The effect of environmental controls on the metal content in ferromanganese crusts and nodules from the Mozambique Ridge and in the Mozambique Basin, southwestern Indian Ocean

Samantha Perritt
Applied Geoscience Research Group, CSIR, P.O. Box 91230, Auckland Park, 2006, South Africa
e-mail: sperritt@csir.co.za

Mike K. Watkeys
School of Geological Sciences, University of KwaZulu-Natal, Durban, 4041, South Africa
e-mail: watkeys@ukzn.ac.za

© 2007 September Geological Society of South Africa

ABSTRACT
Major and minor element compositions of a suite of ferromanganese nodules and crusts dredged from the Mozambique Ridge on the RV Sonne cruise in 2005 are combined with previously published data from both the Mozambique Ridge and adjacent Mozambique Basin, in order to examine the relationship between regional variations in chemical composition and environmental controls on ferromanganese mineralisation. Three principal environmental controls on ferromanganese nodule and crust composition have previously been recognised: primary productivity in the surface waters, the oxygen minimum layer, and the calcium carbonate compensation depth. Of these three, the oxygen minimum layer is identified as having the greatest controlling influence on the composition of the ferromanganese deposits of the Mozambique Ridge and Basin, with primary productivity and the calcium carbonate compensation depth being secondary in importance. As a result, three different mineralisation zones can be defined in the study area: deepwater basin deposits, ridge flank deposits formed below the base of the oxygen minimum layer, and ridge crest deposits formed within the oxygen minimum layer. Nodules and crusts from these different zones display distinct variations in chemistry and mineralisation style.

Introduction
Marine ferromanganese deposits off the east coast of South Africa occur in two distinct forms - as fixed crusts covering exposed outcrops on the Mozambique Ridge and as moveable sediment-hosted nodules occurring on the Mozambique Ridge and on the floor of the adjacent Mozambique Basin (Figures 1, 2). These deposits, occurring under a wide variety of environmental conditions but within a relatively restricted geographic area, represent an ideal opportunity to examine the relationship between ferromanganese chemical composition and possible environmental controls on mineralisation.

Worldwide, three different mineralisation mechanisms have been identified as responsible for the formation of marine ferromanganese deposits; these are hydrogenesis, diagenesis and hydrothermal enrichment (Glasby, 1977). Hydrogenetic deposits form as a result of metal precipitation directly from the seawater column. Diagenetic deposits form where pore waters released by underlying sediments contribute elevated metal concentrations to ferromanganese deposits that would otherwise be reliant on metal enrichment from the seawater only. Hydrothermal deposits, as suggested by the name, form as a result of metal precipitation from circulating hydrothermal fluids. The concentration of metals such as Mn, Fe, Co, Ni and Cu in ferromanganese deposits as a result of these mineralisation mechanisms can be highly variable and environmental factors, including primary productivity in the surface waters, the oxygen minimum layer (O2_min layer) and the calcium carbonate compensation depth (CCD), are frequently identified as potential drivers of these variations (Cronan, 1997; Hein et al., 2000; Verlaan et al., 2004). This paper presents the results of a systematic study of the nature of the relationships between the mineralisation mechanism, environmental parameters and compositional variations of Mn, Fe, Co, Ni and Cu in the ferromanganese nodules and crusts from the Mozambique Ridge and Mozambique Basin.

The study area
The area of interest for this study extends from 25.5°S to 35.5°S and from 30°E to 40°E, and encompasses the Mozambique Ridge and the eastern portion of the Mozambique Basin (Figure 2). The Mozambique Ridge is a predominantly north-south trending oceanic ridge located off the east coast of southern Africa, between the Natal Valley to the west and the Mozambique Channel to the east (Figures 2 and 4) (Watkeys et al., 2006). This relatively shallow (crest depth varies from 1300 m to 2000 m) flat-topped ridge extends south from the “Mozambique Bulge” for a distance of 750 km. The ridge is shallowest near its southern end, where it terminates abruptly with squared-off bluffs at about 35°S. The eastern flank of the Mozambique Ridge forms a steep scarp that extends down to the floor of the Mozambique Basin, while the western flank exhibits a slightly gentler incline into the 3500 m deep Natal Valley, which separates the southern part of the Mozambique Ridge from the steep continental margin of southeastern Africa (Ben-Avraham et al., 1994).
The Mozambique Basin separates the Mozambique Ridge from the Madagascar Ridge to the east (Figures 2 and 4). It has an overall rectangular shape (approximately 1500 km long and 500 km wide) and trends north-south parallel to the adjacent Mozambique Ridge. It has an average depth of ~4500 m, but slopes gently westward and southward to as much as 5500 m in depth, where it merges with the deep ocean floor (Kolla et al., 1980). From about 25°S northward, the floor of the Mozambique Basin shallows significantly and then merges into the Mozambique Channel (the area between Madagascar and Africa), which has an average depth of 3000 m.

Samples from as many localities as possible within this area of interest were included in the study, in an attempt to build a comprehensive database on the chemistry of the ferromanganese deposits. The results of the geochemical analysis of ferromanganese nodules and crusts dredged from the Mozambique Ridge on the RV Sonne cruise in 2005 (Watkeys et al., 2006) were combined with previously published data on the chemistry of ferromanganese nodules from both the Mozambique Ridge and adjacent Mozambique Basin (Appendix 1). Any published sample analyses with missing data for one or more of the elements of interest (Mn, Fe, Co, Ni and Cu) were not suitable for use in this study and were eliminated from the database.

The entries in the geochemical dataset were then divided into three groups, based on the principal geographic setting of the samples – deepwater basin deposits, ridge flank deposits and ridge crest deposits.
The surface productivity dataset

Chlorophyll concentration can be used as a quantifiable proxy for primary productivity (Verlaan et al., 2004). The concentration of the photosynthetic pigment chlorophyll in surface waters is related to the quantity of phytoplankton biomass and provides a reliable gauge of primary productivity in the open ocean (Bidigare and Ondrusek, 1996). The absorption of blue and blue-green wavelengths by photosynthetic pigments enables phytoplankton biomass to be quantified through measurements of ocean colour obtained by satellite (Falkowski et al., 1998). For this study, the publicly available eight-year average of chlorophyll concentrations obtained by NASA’s Sea-viewing Wide Field-of-view Sensor (SeaWiFS) Project, from September 1997 to November 2005, was used to generate contoured chlorophyll values in mg/m³ for the study area, using standard inverse distance squared (1/r²) contouring.

A linear band of elevated surface productivity, where chlorophyll concentrations average 0.35 mg/m³, exists to the south of the study area at around 42°S (Figure 3). From this region of high surface productivity, surface
chlorophyll concentrations decline northwards and north-eastwards to between 0.15 and 0.1 mg/m³ at 25°S. Elevated chlorophyll values also occur along the coastal margins of Africa and Madagascar.

**The O₂ min dataset**
The O₂ min layer occurs where vertical mixing in the water column is inhibited and oxygen depleted through the decomposition of organic matter is not adequately replenished (Verlaan et al., 2004). The publicly available World Ocean Dataset (Reid and Mantyla, 1994) was used to generate contoured O₂ concentration values in ml/l with depth (in metres), for the O₂ min layer in the study area, using standard 1/r² contouring.

The depth of the base of the O₂ min layer progressively increases northwards and north-eastwards, from 2100 m at 40°S to 2600 m at 24°S (Figure 4a). This is associated with the decline in surface productivity away from the high productivity belt around 42°S. Minimum oxygen concentrations within the O₂ min layer are fairly consistent across the study area, averaging 4 ml/l (Figure 4b).

**The CCD dataset**
The CCD is located at the depth where the rate of supply of biogenic carbonates equals their rate of dissolution (Berger, 1978). Above this depth, biogenic carbonates can accumulate as sediments on the sea floor, while...
Figure 4. (a) A 3D terrain model of the study area, based on ETOPO2 bathymetry, with the depth of the base of the O$_2$ min layer indicated in blue (calculated from Reid and Mantyla’s 1994 World Data Set). The crest of the Mozambique Ridge extends above the base of the O$_2$ min layer. The location of the seawater oxygen profile illustrated in Figure 4(b) is indicated in red. (b) A west to east schematic cross-section of the Natal Basin, Mozambique Ridge and Mozambique Basin along latitude ~33°S and associated seawater oxygen profile. The seawater oxygen content was modelled using data from the World Ocean Data Set (Reid and Mantyla, 1994). The crest of the Mozambique Ridge lies within a zone of depleted oxygen, located at a depth from 1200 m to 2200 m.
below this depth, dissolution rates exceed supply rates and no biogenic carbonates are deposited. Within the study area, the CCD has been determined by Kolla et al. (1980) from sediment CaCO₃ content versus depth plots. Overall, the CCD is generally deeper in the south (>5000 m) and becomes shallower (<4500 m) in the north.

**Geochemical classification**

One of the most commonly used methods to express the bulk chemical composition of marine ferromanganese deposits in terms of hydrogenetic, diagenetic and hydrothermal compositional fields is the Fe – Mn – (Ni+Cu+Co) ternary plot developed by Bonatti et al. (1972; 1976) and modified by Halbach et al. (1981). There are, however, some concerns related to the application of this classification scheme as the grouping of Ni + Cu + Co in one apex can be problematic if Ni and Cu vary antipathetically to Co (Banerjee et al., 1999).

In order to eliminate this problem, some authors instead use a series of binary diagrams to discriminate between the genetic types (e.g., Mn+Ni+Cu vs Fe+Co, Banerjee et al., 1999). The successful application of these plots relies on the existence of a positive correlation between Fe and Co in all samples. This is not always the case, as Co can instead show a positive correlation with Mn in some instances (e.g., Ostwold and Frazer, 1973; Cronan, 1977; Halbach et al., 1982). An alternative solution to the problem is used in this study. The variables Fe – Mn – (Ni+Cu) – Co are combined in a tetrahedral plot, thereby permitting the discrimination of geochemical trends without making any prior assumptions regarding the relationship between Co and the other metals (Figure 5a). The Mn/Fe ratio used by Halbach et al. (1981) is retained as an indicator of hydrogenetic and diagenetic contributions.

On the basis of their bulk geochemistry, the ferromanganese deposits from the Mozambique Ridge and Mozambique Basin can be considered the product of predominantly hydrogenetic mineralisation (Figures 5b, c). The crust samples all cluster well within the hydrogenetic compositional field, with relatively low Mn, Ni and Cu contents and relatively high Fe and Co contents. In contrast to this tight clustering of crust samples, the nodule samples exhibit two distinct enrichment trends. The first of these, extending from the cluster of hydrogenetic crust samples towards the Ni + Cu apex, is a typical hydrogenetic-to-diagenetic mineralisation trend, similar to other published examples (e.g., Banerjee et al., 1999). This trend reveals an increasing diagenetic component in nodules from the Mozambique Basin and from the crest of the Mozambique Ridge. Some of the nodules from the flanks of the Mozambique Ridge also fall along this diagenetic trend line, but the majority exhibit a different trend towards the Mn apex. Usually, such a trend would also be considered to reflect diagenetic enrichment, resulting from a rapid supply of Mn from reduced sediments. In this instance, a diagenetic process is unlikely, as few if any sediments occur on the flanks of the Mozambique Ridge (identified as barren erosional zones by Kolla et al., 1980). In the absence of an underlying sediment source, Mn enrichment such as this has previously been attributed...
Figure 5. (a) The Mn-Fe-(Ni+Cu)-Co tetrahedral plot developed for the geochemical classification of the Mozambique Ridge and Basin ferromanganese deposits. The hydrogenetic-diagenetic discrimination line is from Halbach et al. (1981). (b) and (c) Two perspective views of the Mn-Fe-(Ni+Cu)-Co tetrahedral plot showing the distribution of the Mozambique Ridge and Basin ferromanganese samples (red spheres – nodules from the Basin; green spheres – nodules from the Ridge flanks; yellow cones – crusts from the Ridge flanks; blue spheres – nodules from the Ridge crest; blue cones – crusts from the Ridge crest).
to hydrothermal processes (e.g., Usui et al., 1986). In addition, the Mn/Fe ratio of these deposits is unusually high, reaching 18.12 (the average for all other samples is only 1.4), while the concentration of accessory metals Co, Cu, and Ni is very low. These element ratios and concentrations are very similar to those reported for hydrothermal ferromanganese deposits occurring elsewhere in the world (e.g., Usui et al., 1986; Chen and Yao, 1994; Hodkinson et al., 1994; Glasby et al., 1997).

The possibility of a hydrothermal source in the Mozambique Ridge samples is supported by the observation of abundant small, highly angular fragments embedded in the ferromanganese matrix (Figure 6). Morphologically, these are very similar to hyaloclastite fragments (Figure 6a) and are possibly volcanic glass.

**Figure 6.** (a) A simplified sketch of typical hyaloclastite fragment morphologies (after Figure 10-9 in Fisher and Schmincke, 1984). (b) Photomicrograph of a concentrated layer of small, angular fragments embedded within the matrix of a ferromanganese crust sample collected from the southern flank of the Mozambique Ridge. (c), (d) Photomicrographs of the angular fragments occurring within the ferromanganese samples from the Mozambique Ridge. Morphologically, these are similar to hyaloclastite fragments, as shown in (a). (e) Photomicrograph of calcium carbonate and microfossil skeletal fragments occurring within a ferromanganese nodule from the crest of the Mozambique Ridge.
shards. The presence of fresh volcanic glass fragments has previously been reported from the Mozambique Ridge and researchers have proposed the possibility of recent magmatic activity (Ben-Avraham et al., 1995). Such magmatic activity could have resulted in hydrothermal enrichment of the ferromanganese deposits growing on the flanks of the Mozambique Ridge.

**Implications**

The dominance of hydrogenetic mineralisation mechanisms in the formation of the Mozambique Ridge and Basin ferromanganese deposits implies that the level of metal concentration in these deposits is primarily a function of seawater chemistry. Variations in the chemistry of the deposits must then be related to the changing availability of metal elements through the seawater column. Diagenetic enrichment only plays a role on the crest of the Mozambique Ridge and in the Mozambique Basin and, even then, this process is subordinate to hydrogenogenesis. On the flanks of the Mozambique Ridge, a third process, namely hydrothermal enrichment, may act in concert with the hydrogenetic mineralisation.

**Environmental controls on metal content**

The availability of metals in seawater for incorporation into ferromanganese nodules and crusts is a function of three principal environmental controls: 1) primary productivity in the surface waters, which influences diagenetic enrichment through its effect on the supply of labile organic matter to the sediments (plankton can concentrate metals in their tissues and then transport them, on death, to the sea floor) and hydrogenotic enrichment through its effect on the export of metals from surfaces waters; 2) the CCD, which influences diagenetic enrichment through its effect on the concentration of labile organic matter versus carbonate remains in the sediments; and 3) the O₂ min layer, which influences hydrogenotic enrichment through its effect on the availability of metals in the water column (Gronan, 1997; Hein et al., 2000; Verlaan et al., 2004).

All three of these environmental controls have the potential to influence the chemistry of the Mozambique Ridge and Basin deposits. However, given the predominantly hydrogenetic nature of the nodules and crusts, those affecting seawater chemistry and hydrogenetic mineralisation can be expected to dominate. In order to evaluate the relationship between these environmental controls and the chemistry of the ferromanganese deposits, variations in the concentration of each of the metals of interest (Mn, Fe, Co, Ni and Cu) were systematically assessed, both geographically and with depth, in relation to variations in environmental conditions (Figure 7).

**Manganese**

Relative to deposits on the flanks of the Mozambique Ridge and in the Mozambique Basin, ferromanganese deposits on the crest of the Mozambique Ridge show low to moderate Mn concentrations (Figure 7), with an average Mn content of 9.6 weight %, and a maximum of 19.3 weight %. As a result of the elevation of the Mozambique Ridge, these crest deposits all formed within the O₂ min layer and well above the CCD (Figure 4a, b). The principal geochemical effect of the O₂ min layer is on the solubility of Mn (Verlaan et al., 2004). The low oxygen concentrations in the O₂ min layer can act to prevent soluble Mn²⁺, released by decaying organic matter, oxidising to insoluble Mn⁴⁺ (Klinkhammer and Bender, 1980;Verlaan et al., 2004). The seawater in the O₂ min layer is therefore a reservoir for high Mn contents (Klinkhammer and Bender, 1980; Johnson et al., 1996; Verlaan et al., 2004), but not necessarily in a form readily suitable for incorporation in ferromanganese deposits through hydrogenetic mineralisation. This explains the overall low to moderate Mn concentrations in the nodules and crusts from this elevation. The location of these deposits high above the CCD further reduces the degree of Mn enrichment possible, as both the sediments and the deposits themselves are diluted by a high load of carbonate remains (observed as microfossil skeletal fragments embedded within the ferromanganese matrix of many samples, as illustrated in Figure 6e and Sheldon, 1988).

To a limited degree, diagenetic enrichment, originating from the sediments capping the Mozambique Ridge, has contributed to the Mn content of the nodules, but the effect of this enrichment is restricted as hydrogenetic mineralisation processes dominate (Figure 5b,c). Overall, the variations in the Mn content of the crest deposits show a correlation with geographic position, specifically latitude (Pearson correlation coefficient r = 0.57), and can be attributed to variations in surface productivity (which also correlates with latitude, r = 0.74). The increasing surface productivity towards the south of the study area (Figure 3) results in a southwards increase in the export of metals from the surface waters (through processes described in Verlaan et al., 2004), thereby increasing the overall amount of Mn available for uptake by the ferromanganese deposits through hydrogenetic mineralisation.

A notable increase in Mn concentration is recorded in samples from the flanks of the Mozambique Ridge (Figure 7), which have an average Mn content of 19.7 weight % and a maximum Mn content of 30.4 weight %. This increase shows no relationship to latitude or surface productivity in either the nodule or crust samples (r values are all between 0.2 and -0.2). The location of these deposits above the CCD also excludes this as a primary controlling factor. The Mn content of the flank deposits is instead a function of their position below the base of the O₂ min layer, combined with further possible enrichment from a hydrothermal source. As previously mentioned, the O₂ min layer can behave as a reservoir for high Mn contents, predominantly in soluble Mn²⁺ form. Manganese²⁺ is highly particle re-active and readily adsorbs onto the surface of, or is scavenged by, particles...
Figure 7. Schematic illustrations of the variations in Mn, Fe, Co, Ni and Cu enrichment within the Mozambique Ridge and Basin ferromanganese samples with depth, and their relationship to the $O_2$ min layer and the CCD.
traversing the O$_2$ min layer. This results in an elevated supply of Mn to the seawater below the O$_2$ min layer. On reaching the higher oxygen levels that occur below the O$_2$ min layer, the Mn$^{2+}$ oxidises to Mn$^{4+}$, dramatically increasing its availability for incorporation into ferromanganese deposits (Verlaan et al., 2004). The availability of Mn in the seawater column is therefore at a maximum just below the O$_2$ min layer. This explains the elevated Mn contents in flank deposits close to the base of the O$_2$ min layer. Unusually though, elevated Mn values are also found in samples from much further down the flanks of the Mozambique Ridge. Under normal conditions, as Mn is removed from the water column through incorporation into the ferromanganese deposits, its availability subsequently decreases with further increases in depth (Verlaan et al., 2004). Samples from lower down the Ridge flanks should therefore contain progressively less Mn. To some extent, a slight decrease in Mn is noted, with the minimum Mn content of the flank samples decreasing from 15.4 weight % to 9.3 weight % with increasing depth. High concentrations of Mn (up to 30.4 weight %) are, however, recorded in samples from deposits as deep as 3800 m. These elevated Mn values cannot be the result of diagenetic enrichment, due to a lack of suitable source sediments on the flanks of the Mozambique Ridge. In addition, Mn$^{4+}$ is usually a good scavenger of other metal elements (e.g. divalent cations Ni and Cu) (Aplin and Cronan, 1985; Koschinsky and Halbach, 1995; Verlaan et al., 2004) and the lack of associated Ni and Cu enrichment in the samples suggests that hydrogenetic processes are not responsible either. As discussed previously, in regard to the geochemical classification of the ferromanganese deposits, a hydrothermal origin is hypothesised for this Mn enrichment.

The nodules in the Mozambique Basin show overall relatively low to moderate Mn concentrations, with an average Mn content of 12.3 weight %, a minimum of 4.5 weight % and a maximum of 15.7 weight %. Low Mn concentrations are expected to occur in the hydrogenetic deposits at this depth, as the quantity of Mn in the water column typically decreases with increasing depth. This reduces the amount of Mn available at depth for incorporation in ferromanganese deposits through hydrogenetic mineralisation. Higher Mn concentrations within the Basin nodules are related to the effects of secondary diagenetic enrichment and the location of these deposits at a depth just below the CCD. The degree of diagenetic enrichment correlates closely to changing primary productivity in the surface waters ($r = 1.00$), with increasing enrichment occurring southwards in association with increasing productivity. This relationship is a result of the effect of surface productivity on the supply of labile organic matter to the sediments (Verlaan et al., 2004). The Mn enrichment can also be linked to the location of these deposits just below the CCD. Manganese contents in diagenetic ferromanganese deposits increase with proximity to the CCD as the labile organic matter supplied by biological productivity in the surface water is concentrated in the sediments near the CCD as a result of calcium carbonate dissolution. The decay of this material promotes the diagenetic enrichment of Mn in nodules (Cronan and Hodkinson, 1994; Cronan, 2006).

**Iron**

The ferromanganese deposits on the crest of the Mozambique Ridge show relatively low to moderate Fe concentrations (Figure 7), with an average Fe content of 7.9 weight % and a maximum content of 20 weight %. The crusts generally exhibit elevated Fe contents relative to the nodules. This is to be expected, as Fe is preferentially enriched during hydrogenetic mineralisation, which is the sole mechanism responsible for the growth of the crusts (Verlaan et al., 2004), while the nodules have additionally been affected by diagenesis and the associated enrichment of Mn at the expense of Fe. Overall, there is an increase in Fe content with increasing depth ($r = 0.73$). Although these deposits on the Ridge crest formed within the O$_2$ min layer, this has a less pronounced effect on Fe enrichment than it does on Mn. This is because Fe rapidly oxides even at these low oxygen levels and its availability is therefore not limited by the O$_2$ min layer (Verlaan et al., 2004). The availability of Fe is instead primarily controlled by the decomposition of organic carriers. Iron is biologically essential to primary productivity and is therefore generally depleted in the surface waters (Sunda 1994; 2001; Sunda and Huntsman, 1995). With increasing depth in the water column, and increasing decomposition of the organic carriers, Fe is progressively released, resulting in its renewed availability for incorporation in ferromanganese deposits (Gordon et al., 1982; Verlaan et al., 2004). Variations in the Fe content of deposits occurring at similar depths, but in different geographic positions on the Ridge crest, correlate with changes in latitude ($r = 0.56$). As for Mn, this is attributed to variations in surface productivity, with the increase in surface productivity towards the south of the study area resulting in a southwards increase in the export of organic carriers from the surface waters.

Ferromanganese samples from the Mozambique Ridge flanks show low to high Fe concentrations (Figure 7), with an average content of 15.5 weight %, a minimum content of 1.7 weight % and a maximum content of 23.7 weight %. The trend of increasing Fe content with increasing depth noted in the crest samples is partially reflected in samples from the upper parts of the Ridge flanks. Below about 3000 m this trend reverses and the Fe content of the ferromanganese deposits decreases with increasing depth. In the case of hydrogenetic deposits, this is considered to be due to a progressive reduction in the amount of Fe available in the water column at greater depths; the Fe released by decaying organic matter at shallower elevations is progressively depleted through incorporation in the...
ferromanganese deposits and is not replenished at depth. Low Fe contents are, however, also characteristically associated with ferromanganese deposits of hydrothermal origin (e.g. Usui et al., 1986; Chen and Yao, 1994; Hodkinson et al., 1994; Glasby et al., 1997). A hydrothermal influence has been postulated for some of the samples on the lower parts of the Ridge flanks and the low concentrations of Fe occurring in these deposits may also be of hydrothermal origin.

The Mozambique Basin ferromanganese nodules exhibit relatively moderate Fe concentrations, with an average Fe content of 10.5 weight % and a maximum content of 11.7 weight %. The slight variations in Fe content correlate with changing primary productivity in the surface waters (r = 0.95), with increasing enrichment occurring southwards in association with increasing productivity.

**Cobalt**

Ferromanganese samples from the crest of the Mozambique Ridge exhibit a wide range in Co values (Figure 7), with an average content of 0.26 weight % and a maximum of 0.77 weight %. Cobalt values tend to be elevated in the crusts relative to the nodules as Co, like Fe, is preferentially enriched in ferromanganese deposits during diagenetic processes (Verlaan et al., 2004). Down the flanks of the Mozambique Ridge, the ferromanganese samples show a notable decrease in Co values with increasing depth, and nodules from the Mozambique Basin show only very low Co concentrations (average Co content = 0.13 weight %).

Cobalt is not as critical a micronutrient as Fe or Mn, and does not show the same degree of depletion in surface waters as a result of biological uptake (Price and Morel, 1991; Sunda, 1994; Sunda and Huntsman, 1995; Verlaan et al., 2004). As a result, the availability of Co in the water column for inclusion in ferromanganese deposits is not primarily a function of the decay of organic carriers. Instead, Co tends to be removed from the water column by scavenging. A water column profile of Co will therefore typically show surface enrichment and depth depletion (Bruland, 1983; Landing and Bruland, 1987; Verlaan et al., 2004). This decrease in the water column concentration of Co with depth limits the availability of Co for incorporation into ferromanganese deposits and explains the decrease in the Co content in the Mozambique Ridge and Basin samples with increasing depth.

**Nickel**

Ferromanganese samples from the crest of the Mozambique Ridge exhibit moderate to relatively high Ni concentrations (Figure 7), with an average Ni content of 0.41 weight % and a maximum content of 0.65 weight %. Nickel values tend to be elevated in the nodules relative to the crusts as Ni, like Mn, is preferentially enriched in ferromanganese deposits during diagenetic processes (Verlaan et al., 2004).

Overall, Ni contents in the crest samples tend to decrease with increasing depth, a trend that continues down the flanks of the Mozambique Ridge, with Ni values falling to as low as 0.07 weight % at a depth of ~4000 m. Below this depth, samples from the Mozambique Basin show a dramatic increase in Ni content and a return to values very similar to the high concentrations levels observed in the Ridge crest samples. The average Ni content of these Basin nodules is 0.47 weight %, while their maximum Ni content is 0.65 weight %.

Like Co, Ni is not as critical a micronutrient as Fe, Mn or Cu, but it is incorporated in biogenic particles to some extent (Price and Morel, 1991; Sunda, 1994; Sunda and Huntsman, 1995). A water column profile of Ni will therefore typically show some surface depletion and subsequent depth enrichment where Ni is regenerated during biological decay (Bruland, 1980; Verlaan et al., 2004). This liberation of Ni can occur at various levels in the water column, one of the locations being in the relatively shallow O\textsubscript{2} min layer (Bruland, 1980; Verlaan et al., 2004). This accounts for the elevated Ni values recorded in samples from the crest of the Mozambique Ridge. As the regenerated Ni is progressively scavenged from the water column, less is available for incorporation in hydrogenic ferromanganese deposits located at greater depths, explaining the general decrease in Ni contents with increasing depth. The dramatic increase in Ni values in the Mozambique Basin nodules can be attributed to the liberation of Ni from decaying organic matter in the Basin sediments and its subsequent incorporation in the overlying nodules through diagenetic enrichment. The Ni enrichment can also be linked to the location of these deposits just below the CCD, where organic matter supplied by biological productivity in the surface water is concentrated in the sediments as a result of calcium carbonate dissolution (Cronan and Hodkinson, 1994; Cronan, 2006). Variations in Ni content within the Basin samples correlate positively with changing primary productivity in the surface waters (r = 0.97), with increasing enrichment occurring southwards in association with increasing productivity.

**Copper**

Ferromanganese samples from the crest of the Mozambique Ridge show consistently low to moderate Cu concentrations, with Cu values averaging 0.08 weight % and reaching a maximum of 0.13 weight %. The nodule samples tend to contain slightly higher Cu contents relative to the crust samples. This is a result of the preferential enrichment of Cu during diagenesis (Verlaan et al., 2004) and reflects the minor diagenetic component present in the crest nodules. Samples from the flanks of the Mozambique Ridge show very similar Cu concentrations to the crest samples but, overall, exhibit a slight increase in Cu content with increasing depth. Copper values in these flank samples average 0.07 weight % and reach a maximum of 0.21 weight %.
A further increase in Cu content is exhibited by samples from the Mozambique Basin. These nodules average 0.22 weight % Cu and reach a maximum Cu content of 0.3 weight %.

Copper is an important micronutrient and is more biologically necessary to primary producers than either Co or Ni (Price and Morel, 1991; Sunda, 1994; Sunda and Huntsman, 1995). A water column profile of Cu will therefore typically show surface depletion as result of uptake by organic carriers (Verlaan et al., 2004). Normally, elements incorporated in such a way in organic matter are rapidly liberated in the O2 min layer when these carriers decompose. However, the strong bonding between Cu and organic matter results in it when these carriers decompose. The presence of a hydrothermal geochemical signature, combined with the occurrence of abundant angular (volcanic glass?) shards embedded within the ferromanganese matrix of many of the samples, suggests that there has been recent magmatic activity and volcanism on the Mozambique Ridge.

Copper is typically depleted in the O2 min layer, but the Cu enrichment in the Mozambique Ridge crest deposits, as a result of the liberation of Ni from organic carriers in the O2 min layer and its subsequent enrichment in the deposits through diagenetic mineralisation.

• Ridge crest deposits, formed within the O2 min layer, exhibit the highest Co concentrations of all localities. This is due to the availability of Co in the water column for scavenging and its subsequent concentration in the ferromanganese deposits through hydrogenetic mineralisation processes. Elevated Ni concentrations also occur in the Ridge crest deposits, as a result of the liberation of Ni from organic carriers in the O2 min layer and its subsequent enrichment in the deposits through diagenetic mineralisation.

• Ridge flanks deposits, formed below the base of the O2 min layer, show the highest Mn concentrations of all localities. This is due to a combination of the effect of the O2 min layer on the availability and export of Mn to the underlying water column and possible hydrothermal enrichment. The flank deposits also exhibit the highest Fe concentration levels, due to the release of Fe through the decomposition of organic carriers and subsequent incorporation in the ferromanganese deposits through hydrogenetic mineralisation processes.

• Basin deposits show the highest Ni and Cu concentrations, due to elevated supplies from decaying organic matter in the underlying sediments and the subsequent diagenetic concentration of these metals in the overlying nodules. These elevated metal values are linked to the location of the Basin deposits just below the CCD, where organic matter supplied by biological productivity in the surface water is concentrated in the sediments as a result of calcium carbonate dissolution (Cronan and Hodkinson, 1994; Cronan, 2006). The variations in Cu content within the Basin samples correlate positively with changing primary productivity in the surface waters (r = 0.99), with increasing enrichment occurring southwards in association with increasing productivity.

Acknowledgements

The authors are grateful to Wilfried Jokat (Chief Scientist on the RV Sonne Cruise SO-183) for the invitation to MKW to participate in the cruise. The dredge sites were selected with his expertise in combination with marine geophysics, parasound and bathymetry data collected on that cruise by C. Kopsch, K. Kitada, M. Tuachnitz, R. Krocker, A. Laberenz, R. Niebling and S. Riedel. Initial sample descriptions on the cruise were undertaken with the assistance of M. Braysahw and Z. Thackeray. The Master and crew of the RV Sonne are thanked for the excellent cruise. The authors are grateful to the CSIR for providing funding for this project and to Mintek for their assistance in the sample preparation and analysis. The contributions of reviewers David Cronan and John Rogers were very helpful in improving the manuscript. George Henry and Claire Palmer are gratefully acknowledged for their comments on earlier versions of this paper. This is Inkaba yeAfrica contribution number 06.

References


Appendix 1.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Source Sample #</th>
<th>Latitude (DD)</th>
<th>Longitude (DD)</th>
<th>Depth (m)</th>
<th>Mode</th>
<th>Fe %</th>
<th>Mn %</th>
<th>Co %</th>
<th>Ni %</th>
<th>Cu %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mozambique Basin</td>
<td>1 GSS 538(l)</td>
<td>35.850</td>
<td>36.767</td>
<td>5450</td>
<td>Nodule</td>
<td>11.7</td>
<td>15.25</td>
<td>0.163</td>
<td>0.523</td>
<td>0.252</td>
</tr>
<tr>
<td></td>
<td>1 GSS 538(s)</td>
<td>35.850</td>
<td>36.767</td>
<td>5450</td>
<td>Nodule</td>
<td>10.66</td>
<td>15.74</td>
<td>0.135</td>
<td>0.65</td>
<td>0.295</td>
</tr>
<tr>
<td></td>
<td>2 50</td>
<td>31.450</td>
<td>37.600</td>
<td>4960</td>
<td>Nodule</td>
<td>8.6</td>
<td>4.5</td>
<td>0.08</td>
<td>0.11</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>2 33</td>
<td>35.650</td>
<td>37.150</td>
<td>5450</td>
<td>Nodule</td>
<td>11.2</td>
<td>15.5</td>
<td>0.15</td>
<td>0.58</td>
<td>0.27</td>
</tr>
<tr>
<td>Mozambique Ridge</td>
<td>2 21</td>
<td>30.660</td>
<td>37.230</td>
<td>3580</td>
<td>Nodule</td>
<td>16.3</td>
<td>12.3</td>
<td>0.22</td>
<td>0.19</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>2 26</td>
<td>35.550</td>
<td>34.550</td>
<td>3800</td>
<td>Nodule</td>
<td>15.2</td>
<td>16.2</td>
<td>0.62</td>
<td>0.35</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1 GSS 537</td>
<td>31.900</td>
<td>34.267</td>
<td>3800</td>
<td>Nodule</td>
<td>16.8</td>
<td>17.7</td>
<td>0.38</td>
<td>0.23</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1 GSS 545</td>
<td>35.650</td>
<td>37.150</td>
<td>5450</td>
<td>Nodule</td>
<td>11.7</td>
<td>15.2</td>
<td>0.15</td>
<td>0.58</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>1 GSS 538(l)</td>
<td>35.850</td>
<td>36.767</td>
<td>5450</td>
<td>Nodule</td>
<td>10.66</td>
<td>15.74</td>
<td>0.135</td>
<td>0.65</td>
<td>0.295</td>
</tr>
<tr>
<td></td>
<td>1 GSS 538(s)</td>
<td>35.850</td>
<td>36.767</td>
<td>5450</td>
<td>Nodule</td>
<td>10.66</td>
<td>15.74</td>
<td>0.135</td>
<td>0.65</td>
<td>0.295</td>
</tr>
<tr>
<td></td>
<td>2 50</td>
<td>31.450</td>
<td>37.600</td>
<td>4960</td>
<td>Nodule</td>
<td>8.6</td>
<td>4.5</td>
<td>0.08</td>
<td>0.11</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>2 33</td>
<td>35.650</td>
<td>37.150</td>
<td>5450</td>
<td>Nodule</td>
<td>11.2</td>
<td>15.5</td>
<td>0.15</td>
<td>0.58</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>2 21</td>
<td>30.660</td>
<td>37.230</td>
<td>3580</td>
<td>Nodule</td>
<td>16.3</td>
<td>12.3</td>
<td>0.22</td>
<td>0.19</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>2 26</td>
<td>35.550</td>
<td>34.550</td>
<td>3800</td>
<td>Nodule</td>
<td>15.2</td>
<td>16.2</td>
<td>0.62</td>
<td>0.35</td>
<td>0.1</td>
</tr>
</tbody>
</table>


Editorial handling: M. J. de Wit and Brian Horsfield

---

**Notes:**
- The data includes samples from different localities and types of samples (nodules, crusts).
- The columns represent the sample type, location, latitude, longitude, depth, mode, and the percentage concentration of Fe, Mn, Co, Ni, and Cu.

---

**References:**
## Appendix 1. continued

<table>
<thead>
<tr>
<th>Locality</th>
<th>Source Sample #</th>
<th>Latitude (DD)</th>
<th>Longitude (DD)</th>
<th>Depth (m)</th>
<th>Mode</th>
<th>Fe %</th>
<th>Mn %</th>
<th>Co %</th>
<th>Ni %</th>
<th>Cu %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>27A</td>
<td>32.280</td>
<td>34.680</td>
<td>1280</td>
<td>Nodule</td>
<td>4.5</td>
<td>5</td>
<td>0.18</td>
<td>0.35</td>
<td>0.08</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>27B</td>
<td>32.280</td>
<td>34.680</td>
<td>1280</td>
<td>Nodule</td>
<td>1.4</td>
<td>6.7</td>
<td>0.04</td>
<td>0.39</td>
<td>0.06</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>27C</td>
<td>32.280</td>
<td>34.680</td>
<td>1280</td>
<td>Nodule</td>
<td>2</td>
<td>5.6</td>
<td>0.08</td>
<td>0.5</td>
<td>0.09</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>27D</td>
<td>32.280</td>
<td>34.680</td>
<td>1280</td>
<td>Nodule</td>
<td>7.3</td>
<td>8.7</td>
<td>0.35</td>
<td>0.38</td>
<td>0.1</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>27E</td>
<td>32.280</td>
<td>34.680</td>
<td>1280</td>
<td>Nodule</td>
<td>5.5</td>
<td>8.5</td>
<td>0.34</td>
<td>0.51</td>
<td>0.1</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>27F</td>
<td>32.280</td>
<td>34.680</td>
<td>1280</td>
<td>Nodule</td>
<td>1.5</td>
<td>1.6</td>
<td>0.05</td>
<td>0.16</td>
<td>0.03</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>27G</td>
<td>32.280</td>
<td>34.680</td>
<td>1280</td>
<td>Nodule</td>
<td>2.4</td>
<td>2.2</td>
<td>0.05</td>
<td>0.26</td>
<td>0.04</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>28A</td>
<td>32.570</td>
<td>35.780</td>
<td>1250</td>
<td>Nodule</td>
<td>9.6</td>
<td>15.2</td>
<td>0.55</td>
<td>0.65</td>
<td>0.12</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>28B</td>
<td>32.570</td>
<td>35.780</td>
<td>1250</td>
<td>Nodule</td>
<td>4.3</td>
<td>8.8</td>
<td>0.16</td>
<td>0.59</td>
<td>0.08</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>28C</td>
<td>32.570</td>
<td>35.780</td>
<td>1250</td>
<td>Nodule</td>
<td>5.5</td>
<td>11.1</td>
<td>0.17</td>
<td>0.65</td>
<td>0.13</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>GSS 536(l)</td>
<td>32.917</td>
<td>35.317</td>
<td>1250</td>
<td>Nodule</td>
<td>9.6</td>
<td>15.24</td>
<td>0.529</td>
<td>0.645</td>
<td>0.125</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>GSS 536(s)</td>
<td>32.917</td>
<td>35.317</td>
<td>1250</td>
<td>Nodule</td>
<td>4.28</td>
<td>8.82</td>
<td>0.161</td>
<td>0.592</td>
<td>0.083</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>GSS 563(light)</td>
<td>32.917</td>
<td>35.317</td>
<td>1250</td>
<td>Nodule</td>
<td>2.55</td>
<td>3.45</td>
<td>0.023</td>
<td>0.248</td>
<td>0.042</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>GSS 564</td>
<td>32.917</td>
<td>35.317</td>
<td>1250</td>
<td>Nodule</td>
<td>5.52</td>
<td>11.3</td>
<td>0.174</td>
<td>0.647</td>
<td>0.125</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>GSS 564(o)</td>
<td>32.917</td>
<td>35.317</td>
<td>1250</td>
<td>Nodule</td>
<td>15.49</td>
<td>19.13</td>
<td>0.774</td>
<td>0.318</td>
<td>0.048</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>W-57</td>
<td>33.017</td>
<td>34.817</td>
<td>1280</td>
<td>Nodule</td>
<td>4.48</td>
<td>4.98</td>
<td>0.184</td>
<td>0.354</td>
<td>0.083</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>W-59</td>
<td>33.017</td>
<td>34.817</td>
<td>1280</td>
<td>Nodule</td>
<td>1.44</td>
<td>6.65</td>
<td>0.035</td>
<td>0.385</td>
<td>0.061</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>W-40</td>
<td>33.017</td>
<td>34.817</td>
<td>1280</td>
<td>Nodule</td>
<td>1.97</td>
<td>5.57</td>
<td>0.078</td>
<td>0.504</td>
<td>0.091</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>W-43(l)</td>
<td>33.017</td>
<td>34.817</td>
<td>1280</td>
<td>Nodule</td>
<td>13.3</td>
<td>8.74</td>
<td>0.327</td>
<td>0.383</td>
<td>0.102</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>W-43(o)</td>
<td>33.017</td>
<td>34.817</td>
<td>1280</td>
<td>Nodule</td>
<td>5.5</td>
<td>8.45</td>
<td>0.34</td>
<td>0.51</td>
<td>0.098</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>W-64</td>
<td>33.017</td>
<td>34.817</td>
<td>1280</td>
<td>Nodule</td>
<td>1.48</td>
<td>1.57</td>
<td>0.054</td>
<td>0.163</td>
<td>0.025</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>W-65</td>
<td>33.017</td>
<td>34.817</td>
<td>1280</td>
<td>Nodule</td>
<td>2.41</td>
<td>2.23</td>
<td>0.054</td>
<td>0.262</td>
<td>0.038</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>MKW_05_37</td>
<td>33.681</td>
<td>34.605</td>
<td>1898 to 1804</td>
<td>Nodule</td>
<td>19.6</td>
<td>17.9</td>
<td>0.52</td>
<td>0.27</td>
<td>0.086</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>MKW_05_45</td>
<td>33.681</td>
<td>34.605</td>
<td>1898 to 1804</td>
<td>Nodule</td>
<td>19.9</td>
<td>19.3</td>
<td>0.49</td>
<td>0.33</td>
<td>0.066</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>MKW_05_Nod5</td>
<td>33.681</td>
<td>34.605</td>
<td>1898 to 1804</td>
<td>Nodule</td>
<td>16.7</td>
<td>16.4</td>
<td>0.47</td>
<td>0.37</td>
<td>0.11</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>MKW_05_31</td>
<td>33.681</td>
<td>34.605</td>
<td>1898 to 1804</td>
<td>Crust</td>
<td>19</td>
<td>17.8</td>
<td>0.62</td>
<td>0.25</td>
<td>0.057</td>
</tr>
<tr>
<td>Mozambique Ridge (crest)</td>
<td>MKW_05_41</td>
<td>33.681</td>
<td>34.605</td>
<td>1898 to 1804</td>
<td>Crust</td>
<td>20</td>
<td>17.6</td>
<td>0.46</td>
<td>0.27</td>
<td>0.065</td>
</tr>
</tbody>
</table>

1. Willis, J. (1970)
2. Summerhayes, C. and Willis, J. (1975)
4. This study