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GEOCHEMICAL- MINERALOGICAL AND METALLOGENETICAL ASPECTS CONCERNING THE ORIGIN OF SEDIMENTS FROM LEG. 22 D.S.D.P DRILLED SITES 212 AND 213 IN EASTERN INDIAN OCEAN

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Abstract

Basic mineralogical and geochemical data, are presented for sediment core samples from Deep Sea Drilling Project(D.S.D.P) boreholes :Sites 212 and 213 respectively, from the eastern Indian Ocean. In both Sites the Fe-Mn oxides are abundant controlling a numerous suite of trace elements. In Site 212 the Fe-Mn oxides are more abundant in the upper part of the borehole having mainly a diagenetic or hydrogenous origin, whilst in Site 213 these oxides are more abundant in the lower part having mainly a hydrothermal origin. In both Sites clay minerals are consisting mostly of the expandable mixed layered smectite/illite. The geochemical data shows that in both Sites the majority of the sediments have the characteristics of typical deep sea clay being both of detrital and authigenic origin. In Site 212 these clays with considerable amount of palygorskite and the zeolite clinoptilolite, both of authigenic origin, opaline silica, biogenous $CaCO_3$ *,the Fe-Mn oxides and some other detrital minerals together control the bulk chemical composition of the sediments. In Site 213 the clays with large amounts of Fe-Mn oxides and considerable amounts of the zeolite Phillipsite and Palygorskite in small amounts and some other detrital minerals, control the chemical composition of the sediments. The increase in the Ti/Al and Mg/Al ratios with depth in both Sites implies a volcanoclastic input in the bottom sediments probably from the underlying basaltic basement.*

Key words: *Deep sea sediments and clays, Fe-Mn oxides, authigenic minerals.*

Περίληψη

Τα βασικά ορυκτολογικά δεδομένα καθώς και χημική σύνθεση σε ότι αφορά τα κύρια στοιχεία και ιχνοστοιχεία παρουσιάζονται για τα δείγματα ιζημάτων που συλλέχθηκαν στα πλαίσια του προγράμματος DSDP από τους πυρήνες των γεωτρήσεων 212 και 213 αντίστοιχα, από τον ανατολικό Ινδικό Ωκεανό. Και στις δύο περιοχές τα οξείδια Fe-Mn είναι άφθονα ελέγχοντας παράλληλα μια πολυάριθμη ακολουθία ιχνοστοιχείων. Στην περιοχή της γεώτρησης 212 τα οξείδια Fe-Mn είναι αφθονότερα στο ανώτερο μέρος της γεώτρησης έχοντας κυρίως μια διαγεννετική ή υδρογενή προέλευση, ενώ στην περιοχή της γεώτρησης 213 αυτά τα οξείδια είναι αφθονότερα στα βαθύτερα τμήματα έχοντας κυρίως μια υδροθερμική προέλευση. Και στις δύο περιοχές τα λεπτόκοκκα αργιλλοπυριτικά ορυκτά(clay minerals) έχοντας χερσογενή αλλά και *αυτογενή προέλευση,αποτελούν την βασική ορυκτολογική φάση σε σχέση με το σύνολο των παρόντων ορυκτών, με τα διαστελλόμενα μικτά στρώματα Σμεκτίτη/Ιλλίτη (expandable mixed layers smectite/illite) να είναι τα αφθονότερα. Το γεωχημικά δεδομένα δείχνουν ότι και στις δύο περιοχές η πλειοψηφία των ιζημάτων έχει τα χαρακτηριστικά των τυπικών λεπτόκοκκων αργίλων μεγάλων θαλασσίων βαθών. Στην περιοχή 212 αυτοί οι άργιλοι με σημαντικά ποσά Παλυγορσκίτη και του ζεόλιθου Κλινοπτιλόλιθου, αμφοτέρων αυτογενούς προέλευσης, οπάλιο (opaline* SiO_2*) βιογενούς προέλευσης* $CaCO_3$ *,σημαντικών ποσοτήτων οξειδίων Fe-Mn και κάποιων άλλων χερσογενούς προέλευσης ορυκτών, ελέγχουν τη χημική σύνθεση των αναλυθέντων ιζημάτων. Στην περιοχή 213 αυτοί οι χαρακτηριστικοί άργιλοι μεγάλων θαλασσίων βαθών με συμμετοχή Παλυγορσκίτη σε μικρά ποσοστά, με σημαντικές ποσότητες οξειδίων Fe-Mn και σημαντικές κατα περίπτωση ποσότητες του ζεολίθου Φιλλιπσίτη, καθώς και κάποιων άλλων χερσογενούς προέλευσης ορυκτών, ελέγχουν τη χημική σύνθεση των ιζημάτων. Η αύξηση των αναλογιών Ti/Al και Mg/Al με το βάθος και στις δύο περιοχές μας οδηγεί στο συμπέρασμα ότι ηφαιστειακής προέλευσης υλικό έλαβε μέρος στον σχηματισμό των βαθυτέρων ιζημάτων προερχόμενο πιθανώς από το βασαλτικό υποκείμενο υπόστρωμα.*

Λέξεις κλειδιά: *Ιζήματα και άργιλοι βαθέων θαλασσών, οξείδια Fe-Mn, αυτογενή ορυκτά.*

1. Introduction

During Leg.22 of the Deep-Sea Drilling Project (D.S.D.P) in Indian Ocean Sites 212 (latitude:-9.7755 longitude:99.2973) and 213 (latitude -10.2118 longitude 93.8962) were drilled in a water depth of 6243 m. and 5611m. respectively. Site 212 was drilled over the Wharton Basin, whilst Site 213 was drilled over the east site of Ninety-east Ridge of the Indian Ocean (Fig.1).

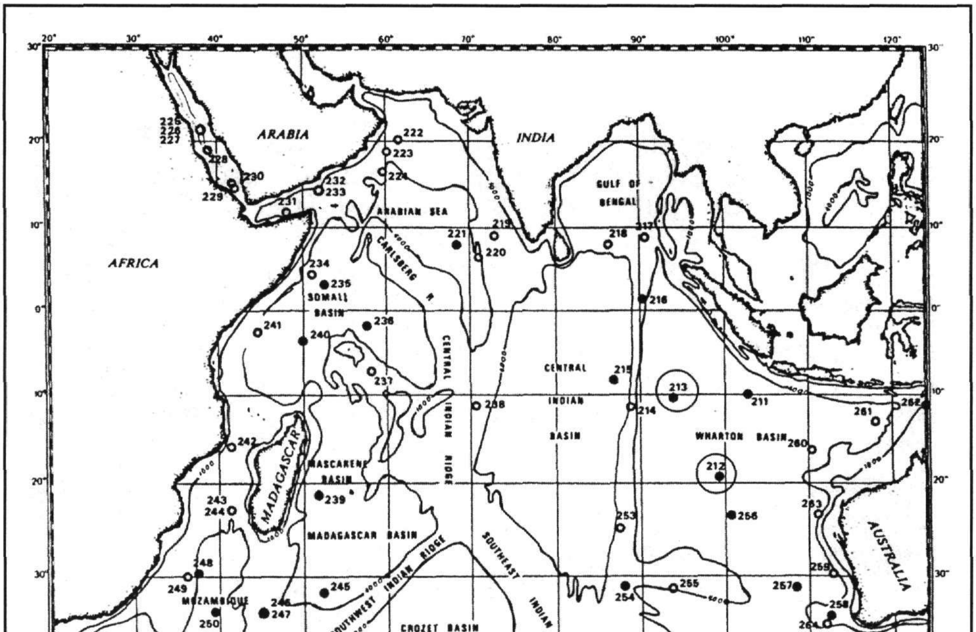

Figure 1 - D.S.D.P Glomar Challenger drill sites in Indian Ocean. The present study Sites 212 and 213 are shown by open circles

The sedimentary sequence for both sites are summarised in Table 1.

Table 1 - Generalised data of the main sedimentological characteristics of Sites 212 and 213 (based to Site reports Von Der Borch and Sclater 1974)

SAMPLES	DEPTH BELOW SEA FLOOR(m.)	AGE	LITHOLOGY
212/15/2	290,00	M.MIOCENE	Fe-oxide rich BROWN ZEOLITIC CLAYSTONE
212/15/3	292,00	“	"
212/16/1	298,50	“	"
212/16/2	300,00	“	"
212/17cc	309,00	“	"
212/18/1	317,50	L.M.EOCENE	"
212/18/2	319,00	“	MODERATE BROWN ZEOLITIC CLAYSTONE
212/23/5	371,00	LATE MIDDLE EOCENE	"
212/27/1	403,00	“	NANNO CHALK-BROWN ZEOLITIC CLAYSTONE
212/28/2	413,80	“	Mn-Fe oxides rich BROWN ZEOLITIC CLAYSTONE
212/35cc	485,50	“	Fe OXIDE RICH CLAYSTONE
212/36cc	489,00	“	ZEOLITIC CLAYSTONE
212/37/1	497,80	“	BROWN ZEOLITIC CLAYSTONE
212/37cc	498,50	“	"
212/38/1	507,50	“	"
213/8/5	73,00	QUATERNARY	RAD-DIATOM OOZE WITH SOME CLAY
213/9/4	81,00	UPPER MIOCENE	ZEOLITIC RAD.BEARING CLAY
213/9cc	84,50	LATE MIOCENE	Mn oxide rich RAD.BEARING ZEOLITIC CLAY
213/10/3	89,50	MIDDLE MIOCENE	Mn oxide rich RAD. BEARING ZEOLITIC CLAY
213/11/2	97,00	“	Mn oxide rich ZEOLITIC CLAY
213/11/5	101,50	“	Mn oxide rich ZEOLITIC CLAY
213/12/5	110,80	“	Mn-Fe oxides rich(goethite?) ZEOLITIC CLAY
213/13/2	116,40	“	Mn-Fe oxides rich ZEOLITIC CLAY
213/13/5	120,50	“	Mn-Fe oxides rich ZEOLITIC CLAY
213/14/3	126,80	E.EOCENE	RAD.RICH Mn-Fe oxides rich ZEOLITIC CLAY
213/15/2	135,40	E.EOCENE	NANNO BEARING Fe-oxides rich ZEOLITIC CLAY

Fifteen samples from the borehole cores of Site 212 and eleven samples from the borehole cores of Site 213 were chemically analysed for nine major elements and seventeen trace elements by an X-Ray Fluoresence Spectometer (Philips PW 1400); CO_2 and H_2O (expressed as loss of weight) were determined gravimetrically.

2. Methods

Chemical analyses of the samples, reduced to rock powder pellets, were produced by X-Ray Fluorescence Spetrometer (Philips PW 1400) at the School of Ocean and Earth Science of the University of Southampton. Water (expressed as loss of weight in the chemical analyses) and CO_2 was determined gravimetrically.

All samples were visually inspected to verify the presence of biogenic phases (calcite and opaline silica). The chemical analyses were processed to correct for such phases, using calcite values and biogenic silica determined both semi-quantitavely.

Calcite was calculated according to a method proposed by Weijden et.al (2006) from total Ca using a correction for clay-bound Ca: $CaCO_{3(sample)} = 2.5 \times Ca_{(sample)} - (Ca/Al)_{clay} \times Al_{sample})$ where (Ca/A1)clay= 0,345 (Turekian and Wedepohl, 1961); also the average of ratios in upper continental crust (Taylor and Mclennan, 1985) and North American shale (Gromet *et al.* 1984).

Biogenic silica values were determined according to a method proposed by Bostrom *et al.* (1976) which is based on the assumption that in sediments with little or no opaline silica the ratio SiO_2/Al_2O_3 usually ranges between 3 and 4,the ratio found in average continental crust (Turekian and Wedepohl 1961); that is, the inorganic Si≈3x Al. The calculated data for both $CaCO_3$ and opaline silica are listed in Table 2.

Table 2 - $CaCO_3$ and Opaline Silica values determined semi-quantitatively

SAMPLES	% OPALINE $SiO_{2(approx.)}$	$CaCO_3$
212/15/2	0	0
212/15/3	0	0
212/16/1	0	0
212/16/2	0	0
212/17cc	0	0
212/18/1	0	0
212/18/2	10,83	0
212/23/5	14,96	0
212/27/1	0	0
212/28/2	0	0
212/35cc	0	11
212/36cc	0	0
212/37/1	11,13	0
212/37cc	18,15	0
212/38/1	15,67	0
213/8/5	9,66	0
213/9/4	0,11	0
213/9cc	4,91	0
213/10/3	4,64	0
213/11/2	1,49	0
213/11/5	0	0
213/12/5	0	1,07
213/13/2	0	1,77
213/13/5	0,19	1,3
213/14/3	4,01	0,6
213/15/2	5,77	40,3

The bulk rock mineralogy data are presented here are originated from the work of the Shipboard Scientific Party of Leg.22 (Kolla 1974, Matti *et al.* 1974) and were also calculated on a semi-quantitative basis.

3. Results

3.1. Bulk Mineralogy

The results of the bulk and clay mineralogical are presented in Tables 3 and 4 respectively.

Comparing the calcite percentages obtained from the method proposed by Weijden *et al.* (2006), presented in Table 2 with calcite percentages derived from the Shipboard Scientific Party of Leg.22 listed in Table 3 it is obvious that the two values are very close.

It is clear from the bulk mineralogical results (Table 3) that clays is the dominant phase in the samples from Site 212 giving values often more than 60 %. Quartz and Plagioclase and K-Feldspars (of terrigenous origin) are the other more abundant phases whilst the Calcite content in most of the samples (except 18/2 and 35 cc) is negligible.

In Site 213 clay is the most abundant phase along with quartz, while K-Feldspars and Plagioclase are most probably detrital and to be the rest most important phases. Calcite is also absent with one exception (sample 15/2) where its content is around 41 %.

Mainly in Site 212 and less in Site 213 the opaline silica (opal-CT) phase was detected (irregular structural interstratification of cristobalite and tridymite layers) which is reflected in the chemical analyses (Tables 3, 5) with enhanced percentages of SiO_2. In marine sediments these phases are usually authigenic of biogenous origin (Chester 1990).

Table 3 - Bulk rock mineralogy(on a semi-quantitative basis; data originated from the work of the Shipboard Scientific Party of Leg.22 (Kolla 1974, Matti *et al.* 1974)

SITE 212 SAMPLES	Quartz	K-Feld	Plag	Clinoptilolite	Phillipsite	Clays	Calcite	Dolomite	Halite	Organic C	B	Minor Minerals
212/15/2	10	2	9	0	0	62	0	0	0	0,36	16,64	Apa, Gib,Op-CT
212/15/3	9	3	7	5	0	52	4	0	0	0,08	19,92	Apa, Gib, Ilm,Op-CT
212/16/1	8	2	7	0	0	64	0	0	0	0,23	18,77	Gib, Op-CT
212/16/2	9	1	5	0	0	66	0	0	0	0,31	18,69	Bar
212/17cc	12	3	5	0	0	54	0	0	0	0,00	26,00	
212/18/1	9	0	7	0	0	61	0	0	0	0,00	23,00	
212/18/2	5	1	5	22	0	51	0	0	1	0,00	15,00	Ilm,Hem, Op-CT
212/23/5	3	1	6	5	0	59	2	0	0	0,45	23,55	Go,Op-CT
212/27/1	7	1	6	0	0	64	0	0	0	0,21	21,79	Go,Gib,Op-CT,Ilm
212/27/5	7	2	6	0	0	64	0	0	0	0,22	20,80	
212/28/2	8	1	4	0	0	66	0	0	0	0,58	20,42	Go,Gib,Op-CT,Ilm
212/29/1	6	1	4	5	0	60	0	0	0	0,21	23,79	Go, Gib, Op-CT
212/35cc	9	2	3	0	0	64	14	0	0	0,32	7,68	Go, Gib, Apa
212/36cc	13	4	12	0	0	64	0	0	0	0,55	6,45	Go, Gib, Hem
212/37/1	14	3	10	0	0	47	0	0	0	0,16	25,84	
212/37cc	8	3	7	37	0	42	0	0	0	0,43	2,57	
212/38/1	7	1	6	33	0	46	0	0	1	0,09	5,91	Op-CT, Go, Hem
SITE 213 SAMPLES												
213/8/5	7		4	0	7	47	0	0	6	0,21	28,79	
213/9/4	5	3	7	0	7	57	0	0	5	0,25	15,75	
213/9cc	3	3	0	0	9	58	0	0	5	0,25	21,75	
213/10/3	5	3	0	0	12	64	0	0	6	0,25	9,75	
213/11/2	3	7	0	0	27	49	0	0	3	0,68	10,32	
213/11/5	6	5	9	0	15	46	0	0	2	1,24	15,76	Gib, Ilm, Apa, Hem
213/12/5	6	5	8	0	12	46	0	0	5	0,33	17,67	Apa, Bar, Gib
213/13/2	5	5	11	0	9	42	0	0	3	0,51	24,49	Bar, Hem, Apa
213/13/5	6	4	8	0	6	52	0	0	3	0,65	20,35	Hem, Gib, Apa,
213/14/3	5	6	11	0	0	59	0	0	0	0,48	18,52	
213/15/2	7	2	3	0	0	30	41	1	2	0,60	13,40	Apa

Ilm = Ilmenite Apa = Apatite B = 100 -(Qtz + Kf + Pf + Clin + Phill + Clay + Calc + Dolo +
Go = Goethite Hem = Hematite Halite + Pyrite + Org C)
Gib= Gibbsite Zir = Zircon B = amorphous material (biogenic silica, volcanic glass) +
Bar = Barite Gar = Garnet minor minerals + Opal-CT
Op-CT = Opal-CT * minor minerals were identified by SEM and/or XRD.

Two important zeolitic minerals were detected in this study. In Site 212 Clinoptilolite $(Na,K)_{3.6}$ $Al_{3.6}$ $Si_{14.4}$ O_{36}. 8.8 H_2O was detected in various samples with considerable amounts (Table 3). On the other hand in Site 213 Phillipsite $[(K,Na,Ca)_2(Si,Al)_8\ O_{16}.6H_2O]$ is present in considerable amounts in most of the samples reaching values up to 27%. In most of the cases both zeolites in deep sea sediments are authigenic (Chester 1990, Cosgrove and Papavassiliou 1979).

3.2. Clay Mineralogy

Clay Mineralogy was carried out in the Institute de Mineralogie of the University of Leige. The <2 μm fraction was examined by X ray diffraction technique. A first run was completed in routine through three usual tests (air dried, solvated with ethylene glycol vapours, heated to 500 °C). Afterwards some samples were subjected to postreatment (Gationic saturations) in order to achieve a more accurate identification particularly at the level of swelling clay components.

Oriented mounts for X-R-Diffraction were prepared leaving dilute aqueous suspensions of the <2 μm fraction to dry in air on glass slides. X-ray diffractograms were obtained using a Philips diffractometer with L-ka radiation. Semiquantitative determinations were carried out by using the techniques applicable by J.THOREZ in the Institut De Mineralogie in the Urersity of Liege.

The results of this semiquantitative analysis are presented in Table 4.

The expandable mixed layerd Smectite/Illite is the most abundant clay minerals phase concerning the clay mineralogy results reaching values up to 90 % in both Sites. This phase seems to have originated from two sources. The most important is authigenic. In the central Indian Ocean, smectite-rich clays appear to have derived mainly from the alteration of in situ submarine basalts and the associated volcanic products (Griffin *et al.* 1968, Kolla *et al.* 1976). This suggestion is confirmed by the fact that in both Sites (212 and 213) the basement drilled was metabasalt with limestone inclusions in Site 212 and basalt in Site 213 (Sclater *et al.* 1974, Subbaro *et al.* 1979).

The other source for smectites and the expandable layerd smectite/illite is detrital. According to Kolla *et al.* (1973) the Quaternary smectite-rich province of Indonesia with higher abundance of smectite adjacent to the Indonesian Islands, on the Cocos-Roo Rises and on the Ninety-east Ridge between 5°N and 14°S can be an important source. This province is influenced by aeolian transport of silicic volcanic ash from the Indonesian island arc.

Table 4 - Clay Mineralogy results

Sample No.	Mixed Layer Illite/Smectite	Illite	Kaolinite	Chlorite	Palygorskite
212/15/2	54	28	10	5	2
212/16/1	74	11	15		
212/17/cc	73	22	5		
212/18/1	78	21	1		
212/18/2	88	9	1		2
212/23/5	91	9			
212/27/1	51	27	13	4	5
212/27/5	70	6	24		
212/28/2	82	5	13		
212/29/1	78	3	19		
212/35cc	73	19	8		
212/36cc	43	36	15	6	
212/37/1	83	10	3		4
212/37cc	65	27			8
212/38/1	45	35			20
213/8/5	83	8	3	5	
213/9/4	96	2	2		
213/9cc	92	4	4		
213/10/3	90	6	4		
213/11/2	89	6	5		
213/11/5	84	10	6		
213/12/5	77	18	5		
213/13/2	74	22	4		
213/13/5	74	20	4		2
213/14/3	77	14	2	2	5
213/15/2	83	11	6		

The other clay minerals i.e Kaolinite, Illite/Chlorite have a detrital origin. The relatively high percentages of Kaolinite and Illite in the clay fraction off the coast of western and north west Australia, southern Wharton Basin and on the Ninetyeast Ridge, has an aeolian origin from western Australia (Griffin *et al.* 1968, Kolla *et al.* 1981).

One important aspect in the clay mineralogy is the presence of Palygorskite mainly in a number of samples from Site 212 and to a lesser extent in a few samples from Site 213 (Table 4).

Palygorskite a Mg-rich aluminosilicate $(Mg,Al)_2Si_4O_{10}(OH)\cdot 4(H_2O)$ in deep sea sediments may have a detrital or authigenic origin. However its origin (at least for the most of it) in both Sites and mainly in Site 212 seems to be authigenic. As pointed out by Weser (1974) its association with the authigenic minerals smectite-Clinoptilolite and opal-CT implies an authigenic origin.

3.3. Chemical analyses results

The chemical analyses of bulk samples are presented in Table 5.

In order to normalize the values for the non-biogenic sediments (i.e removing biogenic carbonate and/or opal) values of Ti, Mg, Fe, K, and Mn are commonly reported as the atomic ratios Ti/Al, Fe/Al etc. (Donnelly and Wallace 1976, Weijden *et al.* 2006). In order to show more clearly the presence of opaline silica in the samples the Si/Al atomic ratio was also calculated.

In Table 6 these atomic ratios from the analysed samples are shown, with their averages whilst in Table 7 the average chemical composition of some important marine sediments and igneous rocks with their atomic ratios are shown for comparisons.

Table 5 - Chemical analyses of bulk samples(major elements, included Mn in %, trace elements in ppm)

SITE 212 SAMPLES	Si	Ti	Al	$Fe_{(total)}$	Mg	Ca	Na	K	P	L.O.I.	CO_2(	Mn	V	Cr	Ni	Cu	Zn	As	Rb	Sr	Y	Zr	Nb	Mo	Ba	La	Ce	Pb
212/15/2	22,30	0,53	9,04	8,22	1,96	0,79	1,71	2,23	0,18	9,48	1,31	2,30	212	97	372	294	140	41	95	425	92	210	20	76	680	93	143	78
212/15/3	21,58	0,49	8,52	8,67	1,77	1,83	1,51	2,14	0,16	9,58	2,30	2,26	211	85	365	291	131	40	90	473	84	190	17	74	529	88	122	71
212/16/1	22,99	0,58	9,36	8,56	1,76	0,74	0,34	2,18	0,15	10,65	1,64	1,87	225	87	337	240	162	35	98	418	82	185	15	19	684	129	137	56
212/16/2	22,85	0,50	9,41	7,85	1,59	0,67	0,19	1,92	0,11	13,92	1,90	1,84	244	200	311	254	142	47	99	425	84	193	14	46	565	100	155	62
212/17cc	23,01	0,55	8,76	9,40	1,72	0,82	1,19	2,56	0,21	8,58	0,90	1,92	281	65	239	193	174	57	97	553	82	184	12	59	792	76	153	64
212/18/1	23,06	0,51	9,46	9,04	1,79	0,61	1,47	1,99	0,14	8,50	0,66	1,69	260	59	204	188	163	56	79	403	69	186	10	45	595	115	127	56
212/18/2	26,17	0,51	7,97	6,49	2,04	0,61	1,72	2,57	0,07	7,50	1,02	0,40	129	60	92	113	123	23	82	545	44	139	11	5	741	44	126	33
212/23/5	26,85	0,35	7,49	7,61	2,59	0,66	1,92	1,90	0,07	7,00	2,33	0,16	162	133	103	55	131	Bd	82	257	40	109	10	0	348	74	92	16
212/27/1	21,40	0,56	12,90	8,10	1,27	0,61	1,31	1,88	0,17	9,03	0,78	0,23	186	93	91	161	181	42	90	197	73	159	11	13	688	119	161	48
212/28/2	21,93	0,50	13,34	7,71	1,32	0,59	1,22	1,61	0,15	10,00	2,12	0,51	224	178	144	112	145	39	77	200	62	154	17	29	519	116	174	40
212/35cc	21,68	0,44	8,62	5,65	1,66	5,62	1,34	2,30	0,09	12,55	7,43	0,17	141	94	89	151	136	12	90	273	45	122	9	21	622	42	126	34
212/36cc	25,30	0,52	9,90	5,98	1,63	0,46	0,67	3,02	0,09	7,88	2,50	0,12	132	118	122	102	158	17	131	147	53	174	14	9	723	76	144	38
212/37/1	27,06	0,58	8,25	5,70	2,11	0,50	1,13	2,91	0,07	7,23	0,60	0,35	103	69	91	187	145	0	116	155	45	199	14	7	638	101	174	50
212/37cc	27,92	0,46	7,34	4,94	1,96	0,66	1,66	2,60	0,11	7,78	2,27	0,70	77	48	117	129	158	9	96	329	60	147	8	0	701	65	136	34
212/38/1	27,36	0,53	7,56	5,34	1,95	0,64	1,51	2,69	0,10	7,83	1,04	0,50	86	48	84	157	149	7	97	316	58	169	10	4	916	68	155	37
SITE 213 SAMPLES																												
213/8/5	26,71	0,32	8,38	3,70	1,26	0,61	3,26	1,98	0,07	9,18	0,76	0,62	73	72	206	182	70	11	81	108	59	136	6	16	324	55	48	31
213/9/4	24,20	0,41	9,11	5,41	2,13	0,99	3,35	1,62	0,17	8,75	0,90	1,10	124	159	244	291	110	15	83	143	110	174	9	28	599	101	119	43
213/9cc	24,35	0,30	8,33	4,62	2,21	0,99	3,44	1,43	0,26	10,20	0,90	1,30	74	145	277	329	116	17	64	175	152	154	9	49	240	99	63	43
213/10/3	24,49	0,29	8,43	4,40	2,18	0,97	3,14	1,45	0,25	9,43	0,90	1,60	96	26	320	346	102	13	55	151	129	138	0	32	384	86	95	44
213/11/2	23,87	0,28	8,75	4,67	1,85	0,96	3,52	2,70	0,27	8,68	2,51	1,94	93	91	418	335	102	15	73	129	121	133	11	44	326	88	119	45
213/11/5	22,33	0,39	8,82	6,34	1,79	1,12	2,69	2,42	0,36	9,63	4,55	2,35	147	59	606	372	147	29	83	178	155	169	15	67	426	129	146	55
213/12/5	21,83	0,50	8,32	7,43	1,88	1,58	3,23	2,57	0,44	9,55	1,21	2,17	162	52	462	244	145	31	75	197	172	188	15	40	458	161	141	49
213/13/2	22,13	0,47	8,52	7,14	1,86	1,89	2,74	2,71	0,56	8,60	1,87	2,32	175	61	479	280	170	33	77	196	229	191	13	41	397	126	131	49
213/13/5	22,37	0,56	8,41	7,43	2,07	1,68	2,30	2,43	0,47	8,93	2,31	2,16	188	43	416	234	179	30	0	0	0	0	0	0	538	169	157	52
213/U/3	23,97	0,50	8,34	6,47	2,58	1,39	1,84	2,82	0,40	8,28	1,70	0,82	121	53	229	134	143	7	88	144	117	163	15	19	513	141	152	40
213/15/2	13,33	0,28	4,01	6,71	1,38	16,71	1,22	1,95	0,33	22,18	18,60	0,81	137	170	131	125	116	43	47	352	82	107	16	21	324	102	77	44

Table 6 - Critical Chemical ratios for the under study samples from Sites 212 and 213

SAMPLES	Si/Al	Ti/Al	Mg/Al	Fe/Al	Na/Al	K/Al	Cr/Al	Ni/Al	Mn/Al	Fe/Mn	DEPTH BELOW SEA FLOOR(m.)
212/15/2	2,369	0,033	0,241	0,439	0,222	0,090	0,00056	0,00189	0,12494	3,573	290
212/15/3	2,432	0,032	0,231	0,491	0,207	0,091	0,00052	0,00197	0,13024	3,834	292
212/16/1	2,359	0,035	0,208	0,442	0,043	0,085	0,00048	0,00165	0,09813	4,578	298,5
212/16/2	2,332	0,030	0,188	0,401	0,024	0,074	0,00110	0,00152	0,09601	4,250	300
212/17cc	2,523	0,035	0,219	0,518	0,159	0,106	0,00038	0,00125	0,10764	4,896	309
212/18/1	2,342	0,030	0,210	0,462	0,182	0,076	0,00032	0,00099	0,08774	5,351	317,5
212/18/2	3,155	0,036	0,284	0,391	0,254	0,117	0,00039	0,00053	0,02466	16,139	319
212/23/5	3,441	0,026	0,383	0,485	0,301	0,092	0,00092	0,00063	0,01048	47,035	371
212/27/1	1,593	0,025	0,109	0,301	0,119	0,053	0,00037	0,00032	0,00875	34,970	403
212/28/2	1,579	0,021	0,110	0,278	0,107	0,044	0,00069	0,00050	0,01878	15,030	413,8
212/35cc	2,416	0,029	0,214	0,311	0,182	0,097	0,00057	0,00047	0,00969	32,666	485,5
212/36cc	2,455	0,029	0,183	0,280	0,079	0,111	0,00062	0,00057	0,00595	47,792	489
212/37/1	3,150	0,039	0,284	0,331	0,160	0,128	0,00043	0,00051	0,02083	16,146	497,8
212/37cc	3,655	0,035	0,297	0,325	0,266	0,128	0,00034	0,00073	0,04686	7,054	498,5
212/38/1	3,475	0,039	0,287	0,339	0,234	0,129	0,00033	0,00051	0,03246	10,631	507,5
AVERAGE SITE 212 VALUES	**2,618**	**0,032**	**0,230**	**0,386**	**0,169**	**0,095**	**0,00054**	**0,00094**	**16,92964**	**16,930**	
213/8/5	3,062	0,021	0,167	0,212	0,457	0,086	0,00045	0,00113	0,03634	5,934 €	73
213/9/4	2,550	0,025	0,260	0,287	0,432	0,064	0,00091	0,00123	0,05927	4,921 €	81
213/9cc	2,809	0,020	0,294	0,268	0,485	0,062	0,00090	0,00153	0,07668	3,556 €	84,5
213/10/3	2,792	0,020	0,287	0,252	0,437	0,063	0,00016	0,00175	0,09325	2,750 €	89,5
213/11/2	2,621	0,018	0,235	0,258	0,472	0,112	0,00054	0,00220	0,10889	2,408 €	97
213/11/5	2,431	0,025	0,225	0,347	0,357	0,100	0,00035	0,00316	0,13079	2,696 €	101,5
213/12/5	2,521	0,034	0,251	0,432	0,455	0,112	0,00032	0,00255	0,12815	3,423 €	110,8
213/13/2	2,494	0,031	0,242	0,405	0,378	0,116	0,00037	0,00258	0,13369	3,078 €	116,4
213/13/5	2,555	0,038	0,273	0,427	0,321	0,105	0,00027	0,00227	0,12612	3,442 €	120,5
213/14/3	2,760	0,034	0,343	0,375	0,259	0,123	0,00033	0,00126	0,04827	7,890 €	126,8
213/15/2	3,190	0,040	0,380	0,808	0,356	0,176	0,00220	0,00150	0,09914	8,281 €	135,4
AVERAGE SITE 213 VALUES	**2,708**	**0,028**	**0,269**	**0,370**	**0,401**	**0,102**	**0,00062**	**0,00192**	**0,09460**	**4,398**	

3.4. General Interpretation

3.4.1. Chemical characteristics of the sediments from Sites 212 and 213

In general the average Si/Al ratio for the analyzed samples from Site 212 (2,61) is lower compared to the average values for terrigenous sediments, deep sea clays, shale and average continental crust. (Table 6). The same applies for the average values from Site 213 which are slightly higher compared with the average Si/Al ratios of Site 212. However as it can be seen from Tables 2 and 5 and Figures 2 and 3, samples rich in opaline silica exhibit values well above 3.1 especially in samples close to the basement in Site 212 core. In contrast, in Site 213 samples the presence of opaline silica is negligible with one exception.

The ratio of Ti/AI is of particular interest in the geochemistry of deep-sea sediments. Chester (1965), Chester and Aston (1976) suggested that high Ti contents strongly indicates the presence of basaltic pyroclastics or generally speaking the influence of basic igneous rocks. According to Couture (1977), sediments having Ti/Al ratio of 0,047, a value being half way between that of average ocean tholeiite (0,062) and average pelagic sediments (0,031), could be composed of altered basaltic ash and terrigenous sediments in equal proportion. Although the average Ti/Al ratio for Site 212 sediments is very similar to the average ratios of terrigenous sediments, shale and deep sea clays (Table 7), samples from the lower part of Site 212 (37/1,37cc,38/1) show considerably higher values (between 0,036-0,0393). This is clearly shown in the plot of Ti/Al versus depth (Fig. 2). So it seems quiet possible that these samples have substantial elemental input from alteration of the underlying basaltic basement. The average Ti/Al ratio for Site 213 samples is slightly lower compared with those of terrigenous marine sediments, shale and deep sea clays (Table 7). However, the samples from the lower part of the core shows similar tendency as 212 basement samples. They have considerably higher values compared with average ratios of terrigenous marine sediments, shale and deep sea clays (Tables 6, 7 and Fig. 3). Also in this case it seems that these samples have an important input from altered basalts derived from the basaltic basement underneath.

The Mg/Al ratio shows also some important characteristics (Figs 2, 3). In Site 212 the Mg content is controlled mainly by authigenic phases i.e zeolites and clay minerals (mixed layer Smectite/IlliTe and Palygorskite). This has been confirmed by the Factor analysis as it will be discussed below. For the samples of this Site the average Mg/Al ratio (0,23) is slightly higher when compared with average marine terrigenous matter (0,216) and shale (0,186) but considerably lower than the average values of deep sea clays (0,277) and continental crust (0,42). However sample 23/5 and the samples from the lower part of the core (37/1,37cc,38/1) show the highest value in the Mg/Al ratio (Fig. 2).

Table 7 - Average chemical composition with their critical chemical ratios for important sedimentary and igneous rocks associated with marine environment

ELEMENTS	AVERAGE SITE 212 COMPOSITION	AVERAGE SITE 213 COMPOSITION	AVERAGE TERRIGENOUS MATTER[1]	AVERAGE DEEP SEA CLAYS[2]	AVERAGE SHALE[3]	AVERAGE CONTINENTAL CRUST[4]	AVERAGE OCEANIC CRUST[5] (MEAN OCEANIC BASALT)	AVERAGE MAFIC IGNEOUS ROCKS[6]
$Si0_2$	51,55	48,54	53,3	53,5	50,93	57,3	47,85	51,36
Al	9,16	8,13	8,1	8,4	8	8,42	8,11	8,8
Ti	0,51	0,39	0,48	0,46	0,45	0,54	1	0,9
Fe	7,24	5,85	4,9	6,5	4,7	7,07	7,6	8,6
Mn	1.00	1,563	0,088	0,67	0,085	0,14	0,13	0,2
Mg	1,81	1,93	1,58	2,1	1,34	3,19	3,96	4,5
Na	1,26	2,79	1,095	4	0,66	2,3	2,11	1,9
K	2,30	2,19	2,25	2,5	2,3	0,91	0,72	0,8
Ba	0,0649	0,0412	0,054	0,23	0,058	0,025	0,0126	0,03
Cu	0,0175	0,0261	0,0057	0,025	0,0057	0,0075	0,0071	0,01
Ni	0,0184	0,0344	0,009	0,0225	0,0095	0,0105	0,0107	0,016
Zn	0,0149	0,0127	0,0078	0,0165	0,008	0,008	0,0098	0,013
Pb	0,0048	0,0045	0,0018	0,008	0,002	0,0008	0,0001	0,0008
Cr	0,0096	0,0085	0,01	0,009	0,01	0,0185	0,0224	0,02
Zr	0,0168	0,0141	0,019	0,015	0,02	0,01	0,014	0,01
Rb	0,0095	0,0066	0,0128	0,011	0,014	0,0032	0,0013	0,0045
Mo	0,0027	0,0032	0,0002	0,0027	0,0002	0,0001	0,0001	0,0001
As	0,0028	0,0022	0,0005	0,0013	0,0006	0,0001	tr.	0,0002
V	0,0178	0,0126	0,013	0,012	0,013	0,023	0,0296	0,02
Y	0,0065	0,0121	0,0031	0,009	0,003	0,002	0,0039	0,0025
Nb	0,0013	0,0010	0,002	0,0014	0,002	0,0011	0,0015	0,002
P	0,126	0,325	0,084	0,15	0,077	0,087	0,0001	0,14
Ce	0,0142	0,0113	0,0054	0,0345	0,005	0,0033		0,0048
La	0,0087	0,0114	0,0033	0,0115	0,004	0,0016		0,001
Sr	0,0341	0,0161						
Ca	1,06	2,63						
RATIOS								
Al /Al+Fe+Mn	***0,5260***	***0,5230***	***0,619***	***0,540***	***0,626***	***0,539***	***0,512***	***0,500***
Fe/Ti	***14,252***	***14,987***	***10,208***	***14,130***	***10,444***	***13,093***	***7,600***	***9,556***
Si/Al(A.R)	***2,618***	***2,708***	***2,954***	***2,859***	***2,858***	***3,055***	***2,648***	***2,620***
Ti/Al(A.R)	***0,032***	***0,028***	***0,0334***	***0,0308***	***0,0317***	***0,0361***	***0,0695***	***0,0576***
Mg/Al(A.R)	***0,230***	***0,269***	***0,2165***	***0,2775***	***0,1859***	***0,4205***	***0,5419***	***0,5675***
Fe/Al(A.R)	***0,386***	***0,370***	***0,2922***	***0,3738***	***0,2838***	***0,4056***	***0,4527***	***0,4721***
Cr/Al(A.R)	***0,0005***	***0,0006***	***0,0006***	***0,0006***	***0,0006***	***0,0011***	***0,0014***	***0,0012***
K/Al(A.R)	***0,0947***	***0,1020***	***0,1917***	***0,2054***	***0,1984***	***0,0746***	***0,0613***	***0,0627***
Na/Al(A.R)	***0,1693***	***0,4008***	***0,1586***	***0,5588***	***0,0968***	***0,3206***	***0,3053***	***0,2534***
Ni/Al(A.R)	***0,0009***	***0,0019***	***0,0005***	***0,0012***	***0,0005***	***0,0006***	***0,0006***	***0,0008***
Mn/Al(A.R)	***0,0500***	***0,0900***	***0,0053***	***0,0392***	***0,0052***	***0,0082***	***0,0079***	***0,0112***
Fe/Mn	***16,9296***	***4,3980***	***55,6818***	***9,7015***	***55,2941***	***50,5000***	***58,4615***	***43,0000***
			[1]Bostrom et.al.1976	[2]Chester 1990	[3]Krauskopf 1967	[4]Taylor and McLennan 1985	[5]Hart 1976	[6]Krauskopf 1967

In the case of sample 23/5 the very high value of Mg/Al (0,383) is explained by the fact that in this sample the clay fraction contains by more than 90 % expandable layers of smectite/Illite (Table 4) which is Mg-rich mineral. On the other hand the increase in this ratio in the lower part of Site 212 is associated with high contents of palygorskite, (a Mg-rich mineral) ranging between 4-20% (Table 4). However, the proximity of these bottom samples with the altered basaltic basement of Site 212 in combination with the increase in Ti/Al ratios in the same samples (Table 6, Fig. 2) implies also a volcanoclastic input in the sediments. For Site 213 the average value for the Mg/Al ratio (0,269) is considerably higher when compared with that of the average marine terrigenous matter (0,216) and shale (0,186) and very close to the average values of deep sea clays (0,277). Also most of the Mg/Al values for this Site are higher when compared with Site 212. (Table 6, Fig. 3). These higher values are associated with the fact that in contrast with Site 212, in Site 213, most of the Mg content is associated with the higher percentage of clay minerals (mainly expandable mixed layers Illite/Smectite) (Table 4). This has been confirmed by the factor analysis shown below. However, similar to site 212 the Mg/Al ratio shows considerable increase with the increasing depth (Fig. 3). This partly is related to the fact that in this Site there is presence of Palygorskite and small amounts of Dolomite in the samples close to basement (Tables 3, 4). On the other hand the same trend of Ti/Al and Mg/Al ratios in both Sites to increase close to basaltic basement (Figs 2 and 3) and this leads to the conclusion that the volcanic activity in the area had an important contribution concerning Ti and Mg. Goldschmidt (1954) mentioned that high MgO (3–6 %) is observed in the sediments if the original constituents of the sediments were derived from basic igneous rocks rich in Mg and especially when volcanic ash from basaltic, andesitic and related volcanoes were deposited with the residual and hydrolysate sediments.

The Fe/Al and Mn/Al ratios seem to be important. Both ratios exhibit similar trends. In Site 212 both are higher in the upper part of the core whilst there is a considerable decrease in the lower part (Table 6, Fig. 2). This trend is common in the upper part of marine pelagic sediments especially when the environment is oxidizing ($E_h>0$) since Fe^{+2} and Mn^{+2} ions are oxidized to Fe^{+3} and Mn^{+4} forming oxides. For Site 212 samples the average value of the Fe/Al ratio is 0,386, which is well above terrigenous marine sediments (0,29) and shales (0,28) but very close to deep sea clays (0,37) and average continental crust (0,40) (Table 7). The average Mn/Al ratio is 0,05, which is almost ten times more than the corresponding ratio for terrigenous marine sediments, shales (0,005) and average continental crust (0,008) whilst it is closer to the average corresponding value for Deep Sea Clays (0,039) (Table 7).

Based on the above findings it is obvious that an additional source for Mn and partly for Fe is required in order to explain such enrichment which especially for Mn, except for the upper part of the core, where the highest values were found (Tables 5, 6). This extra source for the upper part is due to the authigenic formation of Mn-Fe oxides via diagenetic or hydrogenous processes forming a ferromanganese coating very often reported from deep sea clays (Chester and Aston 1976, Chester 1990).

For Site 213 the trends of the Fe/Al and Mn/Al ratios are also parallel but they follow the opposite trend compared to Site 212 samples. As it is evident from Table 6 and Fig. 3 both ratios have an impressive increase in the lower part of the core close to the basaltic basement. The average Fe/Al ratio for the Site 213 analysed samples (0,37) is also well above terrigenous marine sediments (0,29) and shales (0,28) but very close to deep sea clays (0,37) and average continental crust (0,40) (Table 8), whilst the average Mn/Al ratio is 0,09 almost 18 times more than the corresponding ratio for terrigenous marine sediments, shales (0,005) and average continental crust (0,008) and more than twice for the average corresponding value for deep sea Clays (0,039) (Table 7). Again it is evident that an extra source for Mn and partly for Fe is required in order to explain such enrichments which in the case of Site 213 could be related to some local hydrothermal activity related with the tectonic activity in the basement of this Site, leading to the formation of Mn-Fe oxides in authigenic deep sea clays.

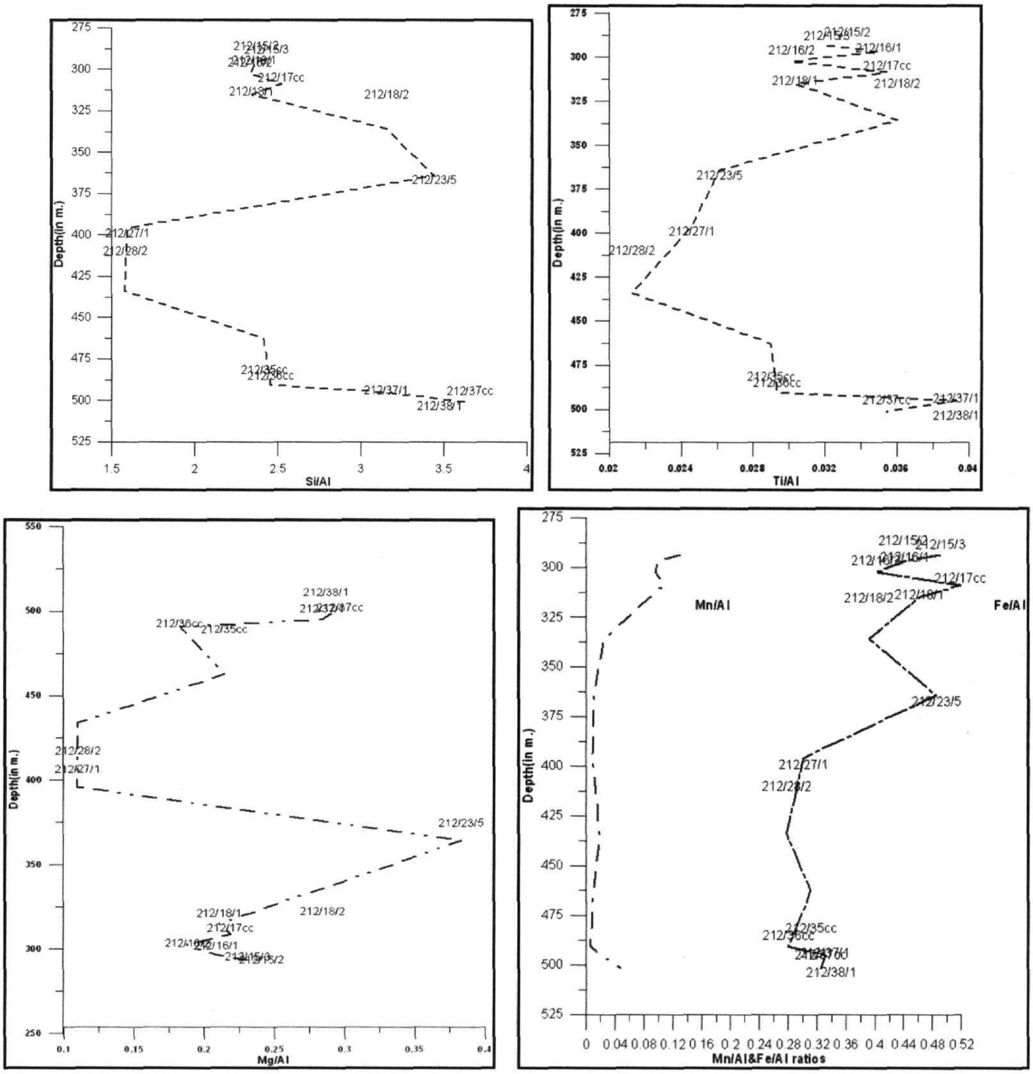

Figure 2 - Plots of the Si/Al, Ti/Al, Mg/Al, Fe/Al and Mn/Al (atomic ratios) versus depth for Site 212 samples

This is evident also from the chemical analysis where Mn values more than 2% have been recorded in both Sites. The description of the upper part of Site 212 sediments as Fe-oxide rich brown zeolitic claystone (Table 1) by the Shipboard Scientific Party of Leg.22 (Pimm 1974) confirms the above conclusion.

According to Sclater et. al. (1974) Around 100-105 m.y. B.P. (Albian – Cenomanian) a spreading centre trending slightly south of east with transform faults trending just east of, north became active in the Central Indian and Wharton Basins and for the next 20 m.y. B.P. India moved in north-north-easterly direction with respect to Antarctica. Therefore, the early Cretaceous sediments of the eastern sites such as 212 and 213 , probably received hydrothermal and volcanic input from this spreading Centre. The existence of the volcanogenic and authigenic inputs as well as the existence of the biogenous component in both 212 and 213 Sites has been confirmed by similar findings in the Broken Ridge (southern to Sites 212 and 213) during the Ocean Drilling Project at ODP Site 752A (Owen and Zimmerman 1991).

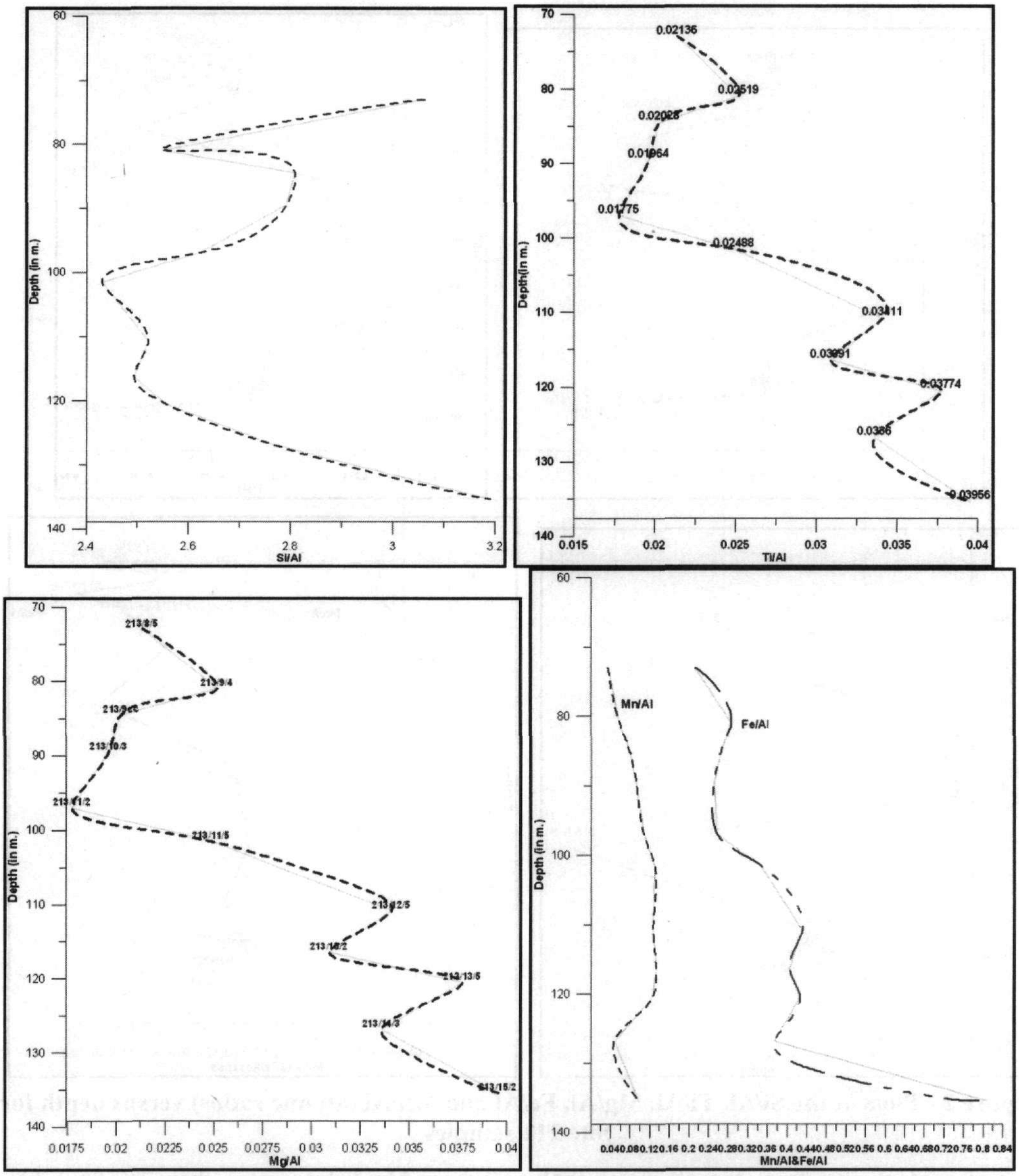

Figure 3 - Plots of the Si/Al, Ti/Al, Mg/Al, Fe/Al and Mn/Al (atomic ratios) versus depth for Site 213 samples

3.4.2. Factor Analysis

Factor analysis using the STATISTICA statistical programme was used in order to identify inter-element groupings in an attempt to understand the geochemical nature and history of the sediments, using only the original bulk chemical analyses. Oblique varimax factors were extracted, these having the advantage of a correlation matrix between the various factors, aiding their interpretation. Factors were derived from orthogonal rotations of principal-component eigenvectors by use of the Varimax method. All communalites are ≥0,90.

The statistical method of factor analysis of the total major and trace element data confirms most of the element associations deduced from the previous analysis for both Sites, and provides a summary of the inter element relationships.

3.4.2.1. Site 212

After the principal components analysis, six factors, accounted for 90,76 of the total variance were extracted. The factor loadings for these 6 factors are shown in Table 8. Factors were derived from orthogonal rotations of principal-component eigenvectors by the use of the Varimax method. All communalites are $\geq 0{,}90$. Low factor loadings, $\leq 0{,}35$, were discarded because they are not statistically significant.

Table 8 - Factor Matrix loadings (Varimax rotation method) for major and trace elements analysed from Site 212 core. Loadings less than 0,45 omitted (see above)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Si	-0,60		-0,61	0,36		
Ti			0,49	0,36	0,53	
Al			0,91			
$Fe_{(total)}$	0,76				-0,35	
Mg			-0,90			
Ca				-0,96		
Na		-0,88				
K		0,37	-0,37		0,74	
P	0,74		0,50			
CO_2				-0,95		
Mn	0,97					
V	0,76		0,35		-0,38	
Cr					-0,81	
Ni	0,93					
Cu	0,87					
Zn			0,63			-0,43
As	0,77		0,49			
Rb		0,79			0,37	
Sr	0,73					
Y	0,88					
Zr	0,66	0,36		0,36		0,38
Nb	0,56					0,66
Mo	0,91					
Ba					0,91	
La			0,54	0,53		
Ce			0,66			0,41
Pb	0,90					
Depth below sea floor(in m.)	-0,83				0,33	
% of total variance	41,18	16,42	13,48	8,39	7,51	3,79
Cumulative %	41,18	57,59	71,08	79,47	86,97	90,76

Table 9 - Correlations between varimax oblique factors for Site 212 values ≥0,30 are shown since they are statistically more significant

	F1	F2	F3	F4	F5	F6
F1	1,00		0,31			0,63
F2		1,00	0,35			
F3	0,31	0,35	1,00			0,33
F4				1,00		
F5					1,00	-0,36
F6	0,63		0,33		-0,36	1,00

Factor 1 is a major one explaining the 41,17 % of the total variance. This factor has high positive loadings for Fe, P, Mn, V, Ni, Cu, As, Sr, Y, Zr, Mo, Pb, medium positive values for Nb and strong negative values for Si and Depth. The positive loadings for the above elements represent the well known covariant group consisting the Fe-Mn hydroxides. The ability of manganese hydroxides to scavenge other transition metals such as Cu, Ni, Pb as well Mo is well known (Cronan 1969, Chester and Aston 1976, Chester 1990). The correlation of P with these oxides is not a surprise. According to Calvert *et al.* (1970), P_2O_5 usually concentrates in Fe-Mn micronodules. However, the high positive loadings of Zr and Nb indicate that this Fe-Mn oxide phase is associated at least partly with the detrital phase, mainly clay minerals. It is known that Fe-Mn oxides coating clay minerals are able to adsorb large amounts of other elements from sea-water. The medium positive correlation of this factor with Factor 3 representing the clay minerals and its strong positive correlation with Factor 6 (representing detrital minerals) (Table 9) confirms this conclusion. On the other hand the strong negative loading of depth in relation to positive loadings of Fe-Mn oxides phase indicate that these oxides are more abundant in the upper part of the borehole. This is shown also clearly in the Fe/Al and Mn/Al ratios versus depth in Figs 2 and 4. The strong negative correlation of Si represents mainly the biogenous opaline silica which is present in considerable amounts in some of the core sections analysed especially in the lower part of the borehole (Table 2). The strong negative loading of depth in this factor confirms this fact which is shown clearly in Fig.2.

Factor 2 explains the 16,41 % of the total variance and has positive loadings for Rb (high) and K (medium) and a high negative value for Na. This factor will be discussed in combination with Factor 3 since there is medium positive correlation between those 2 factors.

Factor 3 explains the 13,48 % of the total variance having strong to medium positive loadings for Al, Ti, P, Zn, As, La, Ce and strong to medium negative loadings for Si, Mg, K. This factor represents the antipathetically related detrital clay minerals with authigenic minerals mainly zeolites and palygorskite and opaline silica. The strong to medium positive loadings of Al and Ti indicate that this factor represents detrital clay minerals which also mainly control the abundance and variance of, Zn, La, Ce and part of P and As. The positive correlation of this factor with F2 means that the positive loadings of F2 i.e part of K and Rb are associated with the positive loadings of F3 i.e the detrital clay minerals. On the other hand the negative loadings of F2 i.e. Na are correlated with the negative loadings of F3 i.e Si, Mg and partly K indicating that these elements represent the authigenic phases of opaline silica, palygorskite and zeolites mainly clinoptilolite.

Factor 4 explains the 8,39 % of the total variance and represents the biogenic $CaCO_3$ factor having very high negative loadings for Ca and CO_2 , contrasting the medium positive loadings for Si, Ti, Zr, La representing detrital silicate minerals mainly feldspars.

Factor 5 explains the 7,5 % of the total variance having high to medium positive loadings for Ti, K, Rb, and very high for Ba, representing the sand fraction with a heavy mineral association (ilmenite, zircon, monazite) and barites. The very strong negative loadings of Cr and medium negative loadings of $Fe_{(total)}$ and V most probably represent a Fe oxide phase. The medium negative correlation of this factor with factor 6 means that the negative loadings of F5 (i.e Cr, part of $Fe_{(total)}$ and V) are associated with the positive loadings of F6 (i.e Zr, Nb, Ce) representing coatings of Fe hydroxides in detrital clays.

Factor 6 explains just the 3,79 % of the total variance and has strong to medium positive loadings for Nb, Zr and Ce and one medium negative loading for Zn. The strong positive correlation of this factor with F1 (Table 9) implies that their positive loadings are associated confirming the fact that elements such as Nb, Zr, and Ce are associated with the main Mn-Fe oxide phase represented by F1. The existence of the strong Zr loadings mean that these oxides are partly associated with detrital clays as coatings. This is confirmed from the medium positive correlation of F6 with F3 which implies that their positive loadings are related i.e part of Zr, Nb and Ce are related with the positive loadings of F3 which represent the detrital clay minerals.

3.4.2.2. Site 213

After the principal components analysis, 5 factors, accounted for 91,54 of the total variance were extracted. The factor loadings for these 5 factors are shown in Table 10. Low factor loadings, $\leq 0,45$, were discarded because they are not statistically significant.

In Table 11 the Varimax factor correlation matrix is shown aiding their interpretation.

Factor 1 explaining the 34,46 % of the total variance has very high positive loadings for Ti, Fe, P, V, Zn, Ba, La, Ce and high to medium positive loadings for K, Mn, Ni and Pb. It represents the coexistence of Fe-Mn oxides with K-Feldspars and Plagioclase and other detrital minerals. This factor is strongly positively correlated with Factor 4 (Table 11) implying that the strong positive loadings (Mn, Ni, Cu, Mo, Pb) of F4 are associated with the loadings of F1 i.e. the abundant Fe-Mn oxides phase in most of the core sections of Site 213. On the other hand the medium negative correlation of F1 with Factor 5 means that the strong to medium negative loadings of this factor (i.e Mg, Cr) are associated with this oxides phase implying that these oxides are associated with deep sea clays, very often coating their surface. It implies also a volcanogenic-hydrothermal origin associated with the basaltic basement of this Site. The fact that in Factor 1 there is also a very strong positive loading of depth confirms the fact that the abundance of Fe-Mn oxides increases in the deeper part of Site 213. This is shown clearly in Fig. 3 where the Mn/Al and Fe/Al ratios are plotted versus depth.

Table 10 - Factor Matrix loadings (Varimax rotation method) for major and trace elements analysed from Site 213 cores. Loadings less than 0,45 omitted (see above)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Si		0,97			
Ti	0,90				
Al		0,95			
Fe(total)	0,91				
Mg		0,48			-0,58
Ca		-0,97			
Na		0,69			
K	0,66				0,61
P	0,86				
CO2		-0,97			
Mn	0,51			0,80	
V	0,88				
Cr		-0,52			-0,51
Ni	0,46			0,76	
Cu				0,85	
Zn	0,92				
As		-0,77			
Rb			0,91		
Sr		-0,80	0,53		
Y			0,82		
Zr			0,95		
Nb			0,79		
Mo			0,66	0,69	
Ba	0,68				
La	0,95				
Ce	0,91				
Pb	0,65			0,71	
Depth below sea floor	0,71	-0,60			
% of total variance	34,47	26,99	16,18	9,25	4,48
Cumulative %	34,47	61,46	77,64	86,89	91,37

Table 11 - Correlations between varimax oblique factors. Values ≥0,30 are shown since are more statistically significant

	F1	F2	F3	F4	F5
F1	1,00			0,44	-0,38
F2		1,00			-0,47
F3			1,00		
F4	0,44			1,00	
F5	-0,38	-0,47			1,00

Factor 2 explaining the 26,99 % of the total variance has high positive loadings for Si, Al, Na, a high to medium positive loading for Mg and high negative loadings for Ca, CO_2, Cr, As, Sr. It represents the clay minerals and quartz (Si, Al, Na, Mg) antipathetically related with calcite (Ca, CO_2,Sr). Calcite is mostly of biogenic origin in the present study. Chester (1990) stated that Sr is of biogenic origin and is supplied by the calcareous marine organisms. The association of Sr with biogenic carbonate has also been reported by Papavasiliou (1979), Turekian (1964), and Bostrom *et. al.* (1974). The negative loadings of Cr and As in this factor need however more explanation. Cr correlation with biogenic calcite could suggest the occurrence of Cr under reducing conditions (The organic tissue of calcareous fossils could provide the necessary organic matter for pyrite formation.). It is well known that under reducing conditions, Cr released from the alteration of basaltic material forms insoluble complexes and could exist as insoluble hydroxide or sulphide in the anoxic layer. In anoxic sediments As is associated often with organic material. In Site 213 samples the organic carbon content is substantially high with values up to 1,24 % (Table 3). So, in marine sediments association of Cr and As with organic carbon under reducing conditions is expected. The strong negative correlation of this factor with factor 5 (Table 11) implies that the strong to medium negative loadings of F5 (Mg, Cr) are associated with the positive loadings of F2 i.e the clay minerals association.

Factor 3 explaining the 16,18 % of the total variance has high positive loadings for Rb, Y, Zr, Nb and high to medium positive loadings for Mo and Sr. It represents detrital fraction of the sediments being rich in heavy minerals (i.e zircon,monazite) and feldspars whilst the presence of Mo and Sr in the positive loadings implies that the deposition of these detrital sediments took place in an anoxic environment. The diagenetic fixation of Mo to organic matter in a reducing environment is well established. (Krauskopf 1967, Calvert 1976, Hirst 1974).

Factor 4 explaining the 9,25 % of the total variance has high positive loadings for Mn, Ni, Cu, Mo and Pb. All these elements form a well known covariant group. The ability of manganese hydroxides to scavenge other transition metals such as Cu, Ni Zn, Pb as well Mo is well known (Cronan 1969, Chester and Aston 1976, Chester 1990). Thus Factor 4 represents a manganese hydroxide phase. This factor confirms the existence of "Mn oxide rich zeolitic clay" described in Table I where the main sedimentological characteristics of the presently studied cores where presented. The strong positive correlation of this factor with F1 confirms its association with Fe-oxides group as it has been mentioned commenting the Factor 1.

Factor 5 explaining the 4,48 % of the total variance has high to medium negative loadings for Mg, and Cr and a medium positive loading for Cr and a medium to negative loading for K. Partly the positive loading of Mg represents the Mg rich authigenic mineral palygorskite which was found in some core sections in Site 213 (see mineralogy section). On the other hand the negative loading of K may represent the existence of the other authigenic mineral being present in considerable amounts in Site 213 core sections. This is the K-rich zeolite phillipsite (Table 3) which varies between 1-27 % in Site 213 core sections. On the other hand the high negative correlation of this factor with Factor 1 and mainly with Factor 2 (Table 11) implies that considerable amount of Mg and Cr are strongly associated with clay minerals and the detrital phases as it has been discussed earlier.

4. Conclusions

The cross examination of the clay mineralogy with the bulk chemical data including the examination of some of the metals to Al atomic ratio and the statistical factor analysis approach leads to a general as well as a few specific conclusions concerning Sites 212 and 213.

A general conclusion

The existence of the volcanogenic and authigenic (diagenetic or hydrothermal) inputs as well as the existence of the biogenous component in both 212 and 213 Sites has been confirmed later by similar findings in the Broken Ridge (south of Sites 212 and 213) in the border area of eastern Indian Ocean during the Ocean Drilling Project at ODP Site 752A (Owen and Zimmerman 1991).

4.1. Site 212

1. The chemical composition of Site 212 sediments approaches more or less the composition of the typical deep sea clays. The sediments of this Site are composed mainly of expandable layered smectite/ illite having both authigenic and detrital origin, with considerable amounts of authigenic palygorskite and the zeolite clinoptilolite.

2. Fe-Mn oxides being more abundant in the upper part of Site 212 control to a large extent the abundance of Fe, Mn, P_2O_5 and trace elements like V, Ni, Cu, As, Sr, Mo, Pb, Ce. These oxides have been formed via diagenetic or hydrogenous processes coating very often the surface of deep sea clay particles. The strong association of these oxides with elements like Zr and Nb implies that part of these oxides are of detrital origin.

3. Ca is controlled mainly by biogenous $CaCO_3$ whilst large amount of SiO_2 is controlled by biogenous silica being present in several Site 212 core sections in considerable amount reaching values up to 18,15 %.

4. Authigenic clay mineral palygorskite and the zeolite clinoptilolite control to a large extent the abundance of Mg and part of K respectively.

5. The detrital heavy minerals and K-feldspars are controlling to a large extent the abundance of Ti, K, Cr, Zr, Nb.

6. The increase of the Ti/Al and Mg/Al atomic ratios in the bottom samples of Site 212 implies a volcanogenic input in these sediments probably from the underlying basaltic basement. The increase in abundance of authigenic minerals like expandable layered smectite/illite and palygorskite, originated often by alteration of the basaltic material, supports further this conclusion.

4.2. Site 213

1. The average chemical composition of Site 213 sediments approaches also more or less the typical composition of deep sea clays. The Site 213 sediments are composed mainly of expandable layered smectite/illite having both authigenic and detrital origin, with large amounts of Fe-Mn oxides and considerable amounts of the authigenic zeolite phillipsite (up to 27 %) and the clay mineral palygorskite in small amounts only in the lower part of the borehole.

2. Large amount of Fe-Mn oxides being more abundant in the lower part of Site 213 control to a large extent the abundance of Fe, Mn, P_2O_5 and trace elements like V, Ni, Cu, Zn, As, Ba, Mo, Pb, La, Ce. The association of these oxides with Ti and part of K represents their coexistence with K-Feldspars. However the considerable increase in abundance of Fe-Mn oxides in the lower part of the borehole, being in parallel with substantial increase of the Ti/Al and Mg/Al atomic ratios (Table 7 and Fig. 3) implies a strong hydrothermal and volcanogenic input in the formation of these oxides. The basaltic basement underneath Site 213 sediments further supports this conclusion.

3. The clay minerals are controlling the abundance of Si, Al, Mg, and the largest part of Na and a proportion of Cr, whilst biogenous $CaCO_3$ is controlling the abundance of Ca, CO_2, and Sr. The association of part of Cr and As with the biogenous fraction (i.e. calcite) especially in the lower part of the borehole is in accordance with the geochemical nature of these elements to form complex insoluble compounds under reducing conditions which seem to prevail in the lower part of Site 213. On the other hand the existence of the authigenic zeolite phillipsite controls considerable proportion of K and part of Na.

4. Feldspars and the heavy detrital minerals are mainly controlling the abundance of elements like Rb, Zr, Y, Nb and a small proportion of Mo and Sr.

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