

Vanadium, manganese and iron in the carbonate rocks of the Rohtas formation

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MS received 23 October 1978; revised 22 December 1978

Abstract. The environmental conditions that prevailed during the formation of the Rohtas carbonates have been delineated on the basis of the Eh-pH diagrams for V, Mn, Fe⁺² and Fe⁺³ compounds. The high content of vanadium in the insoluble residue is indicative of the prevalence of reducing environment. During early-diagenesis manganese seems to have been mobilised from the soft sediments. Higher manganese content in the carbonates is a result of late-diagenesis. Prior to late diagenesis, ferric iron appears to have been precipitated from the waters while manganese remained in solution, and this process accounts for the low iron content of the carbonates.

Keywords. Vanadium; manganese; early-diagenesis; late-diagenesis.

1. Introduction

The carbonate rocks of the Vindhyan basin have been analysed for their mineralogy and Fe⁺², Fe⁺³, Mn and V contents in the insoluble residue fraction and in the carbonate phase. These elements are useful indicators of the redox potential of the environment of their formation. Since Fe⁺³ is an oxidised state of Fe⁺², Fe⁺²/Fe⁺³ ratio is commonly used as an index of oxidation-reduction potentials of environment. Manganese is less mobile under oxidizing conditions while vanadium has a tendency of accumulation under reducing conditions. Behaviour of these elements has been used to evaluate the condition of deposition of Rohtas carbonates and the environment of their diagenesis subsequently.

Chemical parameters have not been used earlier in the study of Vindhyan. For this purpose eleven samples of carbonate rocks, collected from the Gurma area of Mirzapur District, representing a vertical profile, have been analysed. The results have been compared with the concentrations of the same elements in rocks of known environment. The Eh-pH diagrams for metal ions and compounds based on published experimental work have been used.

The geology of the area has been discussed in detail by Auden (1933) and Misra (1969). The Rohtas formation is the upper-most carbonate sequence of the Semri Group of Lower Vindhyan (table 1). They are thinly bedded limestones with intercalations of shales. The location of samples are given in figure 1.

Table 1. Stratigraphy of the Vindhyan basin.

Super group	Group	Formation	Lithology	
Vindhyan	Bhander	unconformity		
	Rewa	unconformity		
	Kaimur	unconformity		
	Semri	Rohtas		limestones, shales
		Kheinjua		dolomites, shales, sandstone
		Chopan		porcellanites
		Kajrahat		limestones, shales
	Arangi		shales, conglc, limestone	
	unconformity			
Bijawar Group (basement) Rb-Sr age $2,500 \pm 50$ million years				

2. Analytical methods

Five hundred grams of each sample has been powdered in an agate mill. The insoluble residue has been separated by treating the powder with the chlor-acetic acid to avoid reaction with micas and organic matter. It has been confirmed that no detectable amount of vanadium is lost during acid digestion. Iron and manganese have been determined by x-ray fluorescence by using arsenic as an internal standard. In this case the Philips XRF unit with Wolfram source and LiF crystal have been used; and analytical method given by Wedephol (1961) has been followed. The accuracy of the data is within $\pm 5\%$ limit. Vanadium has been determined by the 3.4 m Jarrell-Ash emission spectrograph taking the spectrum on Ilford-40 photographic plates. In the vanadium determination, iron has been used as an internal standard and the wavelength pairs used in determinations are: V 3183.4 Å: Fe 3184.9 Å; V 3185.4 Å: Fe 3184.9 Å. To check reproducibility several international standards have been analysed (table 2) which show an accuracy upto $\pm 5\%$. The carbonate fractions of the samples have been dissolved in HCl and from the solution Fe^{+2} has been determined as total iron by atomic absorption. Mineralogy is based on x-ray diffraction, chemical analysis and infrared spectroscopy.

3. Analytical data

Quantitative mineralogy of the samples and variation of different trace elements from bottom to top of the Rohtas formation are shown in figure 2. The analyses given in table 2 show a considerable variation in the amount of insoluble residue fraction of the samples. The total iron content range from 0.15 to 1.5% with an increasing trend towards the top of the sequence (where it is overlain by the quartzite and shales of the Bijaigarh formation of the Kaimur Group). Excluding

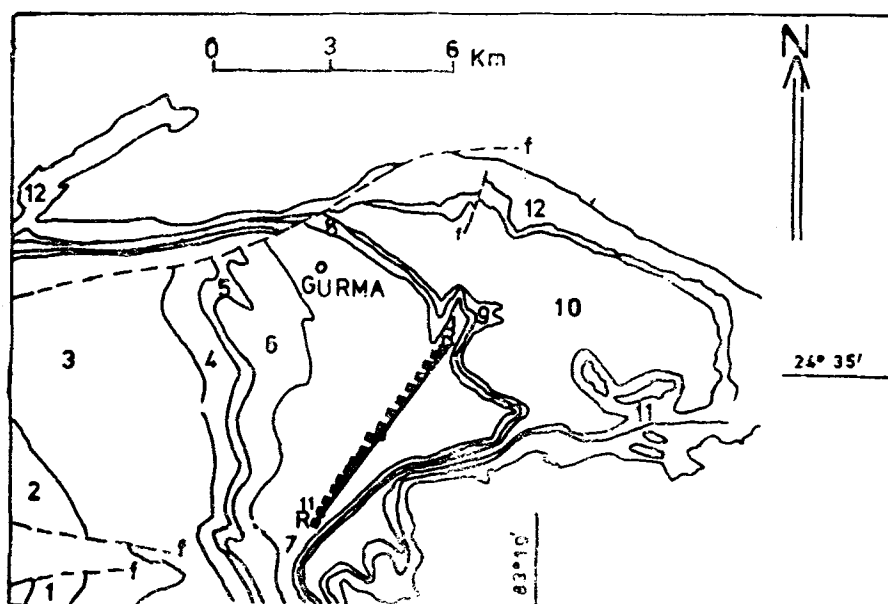


Figure 1. Map showing lithological units of the Gurma area and sample locations from R1 to R11. The units are: 1-Arangi formation, 2-Kajrahat formation, 3-Chopan formation, 4-6 Kheinjua formation, 7-Rohtas formation, 8-12 Kaimur group.

Table 2. Analytical data on the carbonate rocks of the Rohtas formation.

Sample No.	Insoluble residue wt %	Calcite wt %	Dolomite wt %	Fe ⁺² ppm	Fe ⁺³ ppm	Mn ppm	V ppm
R 1	14.6	85.8	..	80	4520	210	33.8
R 2	22.0	74.1	2.4	2380	8110	30	24.0
R 3	11.6	84.0	3.7	1200	2400	30	15.2
R 4	28.1	70.7	1.9	1100	2890	340	19.6
R 5	25.3	74.4	..	760	9650	30	49.4
R 6	12.7	83.5	2.5	720	3380	30	34.1
R 7	9.7	87.4	2.1	900	1190	30	12.9
R 8	9.3	89.5	0.9	1530	1070	230	8.9
R 9	8.9	89.6	0.7	nd	nd	50	nd
R 10	9.2	90.5	1.0	1800	350	50	6.9
R 11	17.9	83.1	..	980	1260	50	19.4

Standards analysed as unknown in triplicate :

	Fe (Σ) %	Mn ppm	V ppm
GSP-1	3.0	314	68
ZGI-BM		1275	
ZGI-TB			101

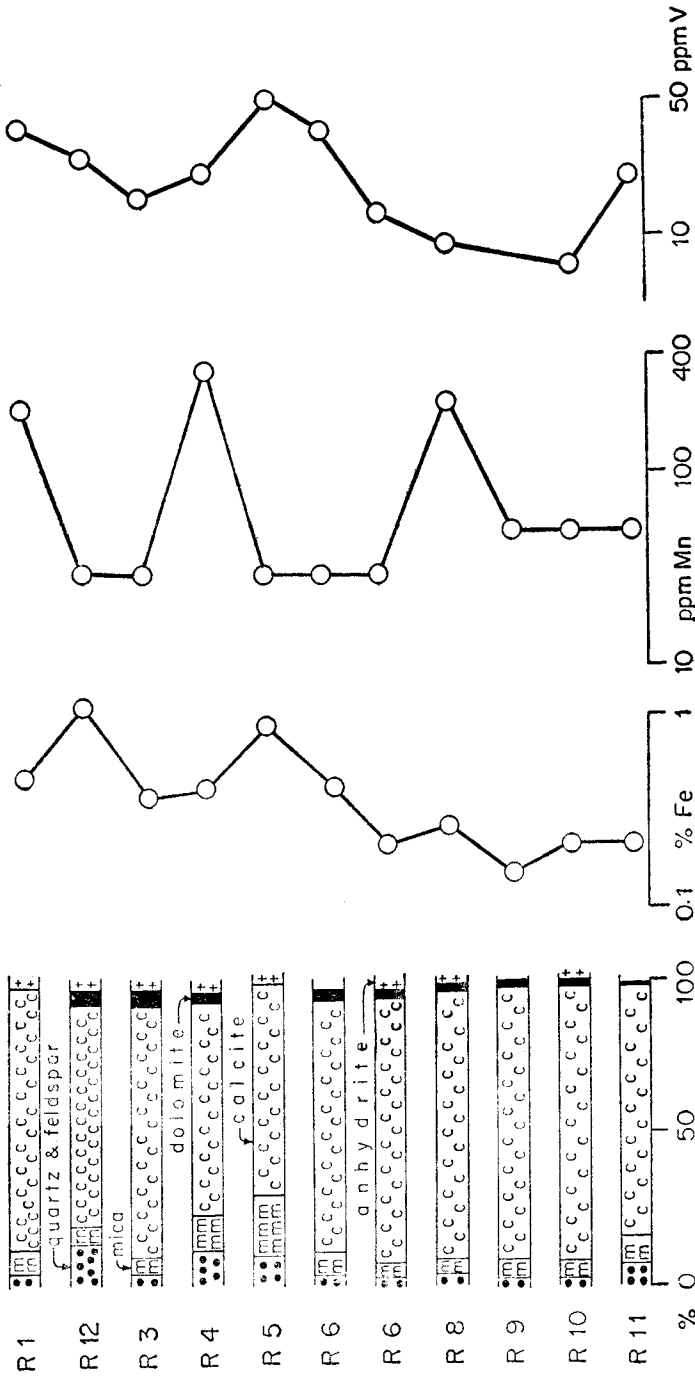


Figure 2. Mineralogical and chemical profile of the Rohrias carbonates. Anhydrite is shown by plus sign.

samples R-2 and R-5, the average iron in the Rohtas sequence comes to 0.29%. The $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio varies from 0.19 to 12.7 (excluding sample R-1). The Fe^{+2} determined here is either in the carbonate or in the sulfide phases. The content of this element is almost negligible in the silicates. Fe^{+3} shows an increasing trend towards the top of the sequence.

The manganese content reported in table 2 is from the carbonate phase, and only less than 5 ppm Mn occur in the insoluble residue fraction (detected by emission spectrography). On the basis of the manganese content, all the samples can be grouped into two categories: (a) those containing 30 to 50 ppm Mn, and (b) those containing 200 to 350 ppm. As compared with the average composition of limestone (550 ppm Mn), the Rohtas samples are very low in this element. Vanadium varies from 6.9 to 49.4 ppm with an average of the sequence 22.4 ppm V, which is comparable to the average vanadium (20 ppm) of limestones given by Wedepohl (1970b). The latter information is of great significance because this indicates that the initial environment of deposition of carbonates is generally similar, irrespective of whether a carbonate is of organic or inorganic origin; the critical component is the organic matter which collects many metals.

4. Fe, Mn and V as part of insoluble residue

The insoluble residue, by its composition, is very close to a shale. Major part of this fraction is of detrital origin. In fact the insoluble residue of carbonates has gone through three distinct chemical environments: (a) weathering and surface waters prior to their deposition, (b) interaction with the waters of a basin characterised by a salinity undoubtedly higher than the former, and (c) of late-diagenesis. The limestones and dolomites are a mixture of shales and carbonates. Therefore insoluble residue and carbonates have been treated as shale *versus* carbonates, and the composition of shale has been assumed to be of average shale. The contribution of Fe, Mn and V as a part of the insoluble residue fraction has been calculated (table 3) with reference to the average composition of shales given by Wedepohl (1970a). The following method has been used:

$$X \text{ element in } Y \% \text{ of residue} = \frac{\% X \text{ in the average shale}}{100} \times Y\%$$

$$\text{Factor} = \frac{\text{wt } \% X \text{ element in the whole rock}}{\text{wt } \% X \text{ element as average shale in residue}}$$

The factor is a quantitative indicator as to whether the rock is enriched in a particular element with reference to the insoluble residue (assumed as having an average shale composition). For example take the case of sample R-1. The insoluble residue as an average shale should contain 18.9 ppm V but the whole rock contains 33.8 ppm V; this means that the rock has been enriched in this element by a factor of 1.8. Such an increase in the V content is only possible in a highly reducing environment and in the bituminous sediments. On the basis of such comparisons with respect to other elements, the rocks of the Rohtas formation are low in iron content, while vanadium is high in samples R-1, 5 and 6, and low in the rest of the samples. A few samples are fairly high in Mn while the rest are considerably low in Mn. Since the insoluble residue contains less than 5 ppm Mn which is

Table 3. Probable concentration of elements equivalent to the proportion of insoluble residue of the rocks calculated with reference to average composition of shales. Insoluble residue has been considered as shale. Eh has been calculated for $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio of the whole rock with $\text{Fe}^{+2} \rightleftharpoons \text{Fe}^{+3}$ at +0.77 volts.

Sample No.	Fe (Σ) ppm	Mn ppm	V ppm	Eh volts	A	B	C
R 1	7037	43	19	0.88	0.65	4.86	1.78
R 2	10604	66	28	0.80	0.99	0.45	0.86
R 3	5591	34	15	0.95	0.64	0.88	1.01
R 4	13544	84	36	0.95	0.29	4.05	0.54
R 5	12194	76	32	0.84	0.85	0.39	1.54
R 6	6121	38	16	0.81	0.61	0.79	2.13
R 7	4675	29	12	0.76	0.45	1.03	1.08
R 8	4482	28	12	0.76	0.58	8.21	0.74
R 9	4289	26	11	nd	nd	1.92	nd
R 10	4434	27	12	0.73	0.48	1.85	0.58
R 11	8627	53	23	0.78	0.26	0.94	0.84

Note : The average composition of shales given by Wedepohl (1970a) is 4.82% Fe (Σ), 600 ppm Mn, and 130 ppm V. The average composition of limestones given by Wedepohl (1970b) is 1.46% Fe (Σ), 700 ppm Mn, and 20 ppm V.

A, B and C are ratios calculated as follows:

$$A = \frac{\text{Fe}(\Sigma) \text{ in the whole rock from table 2}}{\text{Fe}(\Sigma) \text{ as part of the insoluble residue from table 3}}$$

$$B = \frac{\text{Mn in the whole rock from table 2}}{\text{Mn as a part of the insoluble residue from table 3}}$$

$$C = \frac{\text{V in the whole rock from table 2}}{\text{V as part of the insoluble residue from table 3}}$$

very low as compared to the content in average shale, the Mn in the carbonate phase is consequently very high. Averages for limestones computed by Wedepohl (1970b) show an increase of Fe by a factor of 2.3, Mn-6.3, and V-1.2 with reference to the contribution of insoluble residue fraction. Iron and vanadium contents of the sedimentary rocks of different composition are plotted in figure 3, which clearly indicate that in respect of vanadium, the Rohtas carbonates are comparable to the rocks of sapropel environment (the recent shales from the Black Sea of sapropel environment, contain about 100 ppm V). A comparison with these data and the vanadium content of 100% of the insoluble residue indicate a higher concentration in the Rohtas carbonates.

5. Behaviour of elements

The relationship of different elements is shown in figure 3. Positive correlation exists between insoluble residue - Fe^{+3} , insoluble residue -V, V- Fe^{+3} , dolomite- Fe^{+3} ; and a negative correlation between the pair Fe^{+2} -V. As expected the Fe^{+2} - Fe^{+3}

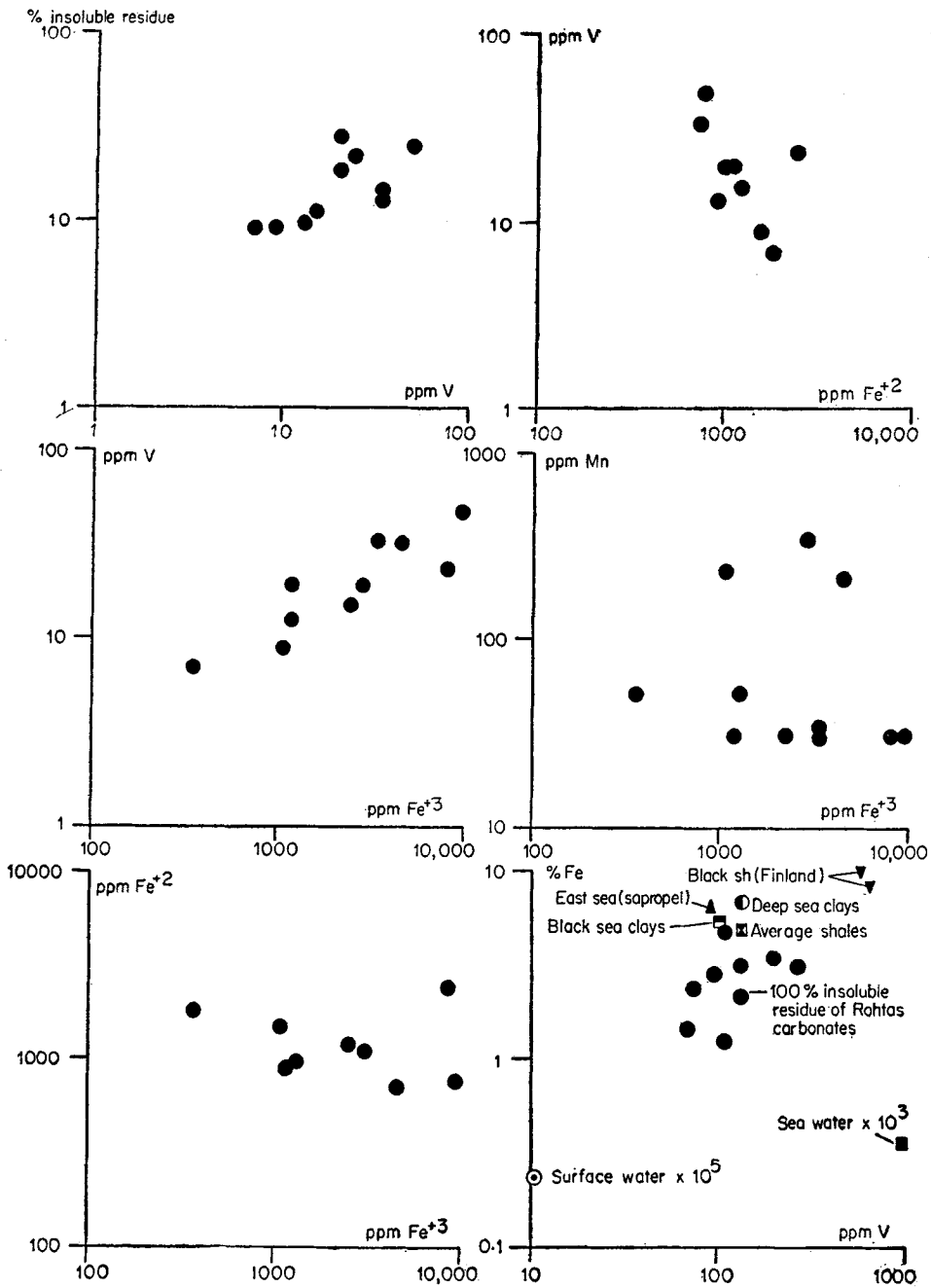


Figure 3. Correlation between different pairs of variables of the Rohtas carbonates and comparison with the recent sediments and averages of shales and limestones. The values plotted in % Fe-V graph are for 100% insoluble residue basis in the case of Rohtas carbonates.

relationship is insignificant. Iron in the rocks is a result of various modes like $\text{Fe}^{+2} \rightleftharpoons \text{Fe}^{+3}$ transformation and Fe^{+3} as detrital component. The iron, manganese and vanadium content of recent sediments of the Atlantic Ocean (Landergrén 1974) show a positive correlation between the pairs V-Mn and V-Fe.

6. Oxidizing and reducing environments

Oxidation state of iron and vanadium in the light of Eh-pH diagrams, mobilisation of manganese, Eh-pH boundaries between Fe_2O_3 and MnCO_3 have been used in the evaluation of data on Rohtas carbonates. $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio is commonly used as an indicator of Eh of the environment. At Eh + 0.77 volts, this ratio is nearly unity. For the $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio of the Rohtas samples, by substituting values in the Nernst equation, the Eh values have been calculated and are given in table 3. These values range from 0.73 to 0.95 which are very high compared to the normal marine and non-marine waters. The Eh of the sea water range from 0.2 to 0.45 volts, with an average 0.35 volts (data from Baas-Becking *et al* 1960; Manheim 1961; Van der Weijden *et al* 1970). At Eh 0.35 volts, the $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio comes to about $10^{-7.12}$, which indicates a very low concentration of Fe^{+3} ions in the medium. The high Fe^{+3} concentration in the Rohtas carbonates may be a result of detrital iron which gets fixed or absorbed on the detrital silicates.

Moreover at such a high Eh like 0.95 volts, vanadium is likely to exist as VO^{+2} or in the form of complex ions, instead of as V^{+3} which is a less soluble compound. Krauskopf (1967) has demonstrated that in a reduced state, V^{+3} seems to be a less soluble compound and gets preferentially adsorbed by ferric iron than by manganese oxide. Positive correlation between V and Fe^{+3} further supports this view. Accumulation of vanadium with the reducing agent like carbonaceous matter is a well-known process. The bituminous sediments have tens of times higher content of this element than the non-bituminous ones (see literature cited in Wedepohl 1974). The Eh necessary for V^{+3} precipitation as $\text{V}(\text{OH})_3$ is between -0.26 to +0.34 volts (data after Krauskopf 1967). According to Van der Weijden *et al* (1970), marine soft sediments are characterised by a pH of 7.6 and a Eh of about 0.1 volts. At this Eh-pH, vanadium forms complex compounds like $\text{CaU}_2\text{V}_2\text{O}_{12} \cdot 8\text{H}_2\text{O}$ and $\text{CaV}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$. But as the Rohtas carbonates do not show any correlation with calcium, it is likely that the vanadium concentration in the rocks may have taken place at negative Eh within the field of V^{+3} ions.

In the case of carbonate rocks, vanadium gets fixed in the insoluble residue and thus the vanadium content can be used to delineate the Eh-pH state at which the insoluble residue was deposited. During late-diagenesis, the vanadium content of the insoluble residue is not altered until the surface water is abnormally enriched in this element (generally surface waters are low in this element). In the case of Rohtas formation, it has been indicated in this paper that the manganese got separated from the ferric iron prior to late diagenesis. This means that much of the vanadium present in the solution has been adsorbed by the freshly precipitated ferric iron; this reduces chances of vanadium introduction during late-diagenesis. Therefore, in the case of Rohtas formation vanadium is an indicator of the initial environment of deposition of carbonate rocks.

Manganese is mobilised under reducing conditions. Whatever manganese occurs in the limestones is in the carbonate phase of the rock. Partitioning of

manganese between calcite and solution has been determined by Bodine *et al* (1965). By extrapolating their data for 40° C, it is possible to state that the marine calcite may contain approximately 20 ppm Mn. Higher manganese content reflects the higher concentration of this element in the medium. Ca/Mn ratio of the sea water is very high (1.3×10^5) as compared with the ratio for fresh water (1.9×10^3). At the site of deposition either in the deep sea or in the restricted basins, the Eh is invariably low and is of the magnitude that permits the Mn^{+2} to become mobile. Therefore chances of high manganese deposition in the soft sediments are rare; particularly when organic matter is deposited in the sediments. The work of Rossman and Callender (1968) and Crerar and Barnes (1974) has clearly demonstrated the mobility of manganese in the soft sediments during early diagenesis. Hem (1963, 1964) has shown that the particles like quartz, orthoclase and plagioclase catalyse manganese oxide precipitation in the environment where Eh-pH make the oxides to dissolve. This surmise seems to be justified in the case of sample R-4 where quartz content is fairly high, but high manganese in other samples like R-8 and R-1 cannot be explained by invoking this mechanism. Lange (1974) has reported a higher manganese content in the pelagic clays of Atlantic and Pacific Oceans, in which sediments with more than 60% $CaCO_3$ contain about 800 ppm Mn. Such higher values are apparently related to the manganese nodule formation and deposition of ferric compounds.

It is now clear that the high manganese content of the Rohtas carbonates is neither a result of early diagenesis nor is a product of adsorption on silicate mineral particles. It seems that late-diagenesis initiated by surface waters is a probable mechanism. Surface water is richer in manganese than sea water, and during late-diagenesis in surface waters chances of higher Eh are very likely. The iron content does not show a proportionate increase with Mn in the Rohtas samples. This appears to be the consequence of a complex geochemical precipitation process just before the late-diagenesis. With slowly increasing pH and an oxidising Eh, the ferric iron precipitation began while manganese remained in solution. In this connection, interpreting the Eh-pH diagrams given by Krauskopf (1967), one can easily find this situation between pH 4 to 6 and Eh around 0.4 volts. Using partition coefficient values for Mn in calcite and solution of sea water composition (by extrapolating data of Bodine *et al* 1965) the Rohtas samples with their high Mn content are certainly a product of at least ten times high Mn containing water than the normal sea. Surface waters can provide such a condition. The surface water of pH 5 when reacts with the carbonate rocks will be rich in Mn and partly depleted in Fe. Soon after the reaction of these waters with the rock, i.e., late-diagenesis, such waters might have been buffered with the dissolution of carbonates, resulting in higher pH. This is the optimum condition when the manganese may have co-precipitated with the carbonate phase. This explains why the Vindhyan carbonates are comparatively low in iron than the average limestones. It may be mentioned here that ferruginous laterite crusts are very common in the areas where carbonates are exposed.

7. Conclusions

The initial deposition of the carbonate rocks of the Rohtas formation has taken place in a negative Eh environment. The organic matter maintained the reducing

environment at the site of deposition. Early-diagenesis has mobilised the manganese out of the system thus resulting in low manganese content in the rocks. Late-diagenesis has taken place in an oxidizing condition during which manganese has been precipitated with the carbonate phase. Higher content of manganese in some of the zones is due to the continuous depletion of this element through spontaneous precipitation during progressive late-diagenesis.

Acknowledgements

The author is grateful to Professor Dr K H Wedepohl for guidance during the course of investigation at the Geochemical Institute, Göttingen, West Germany. This work has been carried out during the 'Alexander von Humboldt-Fellowship' tenure (1974-76), for which the author thanks the Foundation.

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