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DOLOMITIZATION OF PRECAMBRIAN LIMESTONE OF SATARI, NORTH GOA

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Abstract

The limestone comprises dominant dolomite and calcite followed by quartz, micas, chert and chalcedony. The CaO and MgO content varies from 29.88 to 42.68 percent and 2.69 to 16.04 percent, respectively. Insoluble residue varies from 1.03 to 12.70 percent. Based on mineralogy and chemical parameters the Satari limestone has been classified as (i) high magnesium to dolomitized and (ii) high calcium types. There is significant negative correlation between CaO-MgO and MgO-IR, but Fe-Mn and Fe/Mn-IR are positively correlated. Important diagenetic changes included recrystallization of calcite and replacement by dolomite, chert and chalcedony. The replacement origin of dolomite is clearly evidenced by various textural features such as xenotopic mosaic, continuity of cleavage planes from calcite to dolomite and relict features of calcite in dolomite grains. The possible source of Mg required for dolomitization can be ascribed in part to the Mg-rich brines probably result of igneous activity and partly during clay mineral transformations.

Introduction

The satari area forms a part of the Precambrian Dharwar belt of Goa State. The rocks include quartzites, quartz-sericite-schists, crystalline limestone and quartz-biotite schists, along with Deccan Trap, laterite and dolerite dykes. The area was first mapped by Oertel (1959), but the limestone formation was not shown in his map. Gokul and Srinivasan (1963), were the first to record the occurrence of limestone. Broad chemical parameters of the Satari limestone and its suitability for industrial application are given in Gopalakrishnan and Vishwanathan (1985). The present paper attempts an understanding of the texture, mineralogy and broad chemistry for evolving a suitable diagenetic model for the limestone.

Geological Setting

The general stratigraphic succession of the Satari area given by Gopalakrishnan and Vishwanathan (1985) is presented in Table 1.

The limestone formation conformably overlying the quartzite formation extends over a length of 20 km from Derodem in the east to Rivem in the west, with an exposed width of 40-120m (Fig.1). The formation comprises mainly fine to medium grained limestones, dolomitic limestones intercalated with thin bands/lenses/veins of chert and quartzite, banded ferrugenous quartzites and a few lenses of quartz-chlorite-actinolite schist. The outcropping limestone cliffs exhibit a characteristic ribbed appearance due to differential weathering of the calcareous and siliceous bands present in the rock. Owing to gentle dips of the beds and due to erosion, the limestones show a highly sinuous outcrop pattern. The limestone formation is conformably overlain by the metagreywacke formation, which in turn is overlained by Deccan traps. All the rock formations have been intruded by number of dolerite dykes trending in different directions, mostly N30-45°W and N50-65°E.

All the rock units trend in a N30-40°W direction near Derodem in the east, to N60-70°W to the north of Satrem and become nearly E-W in the Surlaghat. Further west, around Rivem and Galauli, the strike once again changes to NNW-SSE direction. The rocks are almost horizontally

TABLE 1: GENERAL STRATIGRAPHIC SUCCESSION OF THE SATARI AREA
(after Gopalakrishnan and Vishwanathan, 1985)

Age	*Formation*	*Rock Types*	
EOCENE		5	Dolerite dykes
		4	Deccan Trap
		-----Unconformity-----	
	Metagreywacke formation	3	Quartz-biotite-chlorite schist, calcareous and siliceous at base
	Precambrian Limestone formation	2	Crystalline limestone with intercalations of thin beds and lenses of chert, quartzite and banded ferrugenous and manganiferous quartzite
	Quartzite formation	1	Quartzite with intercalations of quartz-sericite schist, quartz-actinolite-chlorite schist, talc-actinolite-chlorite schist and thin bands of banded ferrugenous quartzite
		Basement not exposed	

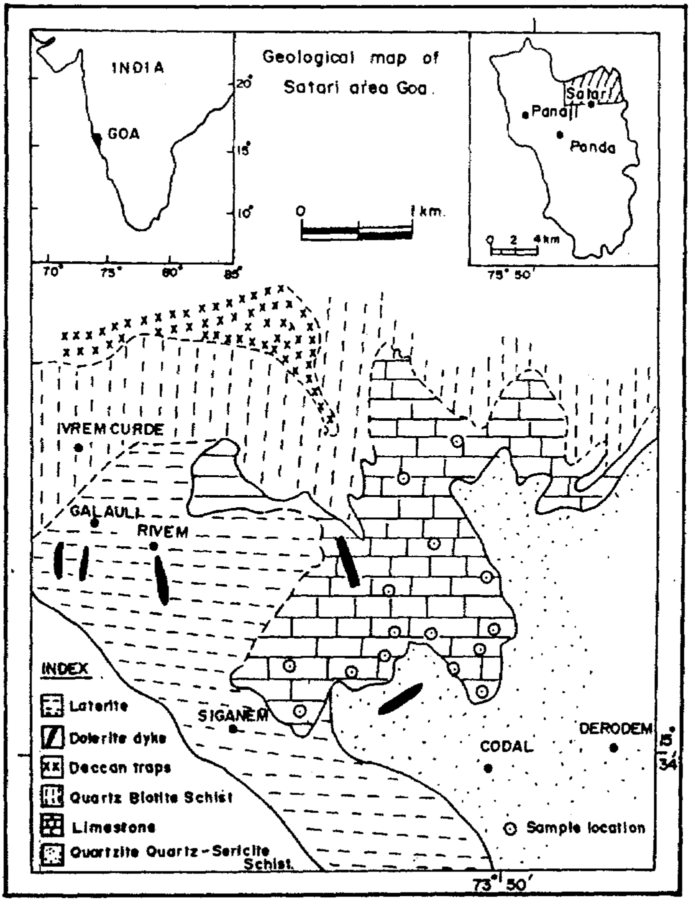
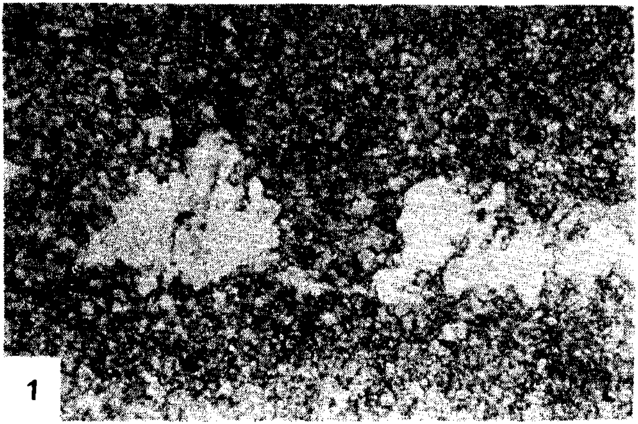
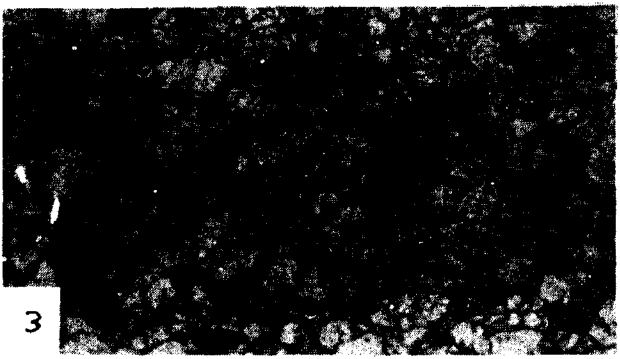


Fig. 1. Geological Map of Study Area Showing Sample Locations



1. Photomicrograph Exhibiting the Recrystallization of Calcite (Aggrading Neomorphism)

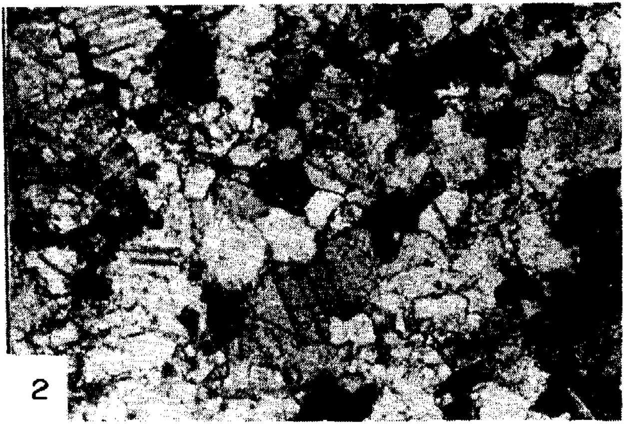
2.



3. Photomicrograph Exhibiting the Typical Xenotopic Mosaic of Anhedral to Subhedral Dolomite Crystals

4.

Plate 1



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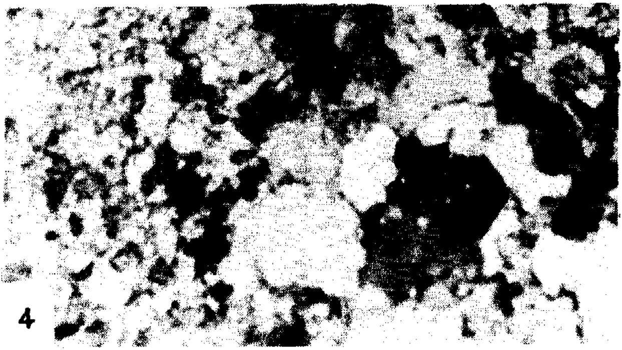
Photomicrograph of Satari Limestone Showing Dolomitization and the Mosaic with Irregular Crystal Boundaries



4

Photomicrograph Showing the Curved Cleavage Planes, Relict Calcite in Dolomite Indicating Replacement Origin of Dolomite Quartz Replacement is also Seen disposed or dip gently at 6° to 12° towards northeast and north. In the area to the west of Rivem, the rocks dip towards west. This part of Satari taluk appears to have been affected by intense recumbent folding, numerous evidences for which could be seen in Satrem, Parvad and Surlaghat areas (Gopalakrishnan and Vishwanathan, 1985). Further, in the Parvadghat and Surlaghat areas the overlying quartz-biotite-chlorite schists are brought below the limestone at many places due to recumbent folding.

Laboratory Methodology

In all about 30 limestone samples were collected form various localities (Fig. 1) and the same were examined for their texture, mineralogy, chemistry and diagenetic modifications. Thin sections of limestones were stained with alizarine red-S and observed under microscope to determine the broad carbonate mineralogy, texture and diagenesis. the detailed mineralogical analyses were carried out using XRD. The chemical parameters of the limestone, viz., CaO, MgO were determined by EDTA titration and Fe and Mn by spectroscopy.

Texture

The limestone is generally fine to medium grained, pale grey to deep grey, hard and compact in hand specimens and exhibits a typical non-clastic crystalline texture consisting of interlocking crystals molded to each other as in a mosaic. The individual crystals are smooth and regular to jagged and irregular in outlines. The individual calcite crystals are subhedral to anhedral whereas dolomite grains show almost a subhedral crystal forms. The more dolomitized varieties of the limestone with approximately uniform size of individual crystal show a typical xenotopic texture (Plate-1: 3) with non-planar, closely packed anhedral dolomite crystals with mostly curved, serrated or otherwise irregular intercrystalline boundaries (Plate-1: 2).

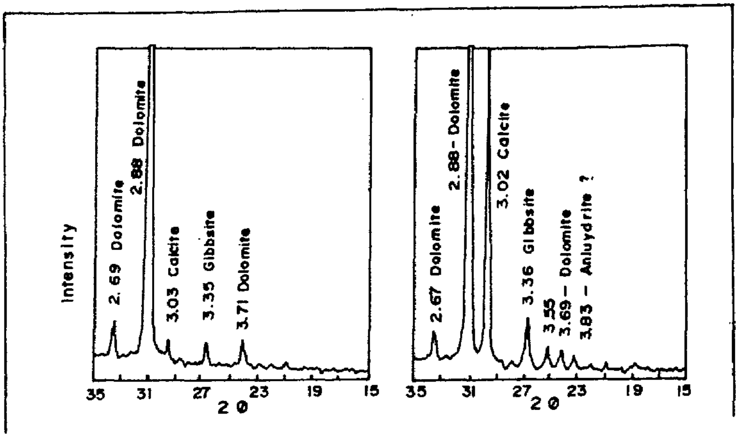


Fig. 2. X-ray Diffractogram of Representative Limestone

Mineralogy

Mineralogical composition as observed under the microscope and as determined by XRD analysis (Fig. 2) reveals the presence of abundant dolomite and calcite followed by quartz and a few grains of micas (biotite and muscovite), chert and chalcedony. Dolomite in the samples can be easily identifiable by uniform subhedral crystals with cloudy centres and clear rims, sometimes with strongly curved cleavage and crystal faces, showing undulose extinction (Plate-1: 4). The dolomite content varies from 12.26 to 74.14 percent with a mean value of 49.44 percent.

The individual calcite crystals are generally clear, fine to medium grained anhedral and show twinkling effect and high order interference colours. Twinning and cleavages are well developed and have optical continuity with dolomite whenever they occur (Plate-1: 2). In some places, cleavage planes in calcite seem to have served as the channels for magnesium rich brines with subsequent minute veinlets branching from these cleavages.

The quartz grains are medium to fine grained showing low relief and sharp extinction. Biotite and muscovite are the common mica minerals observed in these rocks by their characteristic optical properties. Some samples show the presence of fine grained colourless, sometimes isotropic chert grains. Chalcedony is a microfibrous variety of quartz with low R.I. Closer examination of chalcedony in the present samples shows the presence of submicroscopic aqueous bubbles. A form of chalcedony sometimes seen as a replacement of carbonate rock appears at low magnification like clouded quartz that extinguishes uniformly over relatively large areas. Under high magnifications, however, it appears to have a very fine parallel/mesh structure.

Diagenesis

For carbonates diagenesis is essentially the transformation into stable limestones or dolomites. Various factors that determine the nature and the product of diagenesis include (i) the composition of the original sediment, (ii) the nature of the interstitial fluids and their movements, and (iii) the physical and chemical processes involved in and the time subjected to them. The various diagenetic changes that can be observed in this limestone can be ascribed to late diagenetic modifications, that takes place under physicochemical conditions that differ from those of the original deposits, both during burial to increasing depths beneath younger deposits and also uplift and exposure to circulating ground waters or vadose solutions. The important diagenetic changes observed include (i) recrystallization of calcite and (ii) replacement by dolomite, quartz, chert and chalcedony, etc.

The recrystallization is mainly an aggrading recrystallization, i.e., transformation of fine crystalline calcite into coarsely crystalline calcite (Plate-1: 1). The replacements are mainly by dolomite leading to dolomitization of the limestone; some samples also show chert replacements (Plate 1: 4).

Geochemistry

The distribution of major, minor and trace elements are essentially controlled by depositional facies (Veizer *et al.*, 1974). In Phanerozoic rocks with abundant biota, such chemical criteria may be supplementary, but they may be indispensable for interpretation of unfossiliferous Precambrian carbonates. The limestone samples have been analyzed for selected chemical parameters. The chemical data is presented in Table 2 show the distribution of various parameters. In general, the CaO and MgO contents of the limestone vary between 29.88 and 42.68 percent and 2.69 and 16.04 percent, respectively. Insoluble residue varies from 1.03 to 12.70 percent. The Fe and Mn contents of these limestones range from 73 to 188 ppm and 29 to 198 ppm, respectively.

Based on the chemical and mineralogical parameters the limestones of the Satari area can be generalized as (i) high magnesium to dolomitized limestones, and (ii) high calcium or cement-grade limestones with high CaO and relatively low MgO.

The correlation analysis (Table 3 and Fig. 3a-d) of the chemical data show significant negative correlation between CaO-MgO and MgO-IR, Fe and Mn contents of the Satari limestone show almost a similar trend in their distribution, which is also confirmed from correlation analysis

TABLE 2: CHEMICAL DATA OF SATARI LIMESTONES

	Ca	*Mg*	*CaO*	*MgO*	*MgO/CaO*	$CaCO_3$	$MgCO_3$	*I. R.*	R_2O_3	*Fe*	*Mn*	*Fe/Mn*	*Dolomite*
1	24.00	7.56	33.62	12.60	0.375	60.03	26.46	11.50	2.01	170	189	0.899	57.45
2	26.00	6.21	36.42	10.35	0.284	65.03	21.74	8.25	4.98	138	168	0.821	47.20
3	27.40	6.49	38.40	10.82	0.282	68.57	22.72	1.03	0.00	151	182	0.830	49.33
4	22.90	7.84	32.06	13.06	0.407	57.25	27.43	11.80	3.52	188	168	1.119	59.55
5	23.10	7.92	32.36	13.20	0.408	57.75	27.72	9.32	5.21	94	58	1.621	60.69
6	23.90	7.84	33.25	12.88	0.387	59.37	27.05	12.01	1.57	73	29	2.517	58.73
7	29.19	2.21	40.86	3.69	0.090	72.96	7.75	11.08	8.26	186	183	1.016	16.82
8	27.60	3.64	38.66	6.01	0.157	69.03	12.74	10.07	8.16	162	154	1.052	27.58
9	30.49	1.61	42.68	2.69	0.063	76.21	5.65	12.70	5.40	156	176	0.886	12.26
10	24.57	6.41	34.40	10.68	0.310	61.43	22.43	10.80	5.34	165	188	0.878	48.70
11	24.20	7.01	33.90	11.68	0.344	60.53	24.54	5.63	9.30	127	159	0.799	53.27
12	23.99	7.29	33.58	12.15	0.362	59.96	25.51	11.20	3.33	149	177	0.842	55.39
13	22.35	8.31	31.31	13.85	0.442	55.90	29.08	5.88	9.14	163	171	0.953	63.15
14	21.34	9.62	29.88	16.04	0.537	53.36	33.68	4.16	8.80	152	184	0.826	73.14
15	25.04	7.67	35.05	12.79	0.365	62.59	26.86	10.81	0.00	132	181	0.729	58.32
Mean	25.07	6.51	35.10	10.83	0.321	62.66	22.76	9.08	5.00	147	158	1.053	49.44
S.D.	2.59	2.28	3.63	3.79	0.130	6.68	7.95	3.40	3.24	31	48	0.468	17.30
Min.	21.34	1.61	29.88	2.69	0.063	53.36	5.65	1.03	0.00	73	29	0.729	12.26
Max.	30.49	9.62	42.68	16.04	0.537	76.21	33.68	12.70	9.30	188	189	2.517	73.14

TABLE 3: CORRELATION COEFFICIENT MATRIX FOR CHEMICAL DATA OF SATARI LIMESTONES

	Ca	*Mg*	*CaO*	*MgO*	*MgO/CaO*	*I. R.*	*R_2O_3*	*Fe*	*Mn*	*Fe/Mn*	*Dolomite*
Ca	1.0000	–.9457	.9999	–.9456	–.9708	.2052	–.0466	.2391	.2192	–.1775	–.9461
Mg	–.9457	1.0000	–.9457	.9999	.9891	–.3471	–.1941	–.3315	–.2042	.1503	.9999
CaO	.9999	–.9457	1.0000	–.9455	–.9707	.1986	–.0420	.2481	.2298	–.1908	–.9459
MgO	–.9456	.9999	–.9455	1.0000	.9893	–.3509	–.1917	–.3240	–.1947	.1390	.9999
MgO/CaO	–.9708	.9891	–.9707	.9893	1.0000	–.3254	–.0927	–.2908	–.1959	.1492	.9894
I. R.	.2052	–.3471	.1986	–.3509	–.3254	1.0000	–.1833	.0274	–.1894	.3000	–.3505
R_2O_3	–.0466	–.1941	–.0420	–.1917	–.0927	–.1833	1.0000	.2463	.1340	–.1960	–.1906
Fe	.2391	–.3315	.2481	–.3240	–.2908	.0274	.2463	1.0000	.8425	–.6867	–.3271
Mn	.2192	–.2042	.2298	–.1947	–.1959	–.1894	.1340	.8425	1.0000	–.9324	–.1990
Fe/Mn	–.1775	.1503	–.1908	.1390	.1492	.3000	–.1960	–.6867	–.9324	1.0000	.1485
Dolomite	–.9461	.9999	–.9459	.9999	.9894	–.3505	–.1906	–.3271	–.1990	.1415	1.0000

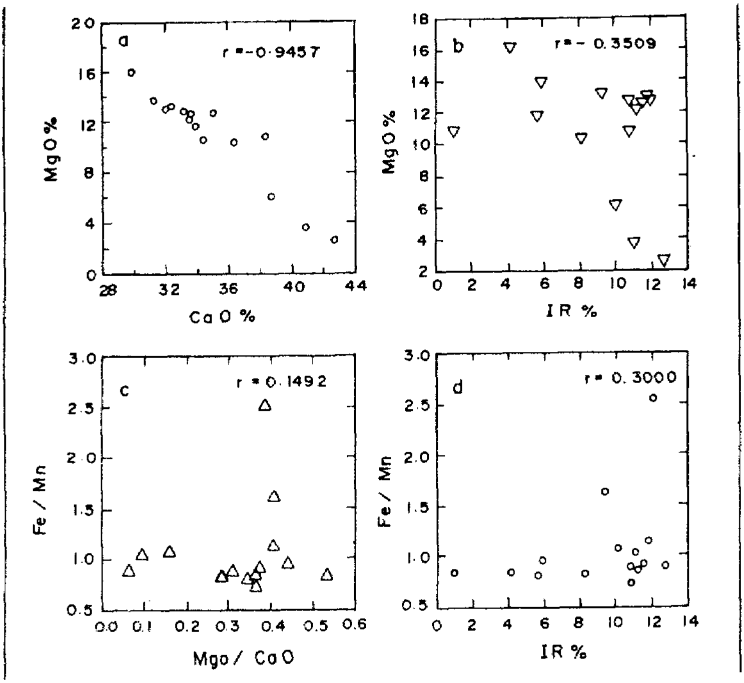


Fig. 3. Scatter Plots of Chemical Data

($r = 0.8425$). Fe/Mn ratio show a positive correlation with IR ($r = 0.3000$), suggesting that Fe and Mn are possibly associated with the non-carbonate residues.

Considerable attention has been paid in recent years to the relationship between MgO, CaO and IR. These studies have indicated (i) a direct correlation between Mg and IR content and (ii) a complete lack of IR-dolomite relation (Fairbridge, 1957; Matfield and Rohrbacker, 1966; Schmidt, 1964). On the contrary, a complete lack of IR- dolomite relationship has been reported in Goldisch and Parmales (1941). The present study of the Satari limestone corroborates the above view.

Discussion

Available compilations of sedimentary rock composition through time (Ronov, 1964) show that dolomite/dolomitic limestones are much more common than pure limestones in the Precambrian compared with the Phanerozoic. The two reasons assigned to account for the predominant dolomite/dolomitic limestones are either primary precipitation from sea water or the existence of conditions (environmental/geochemical) more conducive to dolomitization. Age alone and a longer diagenetic history are not the answer (Tucker and Wright, 1991). A majority of dolomite is of replacement origin, although dolomitic cement is common in the dolomitized limestone. The factors likely to promote direct precipitation from sea water are a higher temperature, higher PCO_2, higher Mg/Ca ratio, lower SO_4 and organic acid effects (Tucker and Wright, 1991). Although there is evidence from a variety of sources and with varying degrees of reliability that in the Precambrian the Mg/Ca ratio was higher (Schwab, 1978), PCO_2 was higher (Holland, 1984), temperatures were higher (Perry and Ahmed, 1983) and that SO_4 was lower (Schopf, 1980), the present study on Precambrian Satari Limestones with abundant dolomitic limestone do not suggest a primary origin of dolomite for various reasons.

The dolomitized limestone types of Satari can be related to late diagenetic dolomitization (replacement of calcite by dolomite) phenomena probably during burial history. Dolomitization can occur on deep burial where interstitial brines can have salinity 0.1 to 200 percent. This dolomite generally shows fine grained, sucrosic clear mosaic texture (Scofin, 1987). The dolomite is often late stage and can be shown to relate directly to voids and fractures. The replacement origin of dolomite is well-evidenced in the present samples by various textural features, such as the continuity of cleavage planes from calcite to dolomite and interconnected branching veinlets of dolomite within calcite and strongly curved cleavage and crystal faces and undulose extinction.

In general, two requirements must be met in order to cause dolomitization, namely, (i) the Mg/Ca concentration of water must be sufficiently high to permit the reaction to take place, and (ii) there must be a mechanism capable of flushing a sufficient volume of the dolomitizing fluid through the rocks so that the reaction can be completed and dolomitization takes place (Blatt *et al.*, 1980). The presence of porosity and permeability is essential for migration of Mg-rich solutions in the limestones. In the absence of this property, intergranular boundaries, cleavage planes and microfractures may serve as channels for migration of solution through the rocks. Generally the composition of formation waters (subsurface fluids) have lower Mg/Ca ratios (1.8 to 0.4) than sea water (Collins, 1975). Formation waters derived from evaporitic sequences, however, are likely to have a higher Mg content. The transformation of clay minerals with increased burial and rising temperatures is well documented and it is frequently suggested that Mg along with Fe, Ca Si and Ma are released on the conversion of smectite to illite (Boles and Franks, 1979; McHayne and Price, 1982) with Ca and Si being released early to precipitate as calcite and quartz cements and Fe and Mg later. The possible source of Mg for dolomitization of the Satari limestones may have been derived from shale or schist during compaction (Mg released during montmorillonite to illite transformation). It could also be from the magnesium content or magnesium calcite. It has been suggested that igneous activity, particularly of effusive nature, can increase the magnesium concentration in formation waters (Bissel and Chillinger, 1958). In the light of this it can be tentatively suggested that a part of Mg may have been derived from Mg-rich brines resulted due to the igneous rocks (effusive and intrusive) present in the area.

In general, the large scale dolomitization of limestones suggests the stability of the basin at the time of deposition and interbedded nature of high calcium limestones and high magnesium limestones reflects a post depositional late diagenetic history of dolomitization. The cross-cutting relationship of calcite to dolomite further supports the above view.

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