

GEOLOGY

Geochemistry

Fe²⁺, Fe³⁺, Mn AND V CONTENTS IN CARBONATE ROCKS OF THE KAJRAHAT FORMATION

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Paleo-physico-chemical environments that prevailed during the genesis of carbonate rocks of the Kajrahat formation are being determined by interpreting concentration of iron, manganese and vanadium in the carbonate phase and in the insoluble residue of the rocks. As compared with limestones, the dolomites record a higher *Eh* of their water of initial deposition. Higher manganese content in the rocks is a result of *late-diagenesis*, of which the waters were rich in manganese as compared with iron.

Keywords: Fe²⁺; Fe³⁺, Mn and V contents in carbonate rocks.

INTRODUCTION

THE purpose of this paper is to evaluate the oxidizing and reducing conditions that prevailed during the genesis of carbonate rocks of the Kajrahat formation of the Vindhyan basin in central India. Nineteen samples of these rocks (Fig. 1), collected from the Dala-Obra area of the Mirzapur district have been analysed for iron, manganese and vanadium as they are indicators of *Eh-pH* condition of the system. Oxidation of Fe²⁺ at a high oxidation potential (high *Eh*), accumulation of Mn under oxidizing conditions and accumulation of vanadium under sapropelic conditions are the basic parameters which have been used in the present study. A comparison with the average composition of limestones, average composition of shales and with the Recent sediments of the known environments seems to be useful to discriminate between sequences of oxidizing and reducing environments.

Using sedimentary structures, Singh (1973) has very precisely lithologged the changes in hydrodynamic energy levels during sedimentation of Kajrahat formation. Based on the boron data, Sharma (1978) has determined the paleosalinity of this carbonate sequence which suggests a rhythmic change in salinity from brackish (lower than marine) to marine conditions. The other aspect of genetic significance of these sediments is a reconstruction of paleo-physico-chemical environment which has been attempted in this paper. Partitioning of Mn in solution and calcite is a useful guide of Ca/Mn ratio of the water with which the limestones have lastly been in equilibrium.

The geology of Dala-Gurma-Obra area has been published by Auden (1933) and Misra (1969). The rocks of the Kajrahat formation constitute mainly limestones in the lower part and dolomite in the upper part of the sequence with intercalations of shales (Table I).

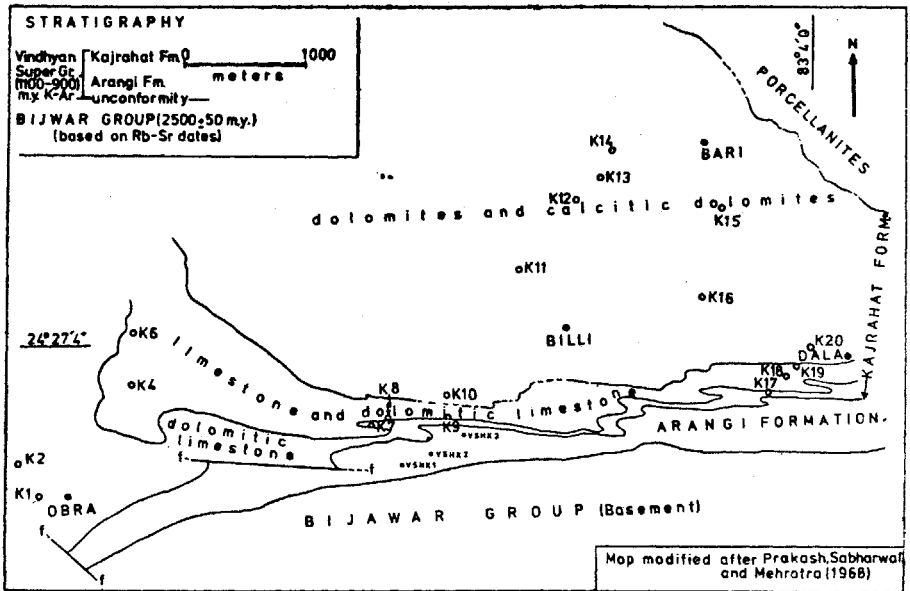


FIG. 1. Geological map of the Dala-Obra area showing lithological boundaries of the Kajrahat formation and sample locations.

TABLE I

Lithostratigraphy of the Lower Vindhyan in the Son Valley of the Mirzapur district

Group	Formations	Lithology
Semri Group	Rohtas Fm.	Limestones and shales
	Kheinjua Fm.	Dolomites, shales and sandstones
	Chopan Fm.	Porcellanites
	Kajrahat Fm.	Limestones, dolomites and shales
	Arangi Fm.	Shales, limestones and conglomeratesunconformity.....
BIJWAR GROUP (BASEMENT)		

ANALYTICAL METHODS

Total iron and manganese have been determined in the whole rock powder by the XRF using arsenic as an internal standard. Fe⁺² has been determined with the help of atomic absorption. Vanadium has been determined in the acid-insoluble residue by the emission spectrography using iron as an internal standard. The insoluble residue has been obtained by dissolving the rock powder in the dilute chloroacetic acid; and it has been confirmed that during this process, vanadium does not go into solution. To check reproducibility of the data several international standards have been analysed. Mineralogy of the samples has been studied

by Sharma (*in press*) by X-ray diffraction, major element analysis and infrared spectroscopy.

ANALYTICAL DATA

The rocks of the Kajrahat formation range in composition from cement grade limestone to dolomitic limestone, dolomites and calcitic dolomites with intercalations of thin calcareous shales grading into limestones. The insoluble residue fraction ranges from 12.7 to 23.8 per cent. The average iron contents of the limestones and dolomites are nearly similar but much lower than the average iron of the average limestone computed by wedephol (1970*a,b*). However, the Fe^{+3}/Fe^{+2} ratio is much higher (0.5 to 8.3) in the lower part of the Kajrahat formation i.e., limestones and dolomitic limestones, while this ratio is comparatively lower in upper part of this formation (0.16 to 0.7) which contains dolomites. This shows that the dolomites are higher in Fe^{+2} content as compared with the limestones. Major part of the Fe^{+2} is situated in the carbonate phase of the rock while less than ten per cent of the total Fe^{+2} of the rock occurs in sulphide phase (Table II).

TABLE II

Analytical data on the carbonate rocks of Kajrahat formation

Sample No	Insoluble residue wt. %	Calcite wt. %	Dolomite wt. %	Fe^{+2} ppm	Fe^{+3} ppm	Mn ppm	V ppm
K1	13.8	72.6	13.3	2400	2280	270	16.3
K2	19.9	54.8	25.1	2030	7100	430	27.7
K7	17.4	65.4	18.1	2540	5060	80	27.8
K9	16.6	78.2	5.9	660	5330	500	31.2
K17	20.5	74.8	4.3	1330	5470	20	25.4
K4	15.7	71.0	13.3	570	4730	180	23.0
K5	18.0	70.5	11.5	—	6300	1080	25.7
K8	13.4	78.1	8.8	3530	1070	960	13.5
K18	12.7	73.4	14.4	3740	1860	1250	12.7
K6	14.9	70.0	14.0	1140	3220	60	23.0
K19	16.9	77.4	4.8	5470	3920	850	12.6
K20	17.0	77.4	6.4	4340	5460	1850	12.8
K10	20.3	9.5	68.9	3640	1950	600	14.1
K11	15.4	11.1	72.7	4460	1930	740	13.8
K12	18.6	11.6	71.0	4880	760	50	6.0
K13	23.8	10.6	64.9	6580	1610	860	11.1
K14	19.3	9.4	70.1	2520	1770	390	14.7
K16	18.2	5.1	88.5	5150	2640	370	22.5
K15	18.9	2.2	74.7	5030	1360	160	14.6
Standards analysed as unknown in triplicate :				$Fe(Z)$ %		Mn ppm	V ppm
GSP-1				3.0		314	68
ZGI-BM						1275	
ZgI-TB							101

The manganese content of the whole sequence ranges from 20 to 1850 ppm. It is in the carbonate phase of the rock. Based on the partitioning coefficient of manganese between solution and calcite of marine environment (as 20 ppm Mn in calcite), the samples have been divided into two groups : (a) containing Mn upto 50 ppm and (b) containing more than 50 ppm Mn. The latter group indicates that the solutions were high in manganese content, i.e., Ca/Mn ratio is lower than the normal marine waters. Three samples which fall in first category are limestones and calcitic dolomites. Of these samples, as expected, the limestone (K 17) is comparatively low in manganese as compared with dolomite. As compared with the average composition of limestones (500 ppm Mn, Wedepohl, *Personal Commun.*), the Kajrahat carbonates are fairly high in this element (Table III). The Mn/Fe(Σ) ratio varies from 0.003 to 0.22. The variation in the manganese content shows a fluctuation in the composition of water at all levels while iron registers a systematic variation from limestone to dolomite.

TABLE III

Manganese and vanadium content in the rocks of the known environments for comparison with the averages of the rocks of Kajrahat formation

Rocks	Mn ppm	V ppm
<i>Kajrahat</i> dolomitic-limestone	627	20.6
<i>Kajrahat</i> calcitic-dolomite	452	13.8
Carbonate rocks of <i>Russian platform</i>	527	
Dolomite-diagenetic	242	
Low-bituminous limestone		70
High-bituminous limestone		300
Limestones (average)	550	20
Bituminous carbonate rocks		300
Non-bituminous carbonate rocks		3.2
Recent-coastal carbonates	43 to 124	
Non-pelagic shales	600	130
Bituminous shales		1650

Data from Rennels and Schleicher (1956) ; Gulbrandsen (1960) ; and Wedepohl (1970a, 1974)

In the Kajrahat sequence, the vanadium content varies from 6 to 31 ppm. However, the dolomites and calcitic dolomites are much lower (13.8 ppm V average) in this element as compared with the limestones and dolomitic limestones (20.6 ppm V) of this formation. Since vanadium is fixed in the minerals of insoluble residue, it represents the environment of deposition of the insoluble residue which did not change during late diagenesis of the carbonate rocks. The average vanadium content of limestones is about 20 ppm V (Wedepohl, 1970). The information about vanadium in the present set of samples discriminates between the chemical environment of limestones and dolomites (Table III).

COMPOSITION OF THE INSOLUBLE RESIDUE

The carbonate rocks contain insoluble residue which is the detrital component of the whole rock. The insoluble residue contains quartz and feldspars, illite, chlorite, kaolinite and organic matter. They resemble the composition of shales. These detrital components of insoluble residue which are mainly silicates pass through various environments like weathering, surface waters, water column of the basin of deposition and environment of soft sediments. During all these processes, the constituents of insoluble residue react with the elements and compounds present in the respective waters. Therefore, the chemical composition of the insoluble residue is comparable with the average composition of shales because the latter pass through a similar sequence of deposition. Accumulation of trace elements in the residue will indicate the environment of deposition. If this insoluble residue is a normal shale, then the equivalent composition of the average shale may be the contribution in the rock. Therefore, iron, manganese and vanadium have been calculated (Table IV) by the following method :

For example sample K 1 contains 13.8 per cent insoluble residue.

The average V for average shales is 130 ppm.

Then 13.8 per cent insoluble residue of K1 will contain

$$\frac{130}{100} \times 13.8 = 17 \text{ ppm V}$$

The sample K1 contains nearly a similar quantity of vanadium, therefore the environment of deposition is of shales of normal condition. In the case of

TABLE IV

Probable contribution of the insoluble residue fraction calculated with reference to average composition of shales

Sample No.	Fe(Σ) ppm	Mn ppm	V ppm	Eh Volts	Sample No.	Fe(Σ) ppm	Mn ppm	V ppm	Eh Volts
K1	6651	82	17	0.76	K19	8145	101	21	0.76
K2	9591	119	25	0.80	K20	8198	102	22	0.76
K7	8386	104	22	0.78	K10	9827	121	26	0.75
K9	8000	99	21	0.72	K11	7422	92	20	0.75
K17	9880	123	26	0.81	K12	8965	111	24	0.72
K4	7567	94	20	0.72	K13	11471	142	30	0.73
K5	8676	108	23	1.00	K14	9312	115	25	0.76
K8	6458	80	17	0.74	K16	8772	109	23	0.75
K18	6120	76	16	0.75	K15	9100	113	24	0.74
K6	7180	89	19	0.74					

[Eh has been calculated for Fe⁺⁺⁺/Fe⁺⁺ ratio of the whole rock with Fe⁺⁺ ⇌ Fe⁺⁺⁺ at 0.77 volts as given by Krauskopf (1967)]

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

sample K9, the whole rock contains 31.2 ppm V and 16.6 per cent insoluble residue. As compared with the average vanadium content in shale (130 ppm V), the insoluble residue (which is a shale) should contain 21 ppm V in sample K9. This means that the actual vanadium content in the rock (31.2 ppm V) shows an increase by 33 per cent of normal shale composition. This increase of vanadium indicates a suitable environment of deposition where vanadium accumulates; that means a reduction or high organic matter deposition. Such evaluations have been made for each sample and for each element. The vanadium content determined in these rocks is found in the insoluble residue fraction and no trace occurs in the carbonate phase. Vanadium has a tendency of accumulation in the sapropelic environment and in bituminous sediments. The sapropelic shales of East Sea and Black Sea contain 90 and 100 ppm V respectively (Wedepohl, 1974). Comparing these values with the data given in Table II, it is clear that the limestones plot very close (Fig. 2) to the sediments of reducing environment while dolomites plot towards the sediments of oxidizing environment. Parsly bituminous limestone from Kansas contains 70 ppm V (data from Rennels & Schleicher, 1956), while highly bituminous limestone from Wyoming contains 300 ppm V (data from Gulbrandsen, 1960).

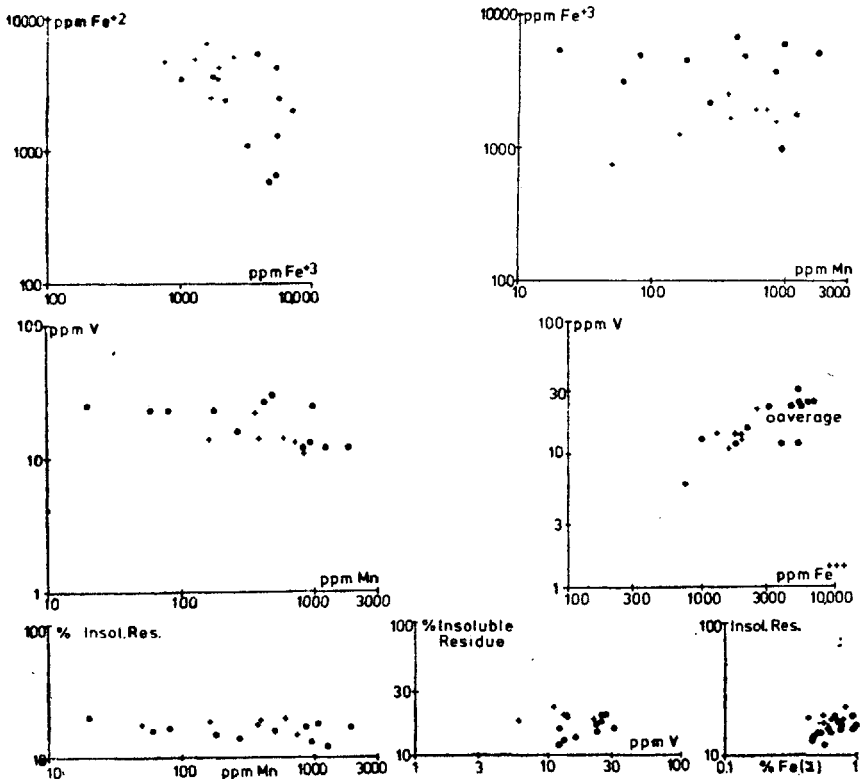


FIG. 2. Plots showing relationship of different pairs of elements and with the insoluble residue of the rocks. Signs used are : plus for dolomite and solid dot for limestone.

The manganese content of the rock is in the carbonate phase and almost negligible amount of this element occurs in the insoluble residue. With respect to manganese, the carbonate phase is much enriched as compared with the insoluble residue proportion of the average shale composition.

RELATIONSHIP AMONGST ELEMENTS

Experiments published by Krauskopf (1956) have demonstrated that the ferric iron oxide is a more effective adsorbent than MnO_2 . Therefore, vanadium may follow Fe^{+3} . Landergren (1974) from the Atlantic Ocean sediments has shown a positive correlation between V-Mn and V-Fe. Various relationships plotted in Fig. 2 show that positive correlation exists between insoluble residue-Fe(Σ), V- Fe^{+3} , Fe^{+3} -Mn in dolomites, V-Mn in dolomites, insoluble residue-V in limestones; and negative correlation exists between Fe^{+3} -Mn in limestones, V-Mn in limestones, Fe^{+2} - Fe^{+3} and insoluble residue-V in dolomites.

EVALUATION OF THE DATA

Fe^{+3} is the oxidized state of Fe^{+2} , and this oxidation is now quantitatively known with reference to Eh and pH of the medium. The greatest problem is to account for the detrital and colloidal iron deposited in the basin without undergoing this oxidation change within the basin. Fe^{+3}/Fe^{+2} ratio is commonly used as an indicator of the Eh of the medium. Another aspect is the behaviour of manganese in different chemical environments. During reducing environment, manganese is mobilised from the system; contrary to this, vanadium accumulates in sapropelic conditions. For the Fe^{+3}/Fe^{+2} ratio of the Kajrahat carbonate samples, by substituting values in the Nernst equation, the Eh values have been calculated and given in Table IV. These values range from 0.72 to 1.0 volts which are very high as compared with the marine and non-marine water. The Eh of the sea water ranges from 0.2 to 0.45 volts with an average of 0.35 volts (Baas-Becking *et al.*, 1960; Manheim, 1961; and Van Der Waijden *et al.*, 1970). Since such a high Eh as indicated by the Fe^{+3}/Fe^{+2} ratio is not normally possible in the basins, it is very likely that Fe^{+3} is also a result of detritus or colloidal ferric iron. The Fe^{+3}/Fe^{+2} ratio of all the samples show that the Fe^{+2} content is more in dolomites than the limestones. On the basis of vanadium content, the dolomites are products of higher Eh than the limestones. This means Fe^{+3} should be higher in dolomites than the limestones; but this is not the case. In fact, overall change in the source material and the environment is responsible for this variation. During the limestone deposition, ferric iron as colloid or detrital was added to the basin. Contrary to this, during dolomite deposition, the content of the ferric iron added to the system was lesser in quantity than the limestones. In this context, the Fe_2O_3 and $FeCO_3$ fields in the Eh - pH diagrams (data after Garrels & Christ, 1965) have to be taken into consideration. By superimposing such diagrams (Fig. 3) for various valency states of vanadium and vanadium compounds one finds a rectangle between pH 6 to 8 and Eh -0.1 to + 0.1 volts which contains boundaries between the fields of V^{+3} , V^{+4} , $FeCO_3$ and Fe_2O_3 . In this rectangle with a little fluctuation in Eh - pH of the system, different proportions of V, Fe^{+2} and Fe^{+3} would form less soluble compounds. At the boundary between

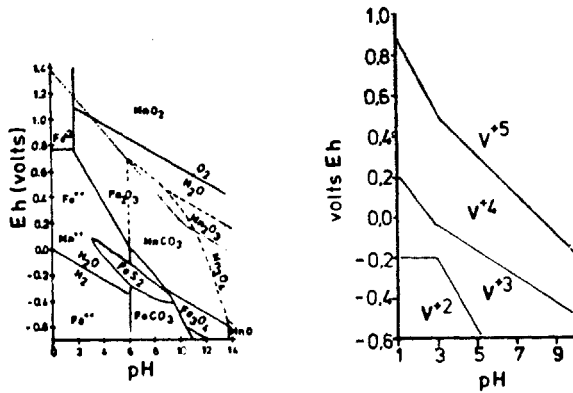


Fig. 3. Eh-pH diagrams showing phase boundaries of different valency states of Fe Mn and V and their compounds after: Garreis and Christ (1965); and Evans and Garrels (1958).

fields of FeCO_3 and Fe_2O_3 , a slight fluctuation in the Eh may have caused coprecipitation of Fe^{2+} in the carbonate phase and Fe^{+3} as oxide. Rapid precipitation of carbonates and eventual burial minimise chances of oxidation of Fe^{+2} into Fe^{+3} , thus resulting in low Fe^{+3} content in the rock.

Vanadium has a tendency of accumulating in a reducing environment. Wedepohl (1974) has given Eh-pA diagram for different valency states and compounds of vanadium. The field of V^{+3} is the most suitable region where less soluble compounds are formed. At a higher Eh, as calculated for $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio of the rock, vanadium is more likely to remain in solution. Of course at a pH higher than 7 and Eh more than 0.1 volt, some complex compounds like $\text{CaU}_2\text{V}_2\text{O}_{14} \cdot 8\text{H}_2\text{O}$ and $\text{CaV}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$ may form. On the basis of vanadium content, the Kajrahat formation can be divided into two regimes of chemical environment: (i) lower Kajrahat carbonates containing limestones of more reducing conditions than the overlying dolomitic sequence; and (ii) upper Kajrahat carbonates showing less reducing conditions than the lower limestone sequence. Since vanadium is found in the insoluble residue of the carbonates, of which the composition does not change during late-diagenesis, it is assumed that the vanadium content in the rocks is a result of Eh-pH condition of early-diagenesis or primary sedimentation. The bituminous material deposited in the sediments generally shows a higher accumulation of this element.

In the case of Kajrahat carbonates, the trend of vanadium indicates changes in the oxidation potential during sedimentation of this formation right from the base to the top of the sequence. This information brings out an important fact to light: why did the more oxidizing conditions prevail during sedimentation of dolomites as compared with the limestones? Had there been similar conditions of deposition then limestones would have formed, or the aragonite/calcite formed may have changed into dolomites. In this case, the vanadium content of limestones may have been retained after dolomite formation. But this is not the case. In fact, on the basis of vanadium, dolomite seems to be a primary product; of

course, it may have formed through various mineralogical changes involving aragonite, calcite, gypsum and hydromagnesium compounds. However, origin of dolomite is not the subject of the present paper.

Partitioning of manganese between calcite and solution has been determined by Bodine *et al.* (1965). By extrapolating their work for 40 °C, a marine calcite will contain approximately 20 ppm Mn. This means that if these carbonates have formed from marine waters then they should not contain more than 20 ppm Mn. This indicates that the manganese content in the calcite is dependent upon the Ca/Mn ratio of water. The Kajrahat carbonates contain from 20 to 1850 ppm Mn with a lot of variations in individual samples. Now the question arises that from where the manganese has come into the system, because whatever manganese is occurring in the rocks is in the carbonate phase and only less than 5 ppm is in the silicates or insoluble residue. Higher values of manganese in the Kajrahat carbonates are the result of water which had hundred times more manganese than the normal sea water while Ca remained constant. Chances of very low Ca/Mn ratio from sea water are remote, therefore, manganese has been added into the system during late diagenesis. Ca/Mn of the surface waters is very low as compared with marine water. Manganese is mobilised under redox conditions. In the deep sea sediments or in the restricted basins, the *Eh* is invariably low and is of the order that manganese becomes mobile. Particularly where organic matter is deposited along with sediments, a redox potential is maintained which helps migration of manganese from soft sediments to the overlying water column. Rossman and Callender (1958) and Crerar and Barnes (1974) have clearly demonstrated the mobility of manganese in soft sediments during early diagenesis. Therefore, chances of higher manganese within the carbonates are less during early diagenesis. During oxidizing conditions, manganese is less mobile.

Therefore, the high manganese content in the carbonate rocks of the Kajrahat formation is a result of late diagenesis. The surface waters rich in manganese have reacted with the early carbonates and have precipitated manganese in the carbonate phase. In the case of dolomites, Fe^{+3} and Mn show a positive correlation while limestones show a negative correlation. It is obvious because the conditions during dolomite formation were oxidizing which resulted in the change from Fe^{+2} to Fe^{+3} and simultaneously manganese was incorporated into carbonate phase a precursor of dolomite. Proportionate to the manganese increase, the iron has not increased in the same proportion in the rocks. Now the question arises, when the surface water is very high in iron (0.23 ppm) then why have not these carbonates been enriched in iron during late diagenesis? It seems that before the reaction of fresh water with the carbonates, water has been depleted in this element while manganese remained in solution. Higher manganese content in some of the samples depends upon the composition of water which changes as the water gradually moves through the rock.

Separation of iron from manganese is a very complicated process and takes place in a very narrow range of *pH*. An *Eh-pH* diagram showing stability fields of common iron and manganese compounds given by Garrels and Christ (1965) and Krauskopf (1967) indicate that between *pH* 4 and 6, Fe_2O_3 can precipitate while

Mn⁺² remains in solution. For this separation, the suitable *Eh* is 0.1 to 0.6 volts. These conditions are normal in surface waters but not in marine conditions. In the case of Kajrahat formation, the regolithic cappings occurring at the top of the sequence may be a product of such separation while manganese was carried in solution to react with the carbonate rocks.

CONCLUSION

As compared with limestones, the dolomites of the Kajrahat formation record a higher oxidation potential of their water of initial deposition. Higher manganese content in the rocks is a result of late diagenesis, of which the waters were rich in manganese as compared with iron. Surface waters which have caused late diagenesis in the carbonate rocks were depleted in iron prior to their reaction with the rocks. The Kajrahat carbonate sequence represents a continuous deposition in a basin. On the basis of vanadium content and Fe⁺³/Fe⁺² ratio, two regimes of chemical environments representing limestone facies and dolomite facies have been distinguished.

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