Geochemical Characterisation And Industrial Suitability Of Mesoproterozoic Carbonate Rocks Near Yellandu, Pakhal Basin, Southern India

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Abstract - *Major element geochemistry has been carried out on carbonate rocks viz., dolomite/dolomitic limestones of Mesoproterozoic age, belonging to Pakhal Supergroup at Yellandu, erstwhile Khammam district, Telangana to understand their geochemical character. The results of this study show that these rocks are enriched in MgCO3 and show paucity in CaO content. Hence the carbonate rocks of Yellandu may be classified as dolomites. Wide range of differences in the CaO content with other major elements is attributed to the variations in the physico-chemical conditions during the course of deposition. At places, effect of metamorphism leading to formation of marble bands is evidenced. The carbonate rocks appear to be suitable for refractory, steel, ferro-alloy and glass industries.*

Keywords- Limestone, Geochemical characterisation, Sedimentary environment, Mesoproterozoic, Pakhal Basin, India.

I. INTRODUCTION

large quantity of carbonate rocks comprising dolomites, dolomitic limestones and marbles is available in the eastern part of Yellandu town of former Khammam district in Telangana. In this paper, an attempt has been made to characterise these carbonate rocks on the basis of major element chemistry and thereby identifying their suitability for industrial usage.

Carbonate rocks act as important raw material in various industries. Different industries require different grades of these rocks which are defined by their chemical compositions. Some of the specifications are liste in Table 1 as per Bureau of Indian Standard (BIS).

II. LOCATION AND GEOLOGICAL SETTING

The study area is situated within the 7 km radius on the east of Yellandu town located in the NW part of the 65C Survey of India (SoI) toposheet. The terrain is rugged and comprised of curvilinear ridges and pediplain with occasional hillocks. The area exposes different rock types of different geological ages.

Table 1. Industrial specifications of dolomite/limestone [1]

Industry/Purpose		CaO%	MgO%	Insolubles
Refractory bricks	Grade-I	30	30	Acid insoluble <4.5%; SiO_2 <2%
	Grade-II	28	18	
Steel Plant	SMS/Flux Grade	29	21	SiO_2- <1%, Al_2O_3- <0.5%, Fe_2O_3- <0.5%, Moisture- <0.5%.
Ferro-alloy/Ferro-Manganese		28-30	19-20	SiO_2 2-5%, Al_2O_3- 2-2.5%.
Glass		53		Lime and magnesia 54.5 or more
Fertilizer	SiO_2- 5%, $CaCO_3$+$MgCO_3$- 90%.			
Lime				$CaCO_3$- 58-75%, $MgCO_3$- 28-48%.
Magnesium metal		58.10	40.5	Fe_2O_3- 0.85 and insolubles 0.6%.
Filler/ Extender	Free from coloring impurities (iron oxide, chromium, manganese etc.)			
Coal mining	SiO_2 <5%			

The oldest rocks in the study area belong to Archaean age comprising biotite-hornblende gneiss and migmatite, followed by Lower to Middle Proterozoic rocks composed of shale, quartzite, dolomite, arkose etc. The Proterozoic rocks are overlaid by Lower Gondwana rocks like green shale, felspathic sandstone, ferruginous sandstone, clays of Upper Carboniferous to Lower Cretaceous age (Fig.1). The Mesoproterozoic carbonate rocks are exposed in a curvilinear band with general strike varying from NW-SE to NNE-SSW with dips in a general easterly direction. The contact between the Talchirs and metamorphics is normal while that of the Kamthi with the latter is faulted. The fault zone is represented by presence of breccia.

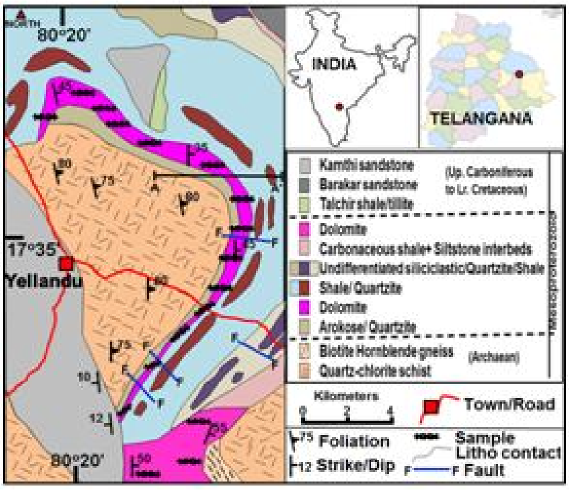


Figure 1. Location and geology of the study area. Modified after [2]

The outcrop trends NW-SE in the northern half and towards NE-SW in the southern part giving rise to serpentinous appearance. At places, the carbonate rocks appear to have undergone metamorphism producing marble. The geological succession of the area is shown Table 1. The curvilinear carbonate rocks are named as Gunjeda/Bayyaram, Formation in the northern part and Echencheruvu Formation in the southern portion of the study area. In field, quartzites, dolomites and sandstones stand as resistant ridges and shales develop depressions due to differential weathering to give present day's landscape. A geological cross-section has been constructed by measuring various strata with the aid of tape and compass method (Fig. 3).

Table 1. Geological succession of the study area [2]

Rock Type	Formation	Group	Supergroup	Geological Age
Ferruginous sandstone and shale with variegated clay	Kamthi Formation	Lower Gondwana	Gondwana Supergroup	Upper Carboniferous to Lower Cretaceous
Feldspathic sandstone, carbonaceous shale and coal	Barakar Formation			
Tillite, green shale and sandstone	Talchir Formation			
Dolomite	Echencheruvu Formation	Mulug Group	Pakhal Supergroup	Mesoproterozoic
Carbonaceous shale with interbeds of siltstones	Polaram Formation			
Undifferentiated siliciclastic	Jakaram Formation			
Shale Quartzite Quartzite Shale	Pandikunta Formation	Mallampalli Group		
Dolomite	Gunjeda/Bayyaram Formation			
Arkose/Quartzite	Bollapalli Formation			
Biotite-hornblende gneiss, migmatite, Quartz-chlorite schist			Peninsular Gneissic Complex (PGC) Khammam Group	Archaean

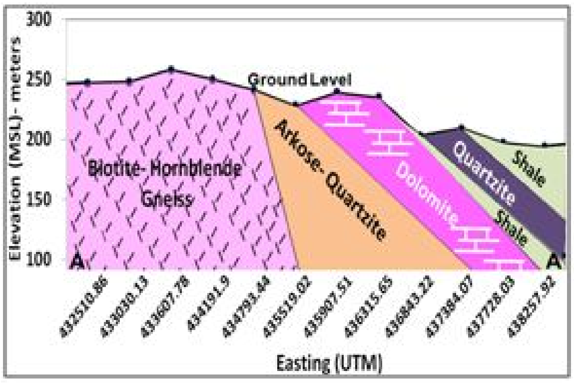


Figure 2. Schematic geological cross-section (A-A' in Fig.1) of various lithological units in the study area.

III. MATERIALS AND METHODS

Field traverses were conducted to ascertain the occurrence and continuity of carbonate rocks as well their relation with other lithological units. About 17 fresh outcrop samples of dolomite/dolomitic limestone have been collected. The samples were crushed and pulverised to a fine powder and major elements were determined using X-Ray Fluroscence Spectrometer (XRF) at an NABL (National Accreditation Board for Testing and Calibration Laboratories) accredited laboratory in Hyderabad. Each sample of this study refers to an average of 2-3 samples collected across an EW section (Table 2).

IV. DISCUSSION

The major element content of the carbonate rocks of Yellandu varies widely and is ascribed to the differences in the physico-chemical conditions at the time of formation of these sediments (Table 2). The data has been plotted to interpret the geochemical character..

Table 2. Major element content of samples in the study area.

	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
SiO_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Al_2O_3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CaO%	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
$CaCO_3$%	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Fe_2O_3%	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
MgO%	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
$MgCO_3$%	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Mg	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Ca/Mg%	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

The binary plots between various major elements and cationic weight percentages have been consturcuted to understand the geochemical character. In the binary plot between MgO and CaO, majority of the samples in the study area plot close to the dolomite region (Fig.3a). This is also supported by the ternary diagram of cationic weight percentages of Ca-Mg-Fe (Fig.3b).

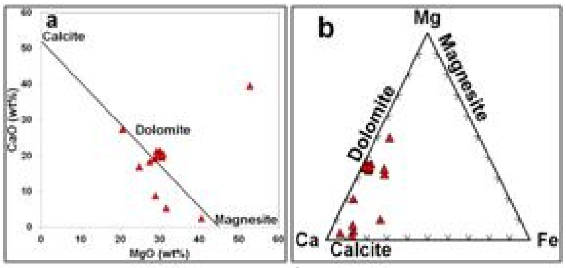


Figure 3 a. Binary plot between MgO and CaO [3] and b. ternary diagram between Ca-Mg-Fe for the samples of the study area.

The variation between CaO and SiO2 displays a positive correlation i.e., higher the CaO content higher is SiO2 indiating impure nature of these rocks (Fig.4a). While the binary plot of MgO versus SiO2 shows an inverse relation, the plot between MgO and MgCO3 demonstrates a clear positive correlation (Fig.4b and c). The bivariant diagram of CaO versus CaCO3 also shows that both the elements are directly proportional to each other in their content (Fig. 4d). In the bivariant diagram of SiO2 versus Al2O3, the samples of the study area show a slight positive correlation (Fig. 4e). The binary plot of MgCO3 versus CaCO3 displays an inverse relation (Fig.4f).

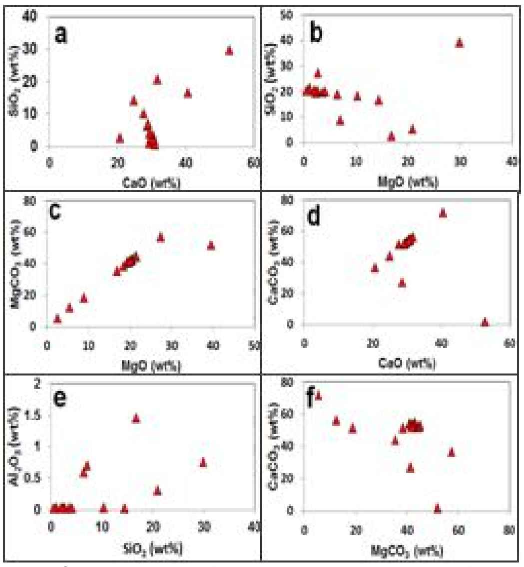


Figure 4a-f. Binary plots between various major elements in the samples of this study.

Majority of the samples appear to be dolomitic limestones while only one sample (YDL-7) possesses a high Ca/Mg ratio of 18.91 implying that it can be a magnesian limestone (Table 1). At this sample site in field, crsytallinity leading to the formation of marble is noticed at Munditog vilalge. The binary plot between Ca and Mg also supports this observation with the samples of the study area plotting in the dolomite field (Fig.5).

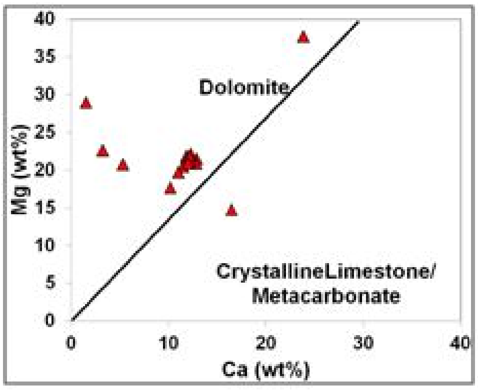


Figure 5. Binary plot between Ca and Mg showing samples of the study area. Fields after [4].

In the Proterozoic Basins, the carbonate-shale horizons widely vary in their depositional milieu spanning from shallow marine such as tidal flat, lagoon [5] to slope to basin [6]. This is in support of the presence of thick autoclastic carbonate mass-flow deposition [7].

It appears that the marbles of the study area, at Munditogu, are formed as a consequence of regional metamorphism of less impure magnesian limestones as evidenced from the presence of numerous needle-like crystals of tremolite. Jayaraman (1940) reported that the tremolite crystals occurring in these marbles are metasomatically unaltered [8]. This inturn indicates a low pressure-temperature metamorphism involving Tremolite facies (dolomite+ calcite+ diopside+ tremolite ± talc). Such a metamorphism in the absence of igneous intrusions in the area could have been caused by great pressure on the strata by folding and other deformation processes. Such processes during the formation and subsequent lithification processes impact the quality of the carbonate rock thus derived. Furthermore, addition of chemical impurities during the formation influences the purity of the carbonate rock. To evaluate carbonate rock purity and chemical characterization, several classifications are available (Table 3, 4 and 5).

Table 3 Classification and Purity of limestones [9].

Purity Category	$CaCO_3$%
Very High (VHP)	>98.5
High (HP)	97-98.5
Medium (MP)	93.5-97
Low (LP)	85-93.5
Impure (IL)	<85

Table 4 Classification of carbonate rocks based on Ca/Mg% [10].

Rock Type	Ca/Mg%
Magnesian dolomite (MD)	1-1.5
Dolomite (D)	1.5-1.7
Slightly calcarepus dolomite (SCD)	1.7-2
Calcareous dolomite (CD)	2-3.5
Highly dolomitic limestone (HDL)	3.5-16
Dolomitic limestone (DL)	16-60
Slightly dolomitic limestone (SDL)	60-105
Calcitic limestone (CL)	>105

Table 5 Classification and Purity of limestones [11].

Classification	MgO%
High-purity limestone (HPL)	0-1.1
Magnesian limestone (ML)	1.1-2.1
Dolomitic limestone (DL)	2.1-10.8
Calcitic dolostone (CD)	10.8-19.5
High purity dolostone (HPD)	19.5-21.6

In order to evaluate the suitability of carbonate rocks of Yellandu, Lime Saturation Factor (LSF) has been calculated [12]. The LSF is determined by the ratio of lime, to silica, alumina and iron oxide and govers the relative proportions of belite (C2S) and alite (C3S) during the lime clinkering process.

$$LSF = \frac{100\ X\ (CaO\% + 1.5\ MgO\%)}{(2.8\ SiO_2\% + 1.2\ Al_2O_3\% + 0.65\ Fe_2O_3)} \quad (4.1)$$

If the value of LSF is above 100% it indicates an excess amount of lime. The samples of the study area show LSF values ranging from 60.48 to 2714.79 indicating enrichment of calcic nature of these rocks.

To check and estimate the potentiality of carbonate rocks of the study area Silica Ratio (SR) has been calculated [13]. The SR is the ratio of silica to alumina and iron oxide.

$$SR = \frac{SiO_2\%}{(Al_2O_3\% + Fe_2O_3)} \quad (4.2)$$

In the study area, the samples show a range of SR values from 0.33 to 4.89 reflecting high proportion of silica and iron oxide.

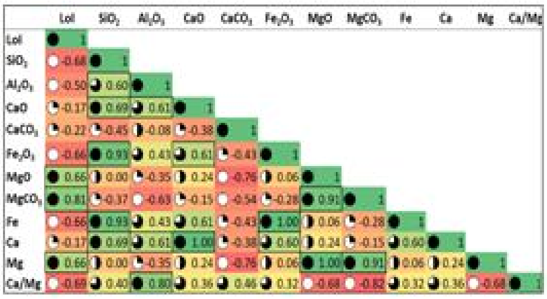
The alumina ratio (AR) is the ratio of Al2O3 and Fe2O3. The samples of the study area show AR values ranging from 0 to 0.48 indicating a high iron oxide content.

In general, insoluble chemical constituents like SiO2, Fe2O3 and Al2O3 are considered as deterious of dolomite for any inductrial use. It is essentially desirable that these insoluble ingredients should be as low as possible in their content. Based on the geochemical parameters, the carbonate rocks of the study area are classified into different categories (Table 4). In the carbonat rocks of the study area, stylolitic structures are observed at many places indicating the impure nature of these rocks.

Table 4.Chemical classification of carbonate rocks of the study. Codes as in Tables 2, 3 and 4.

	LSF	SR	AR	$CaCO_3$%	MgO%	Ca/Mg%
YDL-1	113.76	2.36	0	IL	CD	SCD
YDL-2	60.48	1.94	0.03	IL	DL	HDL
YDL-3	1964.57	1.89	0.06	IL	HPD	D
YDL-4	1025.21	3.14	0.05	IL	HPD	SCD
YDL-5	1443.42	0.49	0.01	IL	HPD	D
YDL-6	784.32	1.05	0.01	IL	HPD	SCD
YDL-7	84.81	2.35	0.26	IL	DL	SDL
YDL-8	121.27	2.38	0.06	IL	HPD	D
YDL-9	646.68	0.81	0.01	IL	HPD	MD
YDL-10	296.01	3.38	0.47	IL	HPD	SCD
YDL-11	2714.79	0.33	0.02	IL	HPD	SCD
YDL-12	570	3.37	0.04	IL	HPD	SCD
YDL-13	701.29	1.27	0.02	IL	HPD	SCD
YDL-14	969	1.94	0.03	IL	HPD	SCD
YDL-15	197.25	3.20	0.48	IL	DL	HDL
YDL-16	182.58	4.89	0.02	IL	HPD	SCD
YDL-17	469.48	2.17	0.02	IL	HPD	SCD

The correlation matrix displays positive relation between - SiO_2- Al_2O_3, CaO, Fe_2O_3, Fe, and Ca; Al_2O_3- CaO, Ca and Ca\Mg; CaO- Fe_2O_3, Ca, Fe_2O_3- Fe, MgO- $MgCO_3$ and Mg; Fe-Ca. The major element $CaCO_3$ shows a negative correlation with Fe_2O_3, MgO, $MgCO_3$, Fe, Ca, Mg and Ca/Mg (Fig. 6).



	LoI	SiO_2	Al_2O_3	CaO	$CaCO_3$	Fe_2O_3	MgO	$MgCO_3$	Fe	Ca	Mg	Ca/Mg
LoI	1											
SiO_2	-0.68	1										
Al_2O_3	-0.50	0.60	1									
CaO	-0.17	0.69	0.61	1								
$CaCO_3$	-0.22	-0.45	-0.08	-0.38	1							
Fe_2O_3	-0.66	0.93	0.43	0.61	-0.43	1						
MgO	0.66	0.00	-0.35	0.24	-0.76	0.06	1					
$MgCO_3$	0.81	-0.37	-0.63	-0.15	-0.54	-0.28	0.91	1				
Fe	-0.66	0.93	0.43	0.61	-0.43	1.00	0.06	-0.28	1			
Ca	-0.17	0.69	0.61	1.00	-0.38	0.60	0.24	-0.15	0.60	1		
Mg	0.66	0.00	-0.35	0.24	-0.76	0.06	1.00	0.91	0.06	0.24	1	
Ca/Mg	-0.69	0.40	0.80	0.36	0.46	0.12	-0.68	-0.82	0.32	0.36	-0.68	1

Figure 6. Correlation matrix between various major elements of carbonate rocks of the study area. Black filled circle/green shade- positive correlaition; While filled circle/ red shade- negative correlation and Quarter or half filled circle/Yellow shade- feeble correlation.

The relations and variations between various major elements might be due to the physic-chemical conditions at the time formation of these sediements and also the processes involved at the time of their diagenesis and lithification. Thus, this study shows that the carbonate rocks occurring at the eastern side of Yellandu are classified mostly as dolomites and may be suitable for steel, ferro-alloys, glass industry requirements.

V. CONCLUSION

The present study shows that the carbonate rocks exposed on the eastern side of Yellandu geochemically range from high purity dolomites to dolomites. The presence of tremolite marble bands within these dolomite horizons indicates regional metamorphism occurred afer the diangenesis and lithificaton processes. The quality parameters like LSF, SR and AR indicate that they are not suitable for cement manufacturing. However, they are useful as roadmetals, in steel industry, ferro-alloys, fertilisers, agriculture, magnesium production etc.

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