Mineralogy & Geochemistry of Iron in Some Recent Continental Shelf Sediments Off Goa

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Fe is present in much higher concentrations in the fine-grained sediments of the inner shelf off the west coast of India than in the predominantly carbonate sediments of the outer shelf. The results of Mössbauer spectroscopic analyses of these sediments and their $<2\,\mu m$ fractions are consistent with X-ray diffraction data and indicate that the Fe is principally associated with clay minerals, particularly montmorillonite. Chlorite and illite are less important sources of Fe in these sediments and Fe oxide hydroxides appear to be present only in small amounts. The inner shelf sediments also contain some pyrite; this indicates a more reducing environment in the inner shelf associated with relatively high detrital sedimentation in this region.

During the last few years, the mineralogy, geochemistry and sedimentology of marine sediments from the western Indian continental shelf have received considerable attention[1-16] and the oceanography of this shelf has been described[17]. Of particular interest is the work of Rao *et al.*[5] in which the form of Fe in Recent sediments of the northern part of this shelf area has been studied using the Chester and Hughes leaching methods and of Kamat and Sankaranarayanan[18,19] on the concentration and form of Fe in the seawater in the region. The present work concerns the application of Mössbauer techniques to the study of the form of Fe in marine sediments from a variety of environments. The results of Rao *et al.*[5] are compared with those obtained by Mössbauer spectroscopy. In addition, standard grain size, mineralogical and chemical analyses of the material have been undertaken.

Materials and Methods

Surface sediments from 4 sites on the western continental shelf off Goa were made available by Dr Ch M Rao of NIO, Goa. Samples G 17/28 and G 17/30 are shallow water (25-30 m), fine-grained sediments from the inner shelf region whereas samples G 18/5 and G 18/24 are coarser grained, biogenic sands from deeper water (100-115 m) on the outer shelf. Station data and brief sediment descriptions are given in Table 1.

Grain size data for the $>62\,\mu m$ fraction of samples were obtained by dry sieving using $1/4\,\phi$ intervals and the grain size distribution of the $<62\,\mu m$ fraction was recorded using Sedigraph equipment. Chemical composition and mineralogy were determined by X-ray fluorescence spectrometry and X-ray diffraction respectively. CO_2 was determined gasometrically. Standard pretreatment techniques were used for X-ray diffraction identification of the clay minerals in the $<2\,\mu m$ and 2-$62\,\mu m$ fractions.

^{57}Fe Mössbauer spectra of selected samples were recorded in transmission mode at room temperature over a velocity range of $\pm 3\,\text{mm.sec}^{-1}$ using a 1024 channel, constant acceleration spectrometer and ^{57}Co source in a rhodium matrix. Calibration of the velocity scale was with sodium nitroprusside dihydrate.

Table 1—Location and Description of Sediment Samples

Sample	Long. (°E)	Lat. (°N)	Depth (m)	Description
G17/28	73°28.0'	15°50.0'	30	Olive-grey (5Y 5/2)* fine-grained sediment
G17/30	73°36.4'	15°40.0'	25	Predominantly detrital with rare shell fragments
G18/5	73°10.7'	15°44.4'	100	Light-grey (5Y 7/2)* calcareous sands with minor mica, rock and pumice fragments. Diverse biogenic fauna includes foraminifera,
G18/24	73° 0.0'	15°32.0'	115	gastropods, bivalves, bryozoans, coral and echinoderm fragments.

*Colour of air dried sediment

Results

Grain size analysis, mineralogy and chemical composition—Grain size distributions of the sediments are shown in Fig. 1. The G 17 inner shelf sediments are clays and the G 18 outer shelf sediments are silty sands. The median size of the inner shelf sediments falls in the very fine clay ($11^\ast$-$12\,\phi$) interval. The outer shelf sediments are much coarser grained and G 18/5 shows a broad grain size distribution which appears to be bimodal. The coarse fraction of this sample is composed mainly of gastropod and bivalve fragments plus benthic foraminifera with lesser coral and rock fragments. This coarse fraction was missing from G 18/24.

X-ray diffraction analysis of the inner shelf sediments shows quartz with lesser amounts of calcite, plagioclase feldspar, pyrite and possibly goethite. The clay mineral component is also significant and consists of montmorillonite, chlorite, kaolinite and illite; the relative abundances of these clay minerals vary with the size fraction of the sediment. Quartz, plagioclase feldspar and pyrite dominate the silt fraction whilst clay minerals dominate the $<2\,\mu$m fraction which contains only minor quartz and plagioclase feldspar[15]. Montmorillonite and kaolinite predominate in the $<2\,\mu$m fraction with minor illite and chlorite. Chlorite and mica are, however, important in the silt fraction where montmorillonite and kaolinite are subordinate.

The outer shelf sediments are dominated by calcite (including Mg-substituted calcite) and aragonite. Quartz together with trace quantities of plagioclase feldspar and clay minerals are also present. The proportions of calcite and aragonite reflect the skeletal composition of the biogenous matter present. Gastropods and corals secrete largely aragonite shells whereas those of foraminifers are predominantly calcite with variable Mg content. The proportions of aragonite and Mg-calcite relative to pure calcite are lowest in the finest fractions of the sediments. The clay mineral fraction of outer shelf sediments is small but these minerals are more abundant in the $<2\,\mu$m fraction than in the 2-62 μm fraction. Montmorillonite is preferentially concentrated in the finer fraction.

The main difference between the clay mineralogies of the inner and outer shelf sediments appears to be the differing relative amounts of chlorite and kaolinite with the kaolinite/chlorite ratio being higher in the outer shelf sediments.

Major and trace element compositions of washed bulk sediment samples show a marked difference between the G 17 inner shelf and G 18 outer shelf sediments (Table 2). The former have higher SiO_2, Al_2O_3, Fe_2O_3 and TiO_2 contents and, with the exception of Sr, higher trace element contents. This reflects the non-biogenous nature of the inner shelf
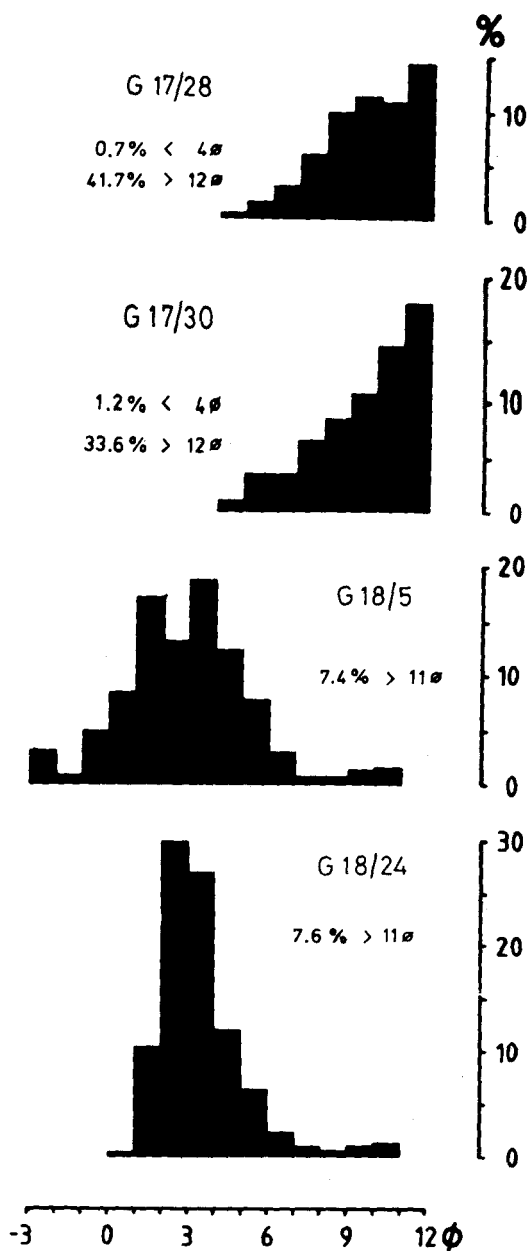

Fig. 1—Grain size distribution of sediment samples studied [Grain size fractions lying outside the analyzed range are given in the diagram]

sediments and the dilution of elements in the outer shelf sediments by $CaCO_3$[9]. Marchig[3] has attributed a terrigenous origin to Fe, Ti, V and Cr in the sediments. The higher overall trace element content observed in the inner shelf sediments is associated with the clay fraction and probably includes both structural incorporation and adsorption onto fine-grained minerals[13]. Of particular note is the concentration of Fe which is considerably higher (by a factor of 5-6) in the inner shelf compared to the outer shelf sediments[5].

Mössbauer spectroscopy—Because of the similarity in mineralogy and composition of the 2 inner shelf and 2 outer shelf sediments, only 1 sediment from each

environment was studied by Mössbauer spectroscopy (i.e. the one with the highest Fe content) and both bulk and $<2\,\mu$m samples were studied. Overall, similarity was observed between the spectra for the bulk and $<2\,\mu$m fraction of these sediments (Fig. 2). The intensity of the central paramagnetic doublet in each spectrum suggests that the majority of the Fe is in the $+3$ oxidation state. A small proportion is, however,

Table 2—Major and Trace Element Composition of Washed, Bulk Sediment Samples

					Conc., %								
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total	Total CO_2
G 17/28	43.99	1.13	17.86	11.13	0.05	3.96	3.46	1.13	1.60	0.44	14.57	99.32	1.43
G 17/30	44.09	1.24	17.81	11.96	0.05	3.91	3.46	0.55	1.45	0.48	14.06	99.06	1.32
G 18/5	8.25	0.17	2.20	2.03	0.00	2.38	44.67	1.03	0.11	0.32	39.11	100.27	36.8
G 18/24	4.32	0.11	1.44	1.81	0.01	1.66	47.06	0.73	0.11	0.23	40.37	97.85	38.1

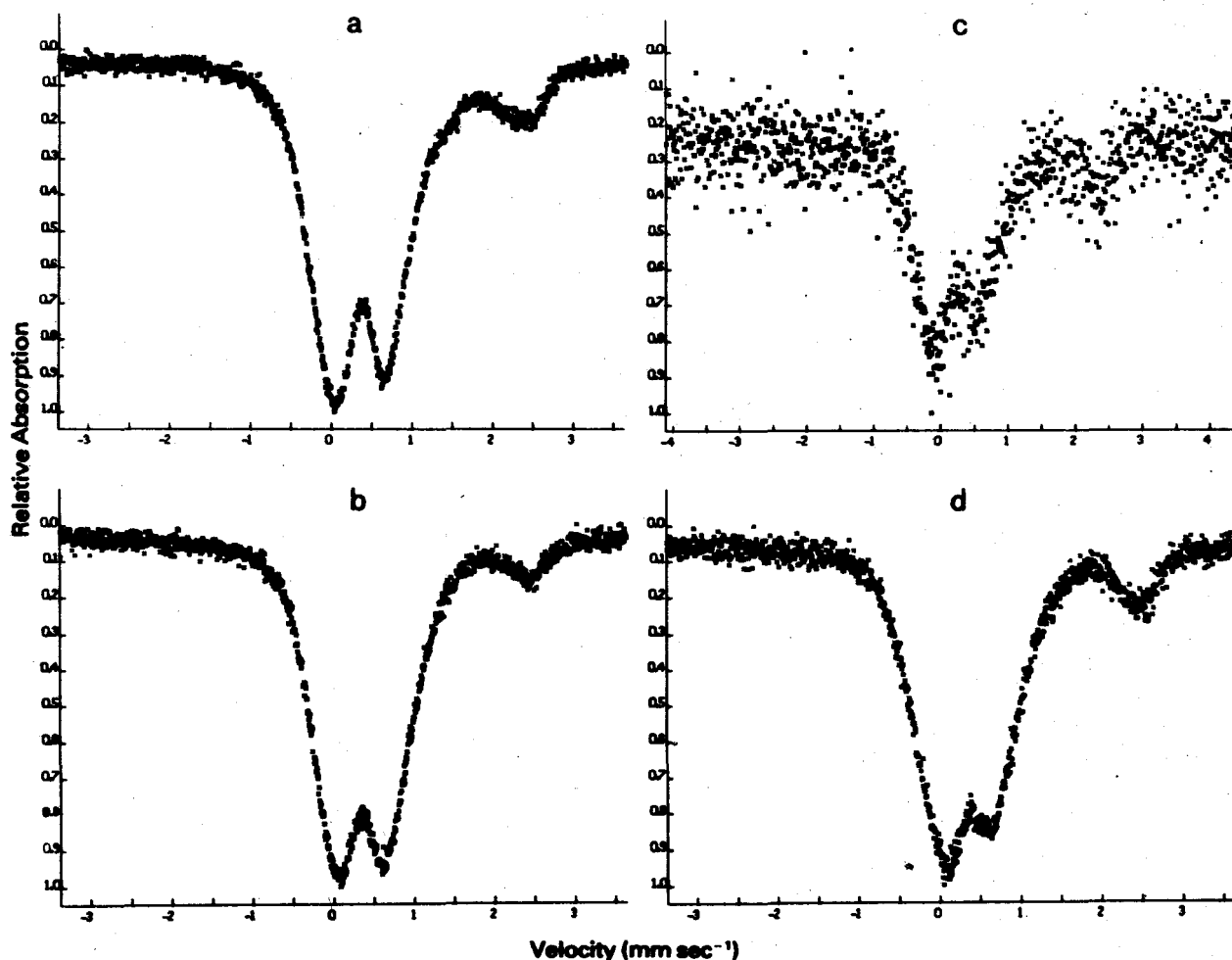|						Conc., ppm								
	Cr	V	Ba	Zn	Cu	Ni	Nb	Zr	Sr	U	Th	Y	Rb	Pb	Ga
G 17/28	237	144	173	101	68	97	11	121	169	2	9	30	72	14	20
G 17/30	254	150	166	107	69	110	13	142	167	3	10	31	70	15	20
G 18/5	63	27	10	30	16	nd*	2	44	2828	0	1	8	8	9	2
G 18/24	36	19	1	24	16	10	1	58	6005	0	0	3	0	4	1

*not determined

Fig. 2—Mössbauer spectra of (a) G 17/30 bulk sediment, (b) G 17/30 $<2\,\mu$m fraction, (c) G 18/5 bulk sediment and (d) G 18/5 $<2\,\mu$m fraction

divalent as indicated by the absorption at approximately $+2.5$ mm.sec^{-1}. Peak breadths and asymmetry probably arise from the distribution of Fe among different sites in one or more minerals.

Quantitative estimation of the contribution of each mineral species to the spectrum requires precise computer fitting because the quadrupole interaction parameter (Δ) and the isomer shift (δ) for Fe^{3+} in montmorillonite, chlorite and illite and low spin Fe^{2+} in pyrite are similar[21-24]. The visually estimated Fe^{3+}/Fe^{2+} ratio for G 17/30 would therefore be overestimated because the inner shelf sediments contain pyrite which has Δ and δ parameters (0.612 and 0.315 mm.sec^{-1} respectively) similar to those for octahedrally co-ordinated high spin Fe^{3+} in clay minerals. In addition, the parameters for high spin Fe^{2+} in montmorillonite, chlorite and illite are similar. Because of the complexity and overlap of the component peaks of the Mössbauer spectra of the sediment samples, satisfactory computer fits were not obtained in this study and qualitative interpretation of the spectra was therefore attempted.

From the mineralogical studies, it is evident that the clay minerals are the major source of Fe in sediments. By way of comparison, the relative amounts of Fe in typical soil clays have been surveyed by Dolničar[25] who concluded that illite and chlorite contain the most Fe followed by montmorillonite[26]; however, Coey[27] has reported that the Fe content of illites is variable. Kaolinite, which is an important constituent of the $<2\,\mu$m fractions, has very little structural $Fe[28]$ but contains significant amounts of surface Fe oxides[29,30].

A comparison of the spectra for the $<2\,\mu$m fraction and the bulk sediment of G 17/30 indicates that the central doublet is more asymmetric and better defined in the latter which also has a broader, slightly more intense absorption at approximately $+2.5$ mm.sec^{-1}. These features are interpreted as arising from fewer mineral contributions to the spectrum of the fine fraction. Despite the lack of computed parameters, it can be concluded from a comparison with reference spectra of chlorite that the contribution of this mineral to the inner shelf sediments must be relatively small. This conclusion is further supported by grain size and mineralogical studies from which it would be expected that the chlorite and illite contributions would be subordinate relative to montmorillonite in both Mössbauer spectra. The significantly narrower absorption, around $+2.5$ mm.sec^{-1}, obtained for the $<2\,\mu$m fraction reflects the smaller amounts of chlorite and particularly illite in this fraction and is consistent with data[23] which list illite and biotite as both having similar δ but slightly lower Δ than montmorillonite.

No consideration has so far been given to the Fe oxide hydroxide components which frequently occur either as surface coatings on clay minerals[26] or independently, and are usually X-ray amorphous. The spectra of G 17/30 indicate no antiferromagnetic Fe oxides or oxide hydroxides to be present but X-ray amorphous superparamagnetic minerals such as goethite might conceivably be present in association with kaolinite and other clay minerals. Sediment colour and the presence of pyrite, however, suggest that, if present, the quantity must be small as does the tentative identification of trace amounts of goethite in the X-ray diffraction trace of G 17/30.

Interpretation of the G 18/5 spectra is difficult because of the poor resolution of the bulk sediment spectrum despite a very long collecting time (over 3 weeks) due to the low Fe content. The better resolved spectrum of the $<2\,\mu$m fraction of this sediment is similar to those obtained for the inner shelf sediment; small differences probably reflect differences in the relative amounts of clay minerals, namely the higher illite content in the $<2\,\mu$m fraction of G 18/5 (compare Figs 2b and d). This would account for the greater asymmetry of the central doublet and slightly higher Fe^{2+}/Fe^{3+} ratio compared with the apparent ratio for the $<2\,\mu$m fraction of G 17/30.

Discussion

The most significant feature of the continental shelf sediments off western India studied here is the difference in composition and grain size between the inner and outer shelf sediments. Fine-grained terrigenous sediments are deposited on the inner shelf whereas the outer shelf favours carbonate sedimentation. From our results, the Fe in these sediments appears to be predominantly associated with the clay minerals and is preferentially concentrated in the finest fractions of the sediments in accordance with the widely noted inverse association between Fe content and grain size[31]. In the inner shelf sediments, montmorillonite is the most important contributor to the total Fe content largely because it is the dominant clay mineral in the sediment. Although chlorite and mica have higher Fe contents than montmorillonite, their contribution to the total Fe content of the shelf sediments is of lesser significance because they are present in lower amounts. These minerals are somewhat more important in the outer shelf sediments which have a higher silt/clay ratio. Other iron containing minerals such as pyrite in the inner shelf sediments and traces of hornblende are less important sources of Fe in the sediments. The origin of the pyrite could not be ascertained from the present study but it probably formed below the sediment-seawater interface in response to a lowering of Eh such as would

occur in areas where there was rapid sedimentation incorporating organic matter[2]. The surface sediments are, however, part of an oxidizing regime as indicated by the presence of small amounts of goethite tentatively identified in G 17/30 and G 18/24, high Fe^{3+}/Fe^{2+} ratios in the sediments and high particulate iron concentrations in the overlaying coastal waters[18,19].

The results of this study are broadly consistent with those of Rao *et al.*[5] who established that 90% of Fe in these sediments is associated with the lithogenous fraction. In particular, clay minerals were identified as the main sources of Fe, although minor pyrite occurs in the inner shelf sediments.

Acknowledgement

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