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(Research Article)

Geochemical suitability of Limestone for Cement making: A case study of Joldhal Formation

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Abstract

In this work, we investigate the industrial potentiality of limestone deposits in the Joldhal Formation of the Shimoga Schist Belt, Dharwar Craton. Based on their mineralogy, petrography, and geochemical characteristics. Twenty-five different limestone samples were collected from distinct locations and analyzed using X-ray fluorescence and X-ray diffraction techniques. Petrographically, these limestone deposits consist predominantly of calcite, quartz, chlorite, mica, micrites, etc. The X-ray diffraction studies indicated the dominance of calcite as an essential carbonate mineral, and quartz, kaolinite, chlorite, and mica/illite are major gangue minerals in the studied limestone. The results of the geochemical investigation of 25 samples indicated that the limestone from the study area exhibits a wide range of variation in LOI (27.99–42.82 wt%), SiO_2 (0.21–19.60 wt%), CaO (27.80–55.50 wt%), Al_2O_3 (0.11–8.48 wt%), Fe_2O_3 (0.23–9.28 wt%), and MgO (0.51–9.79). Traces of K_2O, Na_2O, and TiO_2 are found. This study illustrates how crucial it is to evaluate limestone's geochemical characteristics prior to cement making. Various factor analyses were calculated, like lime saturation factor, silica modulus, and alumina ratio, for suitable high-quality cement production. Bandigudda, Hanne, and Joldhal area valuable for cement manufacturing, unlike Medugondanahalli and Vitalapura, due to their impure quality and below-average parameter values. The results indicate suitability for cement production. The deposit's SiO_2, Al_2O_3, and Fe_2O_3 content meet the ultimate moduli values of the raw material, indicating its suitability for cement production. This study emphasizes the significance of the geochemical evaluation of limestone for cement production

Keywords: Limestone; Cement; Joldhal Formation; Geochemical Evaluation; LSF; Suitability; Major oxides

1. Introduction

India, a developing country requires significant amount of cement production. For this required vast limestone resources, which can be effectively utilized as industrial raw materials. Cement industry in India is among the core industries that is vital for economic growth and development. The quality and availability of industrial raw materials are usually critical prerequisites (Abou Elmagd, K et al 2018). A sedimentary calcareous rock, limestone is mostly made up of calcite with minor gangue minerals like mica, quartz, feldspar, and chlorite (Rao et al. 2011, Ali, K., and Tahir Shah, M. 2008). Limestone is crucial for any cement plant due to its primary raw material components like cement, iron and steel, metallurgy, chemical etc, due to owing major components of lime (CaO). Although limestone is the first raw ingredient used in the cement industry, where chemical characteristics are extremely important, limestone is a raw material that is widely used in various industrial sectors (Bouazza, N et al 2016). The worldwide cement industry is witnessing rapid growth and expansion. From this point of view, in this study, we investigate the required and suitable raw materials for this world. The quality and availability of the raw material components are the main factors influencing the cement industry (Voglis N. et al., 2005). Various researchers conducted an investigation that addressed the crucial goals of geochemical characterization, assessment, and prospecting of limestone raw materials (Cox, F. C et al 1997; Harrison, D. J. 1993; Mahrous, A. M et al 2010; Ismaiel, H. A 2012; Tseni, X et al 2013; Ali, M. A., & Yang, H. S.

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2014; Ozguner, A. M 2014; Azizi, S. H et al 2014; Eltalibi, H et al 2015; Bouazza et al 2016; Ismail, N. R. 2016; Konecny, P., et al 2017). Limestone deposits have contributed to development and construction projects throughout history.

It is considered one of a nation's essential resources. For manufacture of 1 ton cement 1.5 ton of limestone required. The cement grade limestone deposits ore depleting day by day due to over exploitation of high-grade ores Fig.2. Among the limestone production over 90 percent cement industry consumption Fig.1. However marginal grade ore not directly used for cement manufacture. Hence, many Indian cement industries are looking for available marginal grade ore with in the required geochemical range to sustainable in mineral resource and environmental conservation for future generations. India possesses enormous quantities of marginal grade limestone. Because of the overuse of high-grade ore that is necessary for industry, they are not geochemically homogenous. According to Indian cement industry manufacturers specifications, limestone for cement making, should contain more than 45% CaO; Fe_2O_3 as well as Al_2O_3 1 to 2%; free SiO_2 less than 8%. MgO should be ideally less than 3%, although as high as 5% MgO can be used by the cement industry. In order to attain these specifications, low grade limestone needs to be characterized in terms of their mineralogical characterization and as well as geochemistry of the limestone.

The demand for high-quality cement necessitates a meticulous assessment of raw materials, particularly limestone, Therefore, a thorough evaluation becomes imperative to ensure sustainable and cost-effective cement production. The geochemical characteristics of limestone, such as its mineral composition, chemical purity, and trace element content, directly impact the efficiency and quality of the resulting cement. More than 75 percent of the raw limestone required to make ordinary Portland cement. An on average of 80% of cement raw materials owing lime (CaO) bearing material. Ordinary Portland cement is made by reacting a substance comprising silica, alumina, and ferrous elements at a high temperature with limestone. Four primary components make up the product, called clinker: calcium aluminate (C_3A), dicalcium silicate (C_2S), sometimes called belite, tricalcium silicate (C_3S), and tetracalcium aluminoferrite (C_4AF). High-quality cement is produced by balancing the ratios of the four primary components.

The lime saturation factor is a crucial chemical parameter assessed through major oxide composition. It plays a very effective role in cement manufacture because it contains CaO, which is the primary constituent of cement (Ingram and Daugherty, 1991). Along with LSF, some others, like silica modulus and alumina modulus are important in the cement-making process. It controls the mineralogical phases formed during the clinkerization process in the kiln. The primary mineral phases in clinker are alite (C3S) and belite (C2S). Maintaining an appropriate LSF is essential for controlling the quality of clinker. LSF influences the reactivity of clinker. Optimal LSF helps to ensure the clinker phases balance for hydration, setting, and strength development while optimizing energy consumption.

In the present research, Joldhal Formation limestone of Archean age is investigated for its Geological and Geochemical characteristics and computation for cement product manufacturing. Representative limestone samples of diverse kinds were collected from several locations in Bandigudda, Joldhal, Hanne, Medugondanahalli, and Vitalapura, some of the nearby places. The aim of this investigation is to: i) reconcile the need for economic expansion with the obligation to protect the environment. ii) Evaluate the geochemical characteristics of specific geological formations for cement manufacture. iii) To find the raw materials with a minimal impact on the environment and the best utilization of available resources. Hence, geochemical as well as mineralogical characterization of the limestone, along with chemical parameters, are essential to maintaining and manufacturing good-quality cement and ensuring the consistent supply of suitable raw material grades to a cement plant.

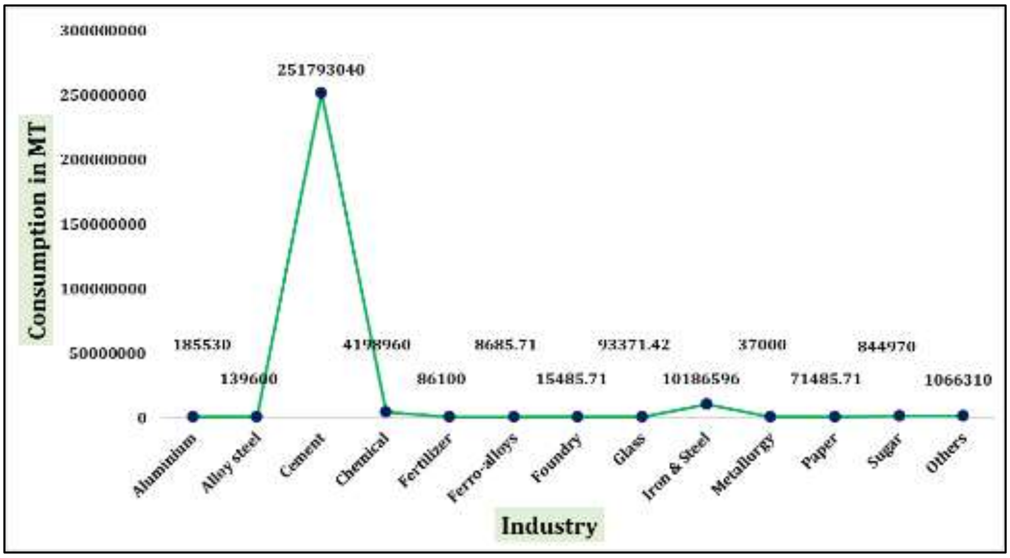

Figure 1 Depicts the consumption of limestone for various industries from 2010-2020. (Source: Indian Mineal Year book of Geological Survey of India)

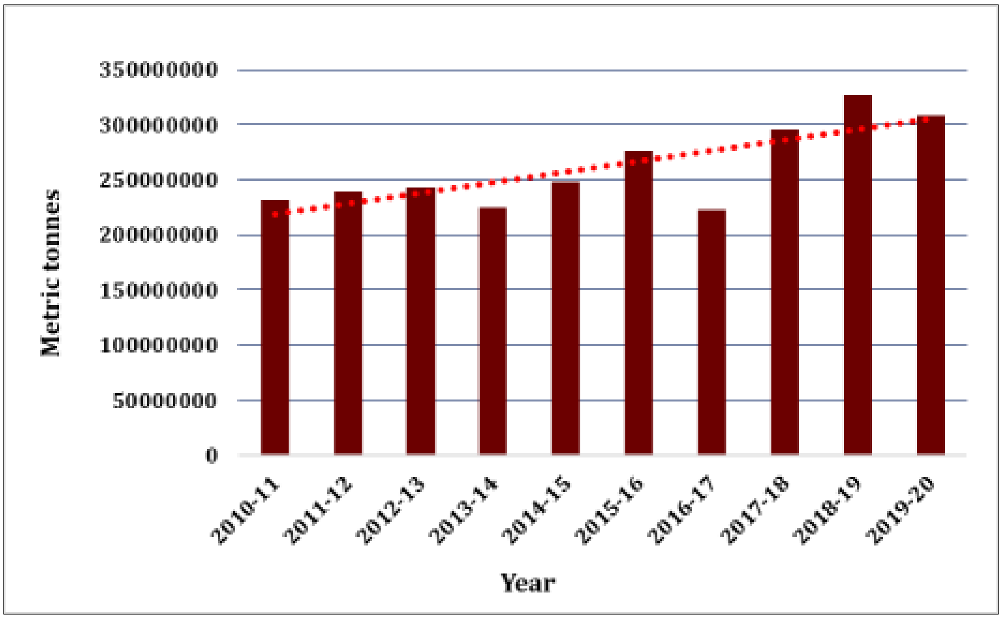

Figure 2 Illustrate the consumption of limestone in the cement production industry from 2010-2020. (Source: Indian Mineal Year book of Geological Survey of India)

1.1. Study area

The limestone in the present investigation is geographically distributed over three districts of Karnataka state of Davanagere, Shimoga, and Chikmagalur. The area extends over longitudes 75°48'00" and 75°59'24" E, latitude13°45'00" and 14°00'00" N and as depicted in Fig.3 In terms of geography, the region is well connected to a dependable road system from the major adjoining cities. It is characterized by a semi-arid climate and thick vegetation, and it has hilly terrain, a broad valley, and an undulating plain with complex elevations ranging from 250 m to about 940 m above mean sea level. A few isolated granite batholiths were exposed in the core of the forest region. The area receives 1813.9 mm of rainfall on average. The southwest monsoon accounts for 58% of total rainfall, whereas the northeast monsoon accounts for 22%. The area comprises a transitional zone of forests, and it enjoys isolated patches of moist deciduous and dry deciduous forests. The major drainage tributary of the Bhadra River flowing in the study region. The study region covers various soil types. The eastern part of the study site is occupied by two small ancient limestone quarries operated by VISL (Vishweshwaraiah Iron Steel Limited) under SAIL (Steel Authority of India Limited) for limestone extraction for steel-making purposes.

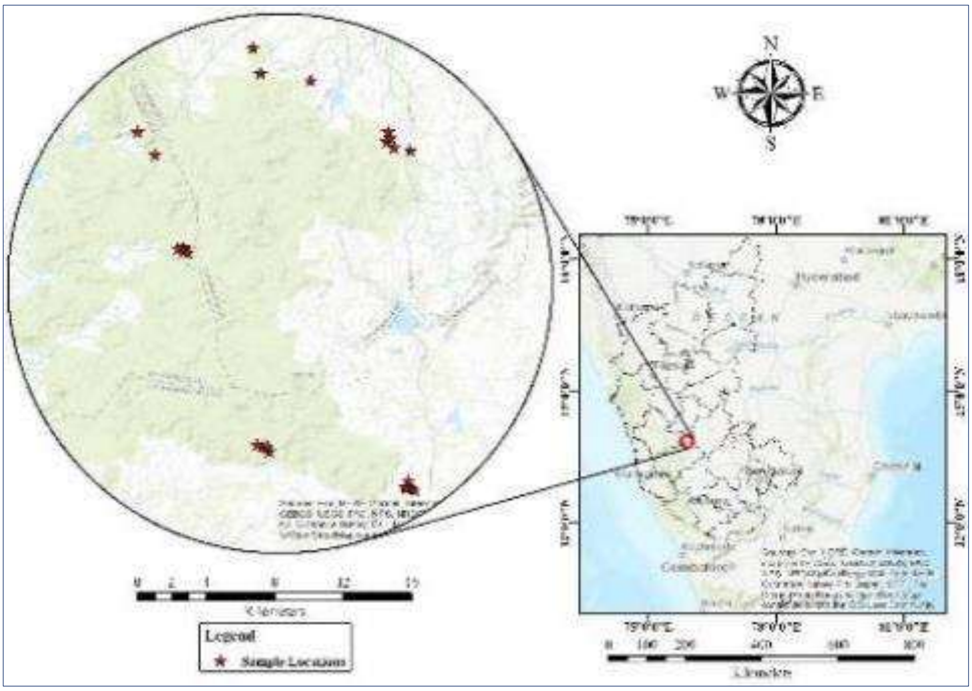

Figure 3 Depicts the sample location of the study area with sample locations

2. Materials and methodology

In the present studies, we have investigated the geochemical suitability of Joldhal limestone for cement production. Field work was carried out in the Joldhal formation, and twenty-five fresh limestone samples were selected from the vicinity of the Joldhal region of the study areas, five samples from each limestone patch. Samples were taken, stored in plastic bags, numbered, and then transferred to the Department of Applied Geology, Kuvempu University, Shankaraghatta, Shivamogga, for the preparation of thin sections of particular individual samples. For detailed petrographic studies, 25 selected limestone samples were prepared into thin sections and observed through an Olympus microscope in the Department of Applied Geology, Kuvempu University, Shankaraghatta. A selected sample was subjected to crushing, grinding (-200# size), preparing powder of the sample, and, after the required amount of sample was taken, analysis. For the detailed mineral phases, the identification of selected samples was examined using the XRD (X-ray diffraction) method analysed at Siddaganga Institute of Technology, Tumkur, Karnataka. The XRD analysis provides information about the mineral phases present in the particular samples. In the geochemical analysis, the major oxides of selected samples were powdered and analyzed using the XRF (X-ray fluorescence) method at the National Centre for Earth Science Studies, Trivandrum, Kerala.

3. Result and analysis

3.1. Mineralogical analysis

The mineralogical study used both megascopic and analytical methods using the X-ray diffractometer method with a Phillips X-ray diffractometer model and Ni-filtered Cu-Ka radiation at Siddaganga Institute of Technology, Tumkur. The limestone in the study area has different varieties; in the Micritic limestone, it looks rusty yellow, and some small microscale vugs fracture filled with quartz veins of fine grain quartz calcite veins and quartz intraclasts were observed in Fig. 4a, f, and h. Calc schist limestone is medium of low-grade variety greyish colour and a thin band of coarse calcite crystal was observed in Fig.4b. Another variety of massive limestone are dark green-coloured high-grade varieties, and visible small pyrite specks were observed in Fig. 4c; these are high-grade varieties. Crystalline limestone is well-developed calcite crystal noticed and ash grey in colour (Fig. 4d), and it is high-grade verities. A calcitic limestone is white with a well-developed calcite crystal (Fig. 4e). The coarse calcite grains of limestone result from metamorphism. This is also high-grade verities. Argillaceous limestone looks thin and muddy in colour and has thin parallel bands of calcite. Fig. 4g, it is low-grade verities of impure limestone.

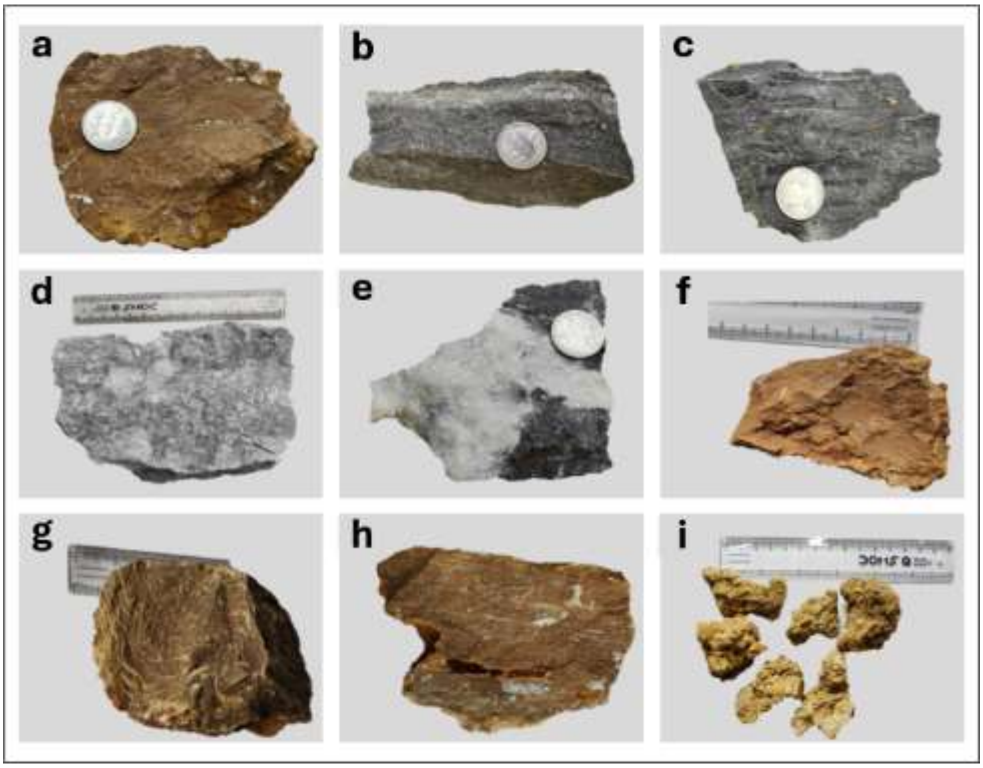

Figure 4 a) Micritic limestone, b) Crystalline Limestone, c) Massive Limestone, d) crystalline Limestone, e) white limestone, f) Micritic Limestone, g) Argillaceous Limestone with carbonaceous bands, h) Argillaceous limestone with elongated quartz intraclasts, i) Kankry nodulus from Hanne village

3.2. X-Ray diffraction analysis

The X-ray diffraction analysis is one of the important methods in the mineral fields, and it is the most efficient, accurate, and reliable technique to identify multiple mineral phases that can be present within the samples (Gunatilaka, H. A., & Till, R. 1971). It plays very important in modern applications; they provide detailed information about the mineral phase composition and crystallographic structure of geological materials. Traditionally, XRD-based quantitative phase identification has been performed using single peak techniques based on integrated intensities or peak heights (Klug, H. P., & Alexander, L. E. 1974). X-ray diffraction is a common technique that determines a sample's composition or crystalline structure, which is essential for understanding a wide range of geological applications. In the current study, we analyzed 25 limestone and related rocks using the Model Rigako, manufactured by Smartlab in Japan. Monochromatized Cu Kα radiation with a Ni filter was used to identify the mineral phases at Siddaganga Institute of Technology, Tumkur, Karnataka. All the sample diffraction data were collected between 5° and 80° and scanned at a speed of 2 theta (θ) degrees per minute. The diffraction pattern was indexed using interplanar spacing (d-value), peak position (2 theta degrees), and peak intensity. The obtained value is further compared with standard reference to identify the mineral. The analysis of the XRD peaks confirmed the existence of calcite ($CaCO_3$) for all the samples because the calcite has a trigonal crystal structure belonging to the hexagonal crystal system, and all samples were compared with JCPDS standards card No. 05-0586. The XRD analysis showed the dominance of calcite in the tested samples, while the associated gangue minerals are quartz, mica, and chlorite with some amounts of pyrite. Important. X-ray diffraction studies pattern shows of some important varieties of limestone mineral phases are provided in Fig. 5.

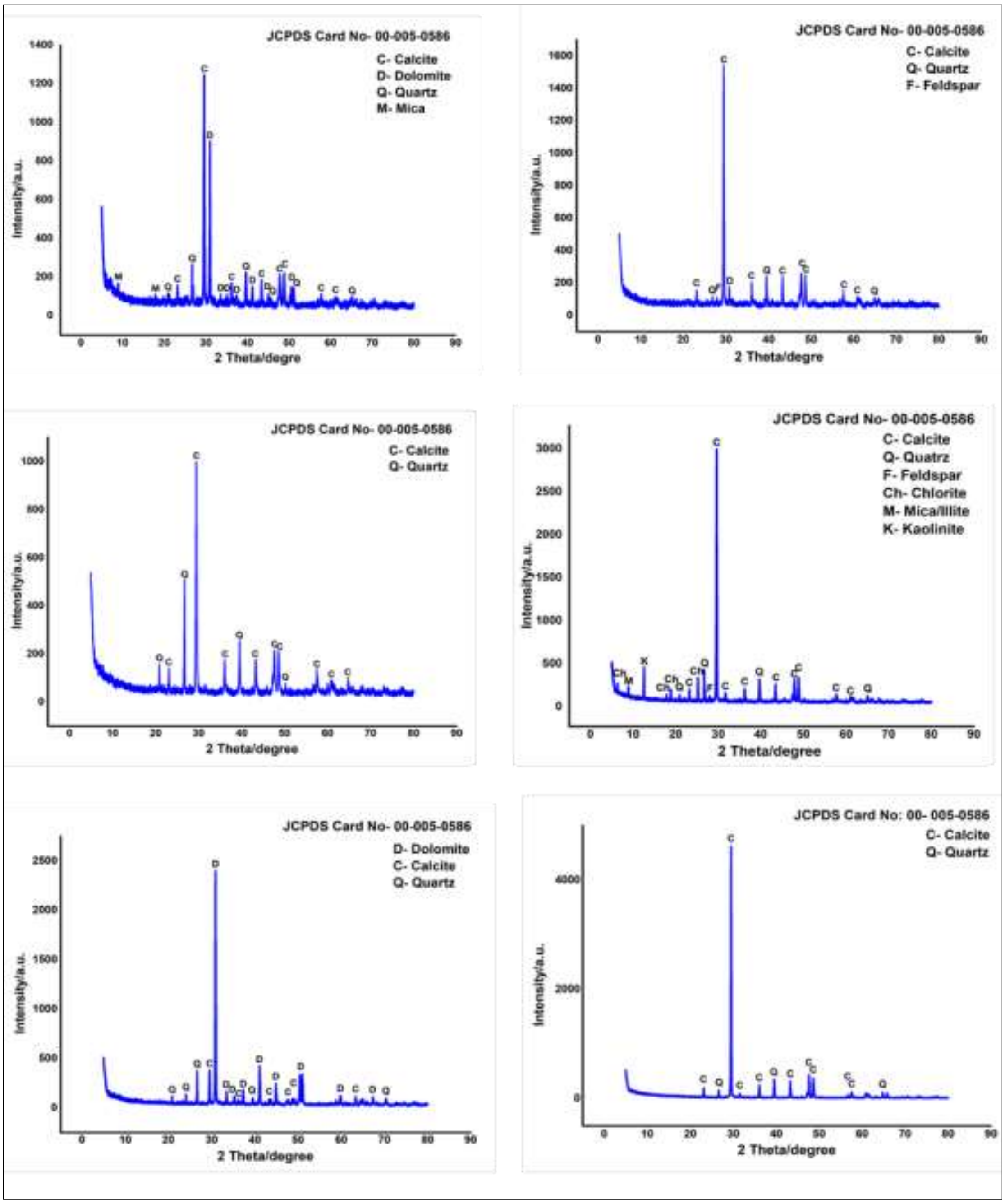

Figure 5 Micritic limestone, Crystalline Limestone, Massive Limestone, Calc schist limestone, white limestone, Argillaceous Limestone, Kankry nodulus

3.3. Petrographic analysis

A detailed petrographic study of Joldhal limestone was carried out through an optical microscope under the plane and cross-polarised light. A detailed description of the petrographic features that were observed in each limestone is provided in Fig. 6a-f. Microscopic petrological study shows that the limestone is greyish to brownish and not homogeneous, with a composition dominantly calcite micrites and quartz. It has been observed that they have an abundance of calcite, which constitutes the main part of the carbonate matrix. The identified quartz appears to be an important part of noncarbonate minerals. These limestone rocks have coarse to medium grain textures, and micritic limestone has a very fine carbonate matrix along with large intraclasts of quartz. The calcite is usually coarse-grained; the quartz is subhedral medium-grained. Fig.6a. The coarse calcite grains of limestone result from metamorphism. Some other noncarbonate minerals, mica and iron oxides (pyrite), are present in a very less and disseminated nature, as observed in thin section Fig. 6c. The microscale vugs fracture filled with quartz veins of fine-grain quartz calcite veins Fig. 6h. Further samples Fig. 6g and h showing micritic nature with quartz and chlorite intraclasts show this micrite deposition far from source areas of clastic sediment. In the calc-schist limestone, chlorite along with mica minerals show crenulated textures. In the massive limestone, quartz mineral books were noticed Fig. 6d. In the banded limestone, alternative mineral bands and microstylolite structure were observed Fig. 6.b. In Fig. 6i, fine carbonate grains were noticed. Moreover, the mineralogical and chemical compositions of limestone depend on its origin and depositional environment, which have had a direct impact on the cement-making process (Pettijohn, F. J. 1975; Blatt, H., et al., 1972; Ghosh, S. P. 1983).

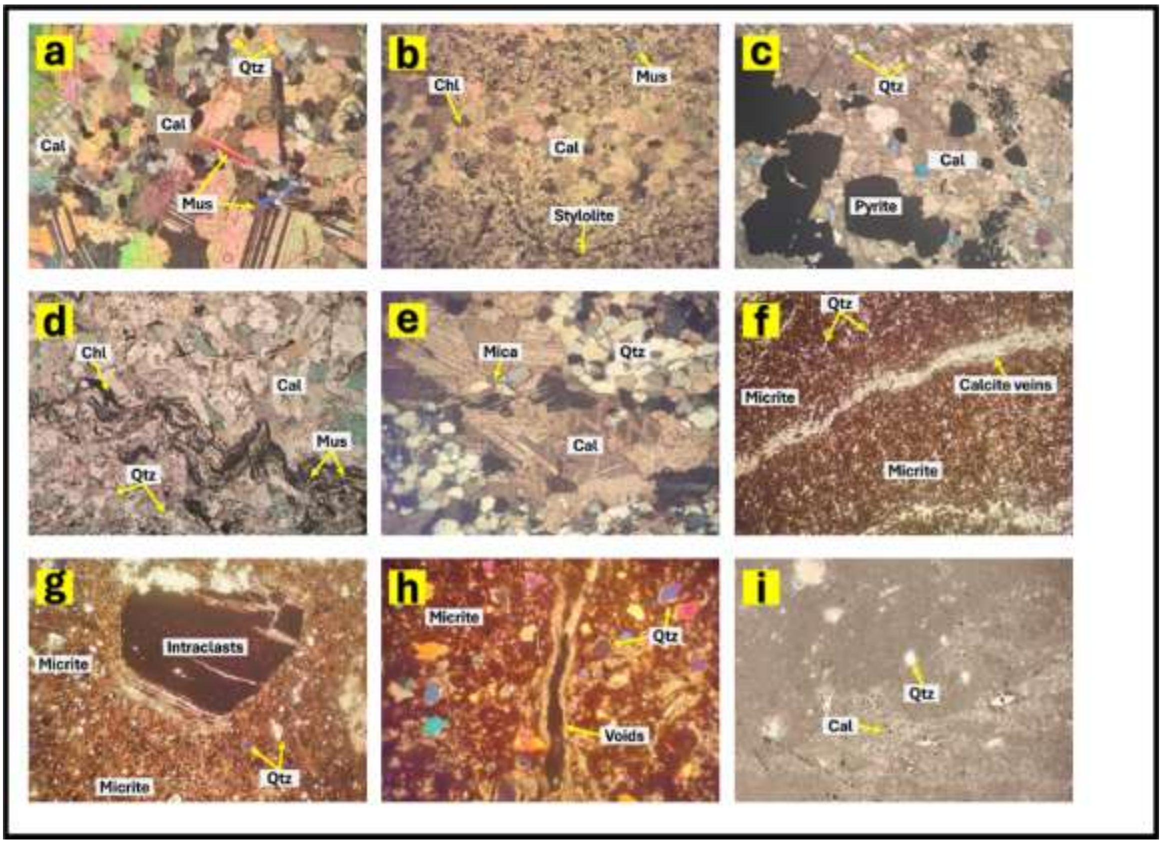

Figure 6 a) Crystalline limestone, b) Banded limestone, c) Massive limestone, d) Calc schist limestone, e) Massive limestone, f) Arillaceous limestone, g) Micritic limestone, h) Micritic limestone, i) Lime kankar

3.4. Geochemical analysis

Geochemical distribution of major oxide elements may provide direct information on the depositional environment. The obtained data on major oxides Table 1-5 for the studied selected limestone samples using the X-ray fluorescence method at the National Centre for Earth Science Studies, Trivandrum-Kerala. All major oxides elements show relative heterogeneity in the composition. CaO ranges from 55.50% to 27.80% Table 1-5. The results of geochemical analysis of the limestone samples show the highest CaO in the Bandigudda region, having 55.21%, and silica was 0.21% due to the calcite presence. In limestones, the increase of MgO content increases the dolomite component and may aggravate the alkali carbonate reactions in favourable conditions. Limestones with less than 4% $MgCO_3$ are termed "low mg-calcite (LMC), while limestones with $MgCO_3$ content greater than 4% are referred to as high mg-calcite (HMC). For applications like concrete, roadstone, cement, and dimension stone, less than 5% MgO by volume is required.

3.5. Major elements concentration:

Quantitative chemical analysis of the major elements indicated that calcite is the predominant mineral in the limestone samples. The geochemical analysis of 25 limestone samples from different parts of the study area revealed CaO concentrations ranging from 55.50% to 27.80% (averaging 41.13%) Tables 1, 2, 3, 4, and 5. The results demonstrate that calcium oxide (CaO) is the dominant component of the limestone, which is due to the fact that the limestone is largely calcite (Pettijohn, 1975), indicating that the limestone of this deposit is suitable for cement manufacturing. Magnesium oxide (MgO) has a value that ranges from 1.35% to 9.79% (averaging 3.85%), and this lower value also supports or indicates an exclusively calcite process. The percentage of silicon (SiO_2) is quite substantial, ranging from 0.21% to 19.60% (with an average of 9.75%). This indicates the existence of noncarbonate silicate minerals like chert silt and clay-sized sand particles. Fe_2O_3 amounts tend to be low, ranging from 0.23% to 9.28% on average (3.84%). This indicates that the depositional environment has a slightly lower oxidation effect. The low values show that the environment that deposits is a reducing type, which means that the pH of the water and the surrounding environment's redox activity do not support the precipitation of iron (III) to iron (II), and therefore the oxides are leached away (Brand, 1983). Major oxide ratios graphical representation is shown in the Fig.6.

Table 1 Chemical composition of limestone from Bandigudda area

Sample No	**BPR-03**	**BPR-07**	**BPR-10**	**BPR-11**	**BPR-16**	**Range**	**Average**
SiO_2	0.21	4.68	1.45	5.26	3.26	0.21 - 5.26	2.97
TiO_2	--	0.0373	--	0.0163	0.0256	0.0163 - 0.0373	0.0158
Al_2O_3	0.11	1.14	0.26	0.78	0.65	0.11 - 1.14	0.58
MnO	0.51	0.72	0.75	0.92	0.81	0.51 - 0.92	0.74
Fe_2O_3	0.36	0.62	0.37	0.23	0.71	0.23 - 0.71	0.45
CaO	55.50	52.30	55.1	48.41	51.25	48.41 - 55.5	52.51
MgO	0.51	1.08	0.71	1.92	1.86	0.51-1.92	1.21
Na_2O	--	0.0721	--	0.0129	0.0527	0.0129 - 0.0721	0.0275
K_2O	0.0053	0.22	0.0227	0.0450	0.0348	0.0053 - 0.22	0.1064
P_2O_5	--	--	--	0.008	0.005	0.005 - 0.008	0.0026
LOI	42.82	39.08	41.30	42.41	41.34	39.08 - 42.82	41.39
Total	100.0253	99.9494	99.9627	100.0122	99.9981	---	99.9895

Table 2 Chemical composition of limestone from Joldhal area

Sample No	**JPR-09**	**JPR-10**	**JPR-11**	**JPR-12**	**JPR-13**	**Range**	**Average**
SiO_2	5.72	10.40	10.50	8.28	7.17	5.72 - 10.50	8.41
TiO_2	0.21	0.24	0.25	0.33	0.26	0.21 - 0.33	0.258
Al_2O_3	3.27	5.20	4.93	4.21	2.69	2.69 - 5.2	4.06
MnO	0.90	0.82	0.21	0.18	0.72	0.9 - 0.72	0.566
Fe_2O_3	8.42	3.26	3.43	5.32	9.28	3.26 - 9.28	5.942
CaO	41.60	42.50	42.70	44.32	40.35	40.35 - 44.32	42.29
MgO	2.61	2.33	2.92	2.01	3.08	2.01 - 3.08	2.458
Na_2O	0.18	0.49	0.0522	0.40	0.16	0.0522-0.49	0.25656
K_2O	0.78	0.66	0.68	0.55	0.73	0.55 - 0.78	0.68
P_2O_5	0.0327	0.248	0.0179	0.10	0.21	0.0179 - 0.21	0.12172
LOI	36.20	34.03	34.26	34.30	35.34	34.03 - 36.20	34.82
Total	99.9227	100.178	99.9501	100	99.99	----	99.86228

Table 3 Chemical composition of limestone from Medugondanahalli area

Sample No	MPR-03	MPR-04	MPR-05	MPR-06	MPR-16	Range	Average
SiO_2	13.01	16.1	12.80	11.34	15.20	11.34 - 16.10	13.69
TiO_2	0.24	0.4	0.34	0.21	0.42	0.21 - 0.42	0.322
Al_2O_3	6.05	7.41	6.04	5.51	4.93	4.93 - 7.41	5.988
MnO	0.48	0.56	0.67	0.39	0.69	0.39 - 0.69	0.558
Fe_2O_3	7.03	5.88	4.40	5.01	4.59	4.40 - 7.03	5.382
CaO	34.02	35.6	33	36.58	35.08	33 - 36.58	34.856
MgO	8.03	2.42	7.11	6.21	5.24	2.42 - 8.03	5.802
Na_2O	0.0454	0.0601	--	0.0556	0.0021	0.0021 - 0.0601	0.0408
K_2O	1.09	1.19	1.62	1.38	1.37	1.09 - 1.62	1.33
P_2O_5	0.0207	0.0204	0.0382	0.0134	0.0228	0.0134 - 382	0.0231
LOI	29.98	30.23	33.65	33.3	32.45	29.98 - 33.65	31.922
Total	99.9961	99.8705	99.6682	99.999	99.9949	---	99.9139

Table 4 Chemical composition of limestone from Hanne area

Sample No	HPR-01	HPR-02	HPR-03	HPR-04	HPR-05	Range	Average
SiO_2	5.03	13.90	8.30	7.63	10.04	5.03 - 13.9	8.98
TiO_2	0.15	0.33	0.45	0.2	0.38	0.15 - 0.45	0.302
Al_2O_3	1.68	4.57	2.31	1.84	5.01	1.68 - 5.01	3.082
MnO	0.0178	0.41	0.051	0.024	0.19	0.0178 - 0.41	0.1385
Fe_2O_3	1.42	3.76	2.81	1.58	3.35	1.42 - 3.76	2.584
CaO	50.50	42.2	44.5	48.01	45.03	42.2 - 50.5	46.048
MgO	1.35	1.93	2.01	1.41	2.09	1.35 - 2.09	1.758
Na_2O	0.18	0.27	0.38	0.24	0.31	0.18 - 0.38	0.276
K_2O	0.0365	0.41	0.10	0.022	0.0238	0.0238 - 0.41	0.1184
P_2O_5	--	0.0145	0.0013	0.0030	0.0197	0.0013 - 0.0197	0.0077
LOI	39.57	32.06	39.08	39.04	33.56	32.06 - 39.57	36.66
Total	99.9343	99.8545	99.9923	99.999	100.0035	---	99.95672

Table 5 Chemical composition of limestone from Vitalapura area

Sample No	**VPR-04**	**VPR-05**	**VPR-06**	**VPR-07**	**VPR-08**	**Range**	**Average**
SiO_2	19.60	17.02	11.60	13.17	12.14	11.60 - 19.60	14.706
TiO_2	0.36	0.41	0.27	0.21	0.32	0.21 - 0.41	0.314
$Al2O_3$	8.48	8.09	5.32	6.37	7.50	5.32 - 8.48	7.152
MnO	0.23	0.17	0.24	0.29	0.31	0.17 - 0.31	0.248
Fe_2O_3	7.12	6.02	4.92	5.04	8.03	4.92 - 8.03	6.226
CaO	27.80	29.03	31.7	30.97	30.02	27.80 - 31.70	29.94
MgO	6	7.36	9.79	8.91	8.18	6 - 9.79	8.048
Na_2O	0.0491	0.0398	0.0725	0.0489	0.0362	0.0362 - 0.0725	0.0493
K_2O	2.20	1.81	1.22	1.48	1.33	1.22 - 2.20	1.608
P_2O_5	0.0488	0.0302	0.0173	0.0248	0.0228	0.0173 - 0.0488	0.02878
LOI	27.99	30	34.79	33.48	32.05	27.99 - 34.79	31.662
Total	99.8779	99.98	99.9398	99.9937	99.939	---	99.94608

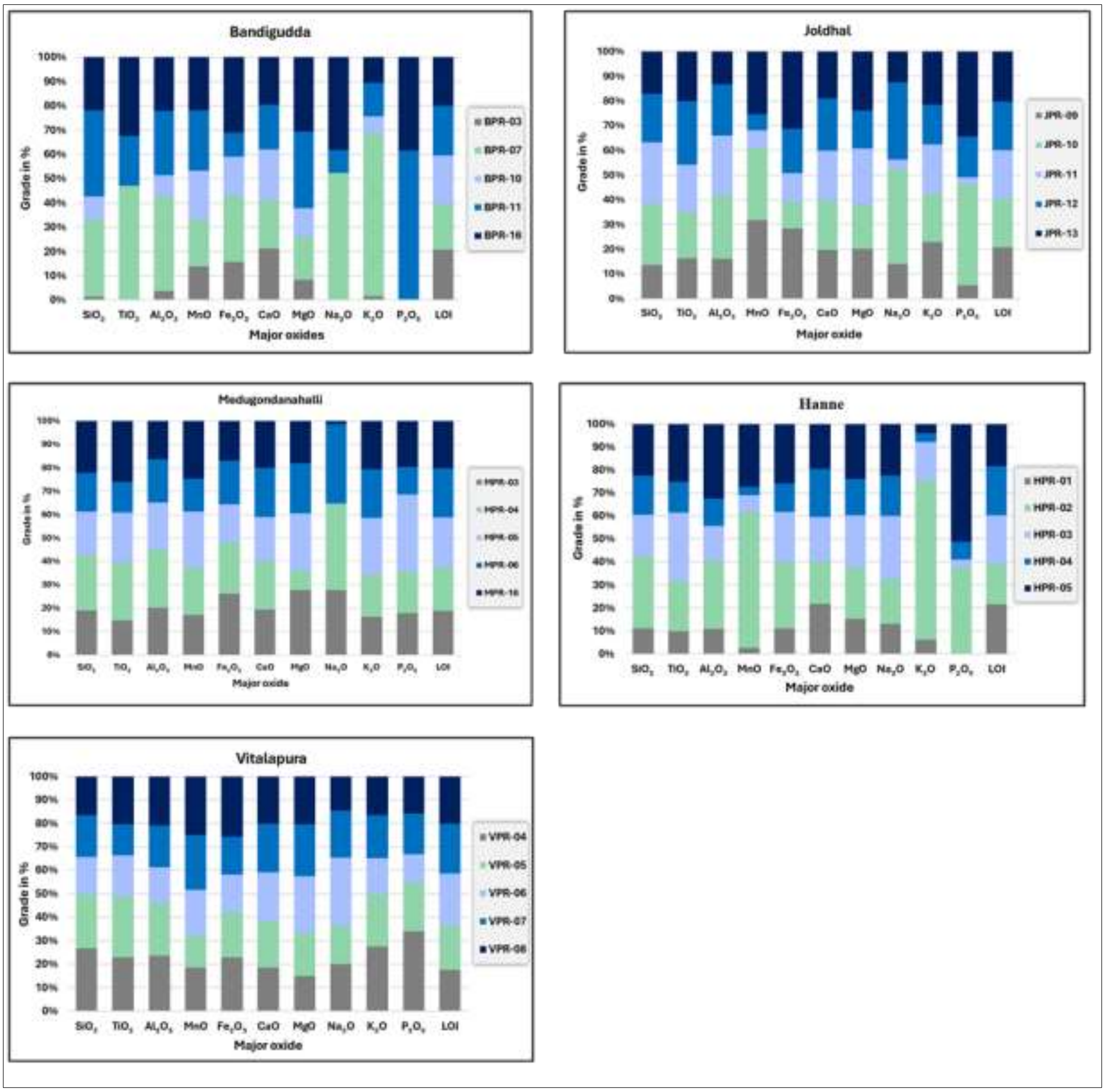

Figure 6 Represent the grade concentration % of major oxide various region of the study area

3.6. Ratio factor Analysis

Cement making requires essential major oxides in the raw material for balancing and proper burning for a good-quality cement product. Major oxides like CaO, SiO_2, Al_2O_3, and Fe_2O_3 require various confirmation tests, such as lime saturation factor (LSF), silica modulus (SM), and alumina modulus (AM) (Marzouki, A. et al, 2013).

Table 6 Illustrate the geochemical modulus result of procured limestone of the study region

Sample Code	Lime saturation factor	Silica ratio	Alumina ratio
BPR-03	58.18	0.45	0.31
BPR-07	3.52	2.66	1.84
BPR-10	11.95	2.31	0.71
BPR-11	3.07	5.21	3.40
BPR-16	4.95	2.40	0.92
JPR-09	1.64	0.49	0.39
JPR-10	1.14	1.23	1.60
JPR-11	1.14	1.26	1.44
JPR-12	1.40	0.87	0.80
JPR-13	1.38	0.60	0.29
MPR-03	0.71	1.0	0.87
MPR-04	0.62	1.22	1.27
MPR-05	0.72	1.23	1.38
MPR-06	0.88	1.08	1.10
MPR-16	0.69	1.60	1.08
HPR-01	2.97	1.63	1.19
HPR-02	0.91	1.67	1.22
HPR-03	1.60	1.63	0.83
HPR-04	1.96	2.24	1.17
HPR-05	1.25	1.21	1.50
VPR-04	0.40	1.26	1.20
VPR-05	0.48	1.21	1.35
VPR-06	0.76	1.14	1.09
VPR-07	0.65	1.16	1.27
VPR-08	0.63	0.79	0.94

3.7. Lime Saturation Factor (LSF)

Lime saturation factor is crucial for cement manufacture because it contains CaO, which is the primary mineral ingredient for cement Ingram and Daugherty, (1991). It is demonstrating that some clay must be added to cement production to compensate for the amount of silica-alumina and iron oxides in the acceptable limestone. Approximately, LSF is 1.0, indicating the amount of lime exactly balances the amount of silica, alumina, and ferric oxide. An excess of 1.0 suggests free lime is present in clinker Champman and Hall 1995). The following equation was used to calculate the LSF.

$$\text{Lime saturation factor} = \frac{\text{CaO}}{2.8\ (\text{SiO}_2) + 1.2\ (\text{Al}_2\text{O}_3) + 0.65\ (\text{Fe}_2\text{O}_3)}$$

The LSF controls the ratio of alite (tricalcium silicate, C_3S) to belite (dicalcium silicate, C_2S) in the clinker. High LSF has a higher proportion of alite and belite than clinker. The LSF is mainly used for kiln feed control (Roa D. S. et al., 2011). If the LSF is higher than 1, the surplus free lime has nothing to be associated with and will remain as free lime. Glasser, F. P. (1998). In practice, the mixing of raw materials is never perfect, and there are always regions within the clinker where the LSF is considerably below the target for the clinker as a whole. Values above 1.0 indicate that free lime is likely to be present in the clinker. In the present limestone samples, LSF ranges from 0.40–4.95, except for two samples: BL-01, which is 11.95%, and BL-03, which is 58.18%, as provided in Table.1. It indicates that CaO values in Bandigudda have a higher concentration, with the remaining other limestone having a uniform range. A value greater than 1.0 suggests that the clinker probably contains free lime. This is because all of the free lime should have been coupled with belite to produce alite at LSF = 1, theoretically considered. The surplus free lime has nothing to do with and will continue to be free lime if the LSF value is greater than 1. Dow, C., & Glasser, F. P. (2003). In the Bandigudda region, a few limestone samples have higher LSF, as shown in Table.6, and it's difficult to burn raw mix. Joldhal and Hanne region limestone have within the acceptable range of LSF values; Vitalapura and Medugondanahalli limestone have <1 values, so these are not suitable for this utilization. Hence, Joldhal and Hanne limestone are most suitable for cement manufacture. In the Bandigudda region, the highest LSF was observed at 58.18 and 11.95%. A large variation in the LSF is observed in Fig,8. Individual distributions of LSF for different regions are provided in Fig.7.

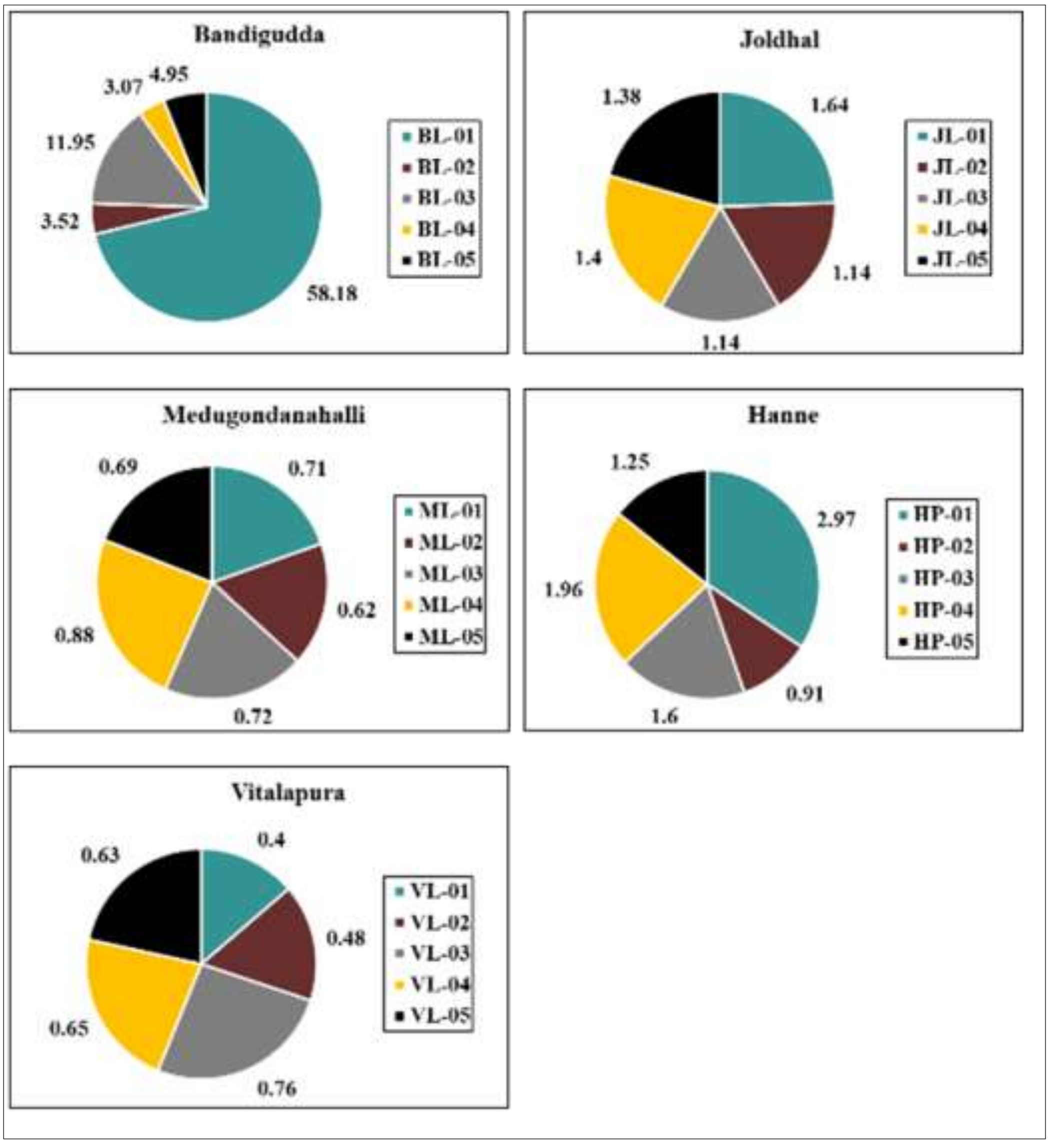

Figure 7 Illustrate lime saturation factor of all 5 regions collected limestone samples from the study area

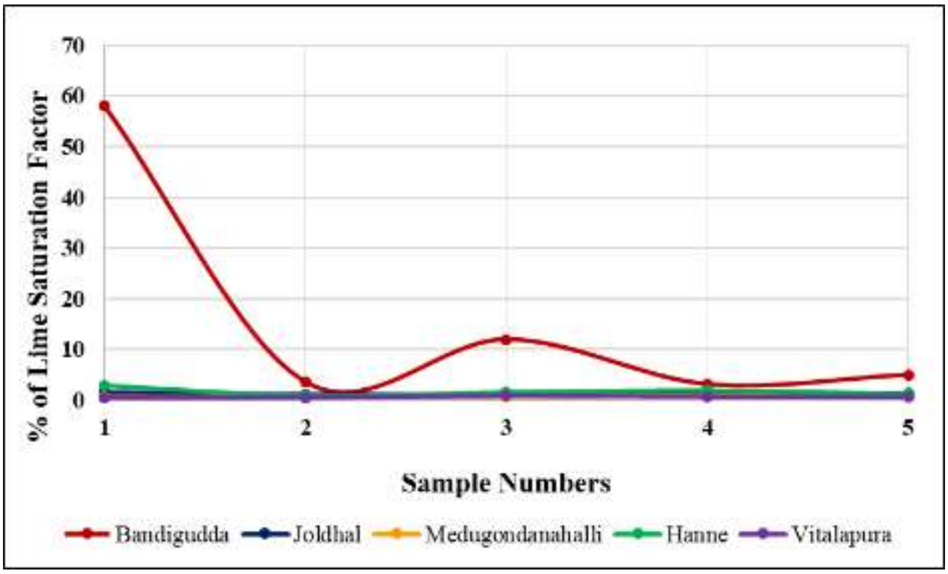

Figure 8 Illustrate average lime saturation factor of all five region collected limestone samples from the study area

3.8. Alumina Modulus (AM):

The alumina ratio is an important factor in the cement-making process. The alumina ratio determines the potential relative ratio of aluminate to the ferrite phase in the clinker. An increase in clinker AR means that there is more aluminate and less ferrite in the clinker. A higher value of the alumina ratio shows more alumina and less ferrite, and lower values indicate vice versa Rao D.S. et al., (2011). The following equation was used for calculating the AM.

$$\text{Alumina Ratio} = \frac{\mathrm{Al_2O_3}}{\mathrm{Fe_2O_3}}$$

In general, the alumina ratio in ordinary Portland cement clinker is usually between 1.0 and 4.0 Rao et al., (2011). The AR in the present samples ranges from 0.29 (Joldhal samples) to 3.40 (for the Bandigudda sample) Table.6. Most of the samples Alumina modulus will be 1 to 2 range. Individual distributions of AM for different regions are provided in Fig.9.

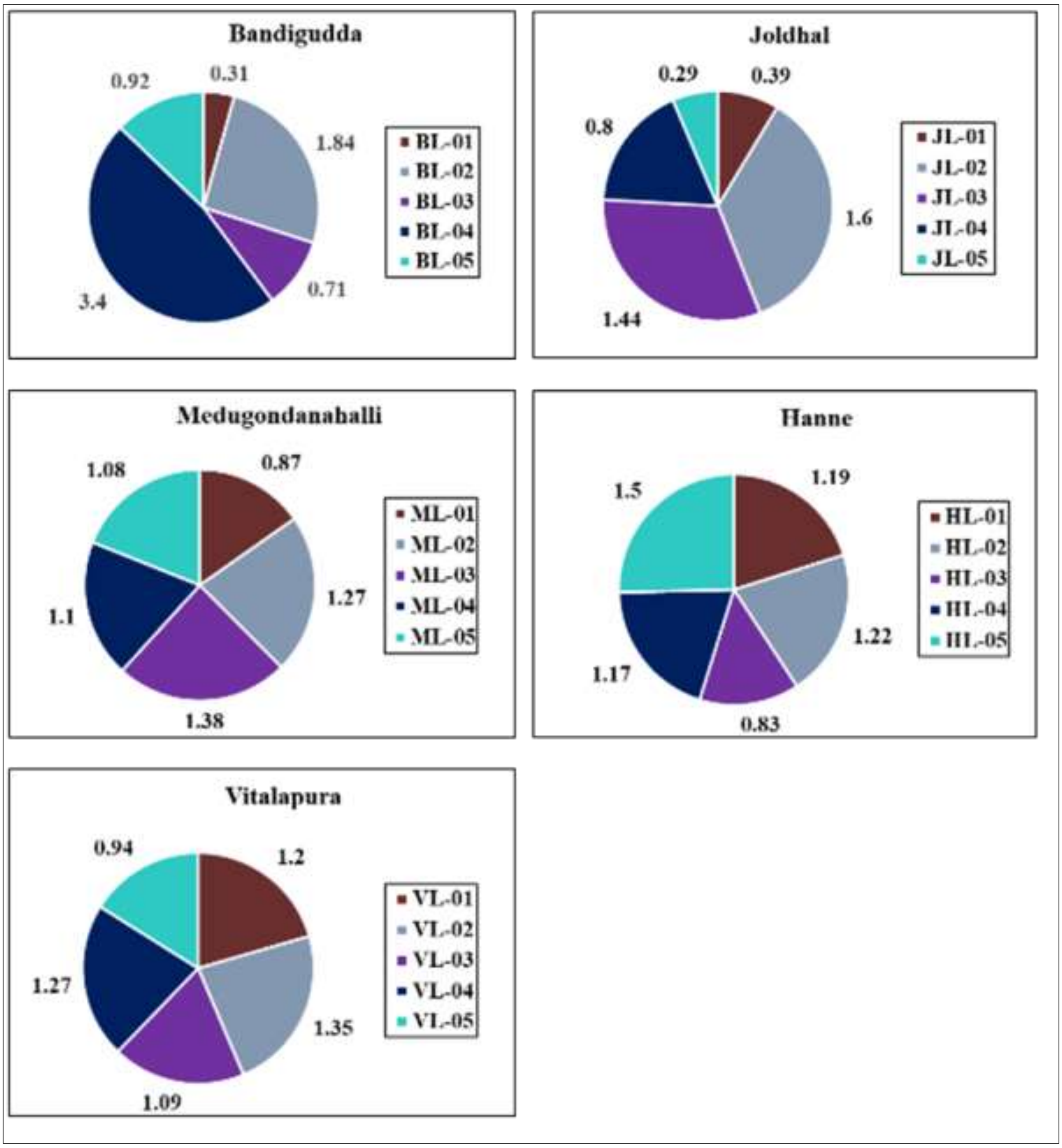

Figure 9 Illustrate Alumina modulus of all 5 regions collected limestone samples from the study area

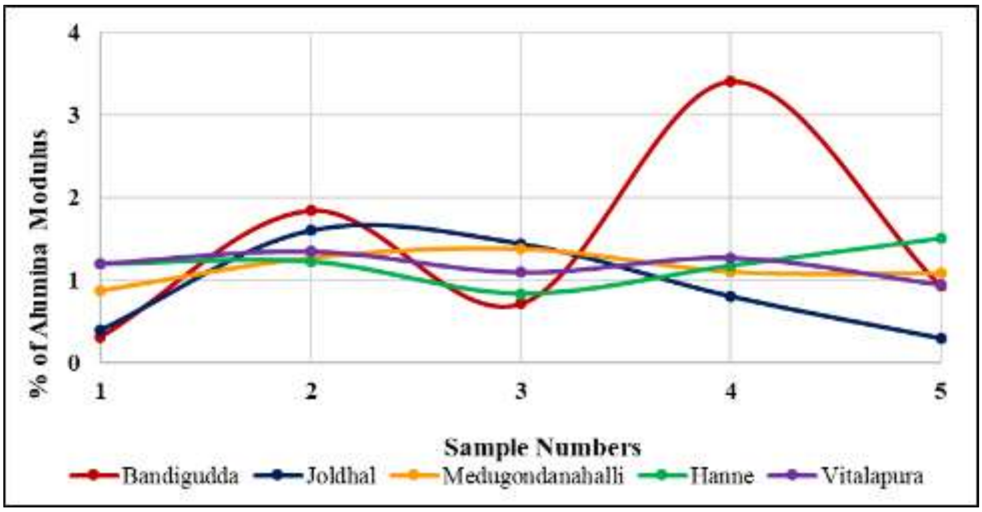

Figure 10 Illustrate average Alumina modulus of all five region collected limestone samples from the study area

3.9. Silica Modulus (SM)

The silica ratio plays a very important role in cement manufacture and has a particularly significant influence on the combustion process Rao et al., (2011). When the silica ratio is increased, the amount of liquid phase is decreased, and vice versa. So, the silica ratio has a major influence on the formation of the liquid phase. The following equation was used to determine the silica ratio.

$$\text{Silica Ratio} = \frac{\text{SiO}_2}{(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)}$$

The higher silica content causes difficulties in combustion and shows poor coating characteristics. As the silica ratio increases, more heat is required to run the kiln Nayak and Mallik (2002). If the silica ratio is lower than the standard ratio, it will develop ring formation in cement. According to Aldieb and Ibrahim (2010), the silica ratio ranges between 1.9 and 3.2. A large variation in the silica ratio in the clinker can be an indication of poor uniformity in the kiln feed. The silica ratio for the present investigation limestone samples ranges from 0.45 to 5.21, as provided in Table 6, which indicates that the samples have a standard specified limit of SiO_2 content and consider this limestone resource for cement production. This limestone is almost within or near the standard ratio; this will not create a grinding problem, so consider ordinary Portland cement (OPC) manufacturing. The present investigation shows that except for the Bandigudda region, all other regions show almost the same range, and the Bandigudda region has a lower silica range and a high CaO range due to its pure form. A large variation in the silica ratio is observed in Fig.12. In the Bandigudda region, the highest silica ratio was observed (5.21%), and the lowest was also observed in this region (0.45%). Individual distributions of silica ratios for different regions are provided in Fig. 11.

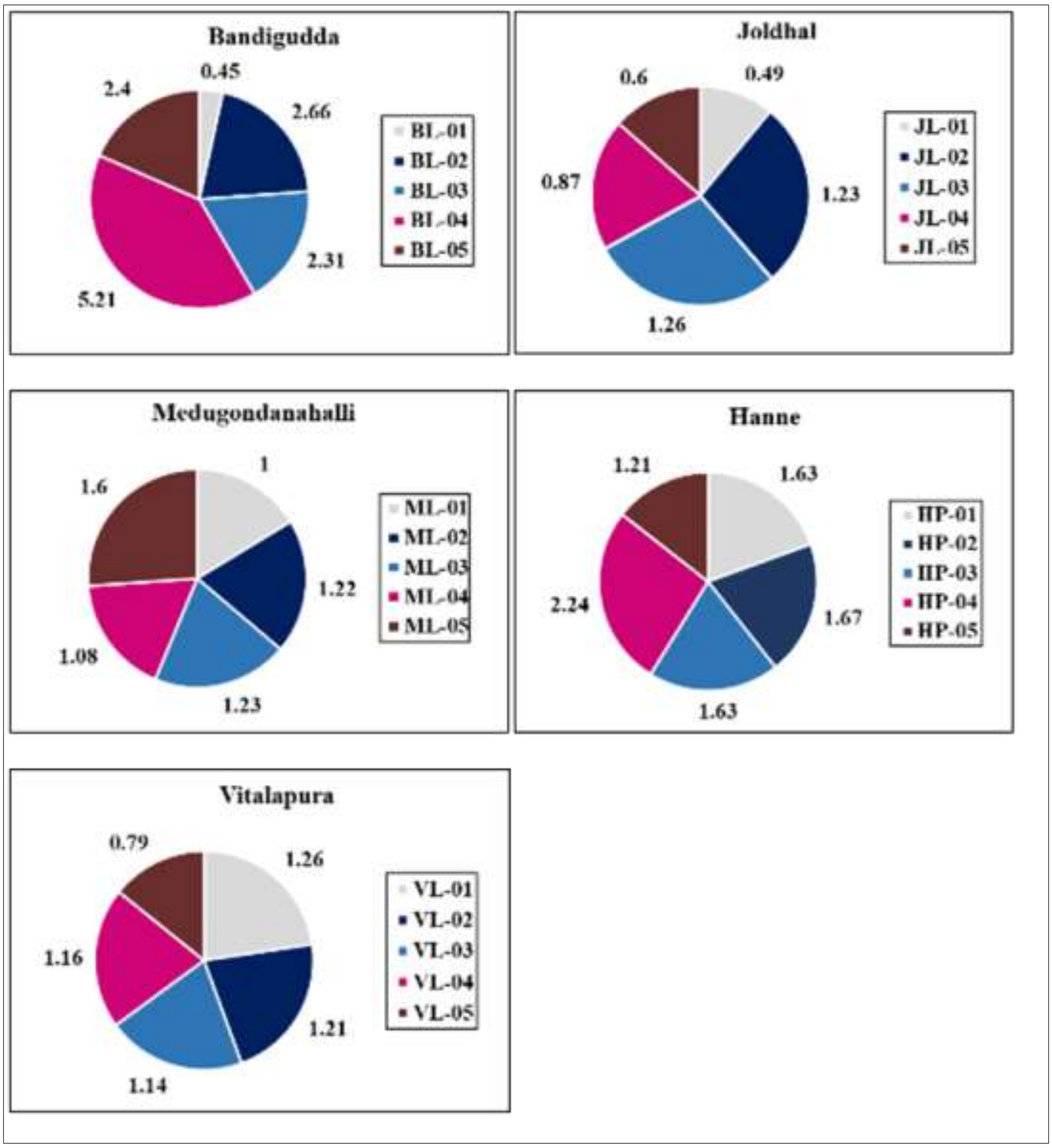

Figure 11 Illustrate Silica modulus of 5 regions collected limestone samples from the study area

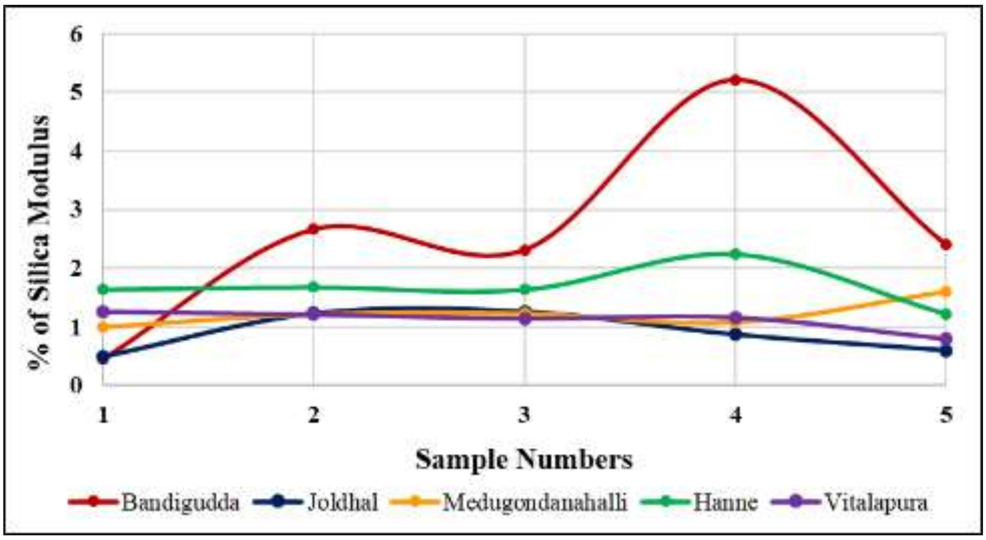

Figure 12 Illustrate average silica modulus of five region collected limestone samples from the study area

3.10. Geochemical suitability of limestone

3.10.1. Bandigudda limestone (BL)

Bandigudda limestone is coarse-grained crystalline nature Fig.4d, is lithologically homogeneous and typically composed of high-grade limestone. and they were closely associated with carbonaceous phyllites. Alternative-banded limestone and various calcite and quartz veins were observed. A petrographical study shows this limestone dominance with coarse calcite crystals and some quartz grains. In Table 1, the all-major oxide elemental concentration ratios display greater chemical variation observed in this region: CaO (48.41% to 55.50%), SiO_2 (0.21% to 5.26%), Al_2O_3 (0.11% to 1.14%), Fe_2O_3 (0.23% to 0.71%), MgO (0.51% to 1.92%), and LOI (42.82% to 39.08%). This limestone is rich in CaO% and poor in MgO% and SiO_2%. SiO_2 has a relatively low and variable concentration in this limestone. The XRD pattern Fig.5 reveals a 90–95% calcite mineral dominance and very few gangue minerals like quartz and mica. The ratio factor analysis of lime saturation factor, alumina modulus, and silica modulus is in a closely acceptable range, except for one sample. Hence, this limestone was most suitable for cement manufacture according to Indian standard specifications.

3.10.2. Joldhal limestone (JL)

Joldhal limestone is a calc-shist variety with a medium- to coarse-grain texture. physically grayish in color Fig.4b. The petrographical study highlights the calcite, quartz, chlorite, and mica grains observed. Calcite is partially deformed, and chlorite has a crenulation or wave-like appearance. Major oxide elemental concentrations are provided in Table 2, and this limestone is homogeneous in chemical composition. From the result, the chemical variation observed in this region was CaO (40.35% to 44.32%), SiO_2 (5.72% to 10.50%), Al_2O_3 (2.69% to 5.20%), Fe_2O3 (3.26% to 9.28%), MgO (2.01% to 3.08%), and LOI (34.03% to 36.20%). This limestone is rich in CaO% and poor in MgO% and SiO_2%. This limestone is highly deformed and in close contact with argillaceous limestone. The XRD pattern Fig.5 shows that 80–90% calcite was dominantly present, with some minor peaks like quartz, chlorite, and mica feldspar. The ratio factor analysis results confirm that the lime saturation factor is within the range, and the alumina modulus and silica modulus are below the acceptable range, except for two samples. Hence, this limestone was suitable for cement manufacture according to Indian standard specifications after some clay adjustments.

3.10.3. Medugondanahalli limestone (ML)

Medugondanahalli limestone is classified into two types: dolomitic and micritic limestone, which have very fine grain textures. physically brownish in colour Fig.4.a, f,g. Lithologically, it is homogeneous. The petrographical study highlights the micrite, calcite veins, and quartz minerals that were observed. Calcite is in the form of a thin, parallel, layered mineral. Major oxide elemental concentrations are provided in Table 3; this limestone is homogeneous in chemical composition. The chemical variation observed in this region is CaO (33% to 36.58%), SiO_2 (11.34% to 16.1%), Al_2O_3 (4.93% to 7.41%), Fe_2O_3 (4.40% to 7.03%), MgO (2.42% to 8.03%), and LOI (29.98% to 33.65%). The XRD pattern Fig.5 shows that calcite, dolomite, and quartz are the major peaks detected in this limestone. The ratio factor analysis results confirm that the lime saturation factor and silica modulus are both below acceptable ranges, are only alumina modulus, and are in a nearby permissible range. Hence, this limestone was not suitable for cement manufacture according to Indian standard specifications.

3.10.4. Hanne limestone (HL)

These limestones are categorized as lime kankar nodules (0.5 to 15 cm range) and brown to cream-coloured Fig.4i, where quartz is present as grains and sparry calcite was developed in small veins. The results of the analyses were presented in Table 4, and chemical variation was observed in this region in CaO (42.20% to 50.50%), SiO_2 (5.03% to 13.90%), Al_2O_3 (1.68% to 5.01%), Fe_2O_3 (1.42% to 3.76%), MgO (1.35% to 2.09%), and LOI (32.06% to 39.57%). This limestone is most suitable for limestone due to its high CaO%. XRD patterns Fig.5 shows that calcite, quartz, and some clays are the major detected peaks in this limestone. The ratio factor analysis results highlight that the lime saturation factor and alumina modulus are within the range, while the silica modulus is below the acceptable range. Hence, this limestone was suitable for cement manufacture according to Indian standard specifications after some clay adjustments.

3.10.5. Vitalapura limestone (VL)

These limestones are categorized as dolomitic and argillaceous limestone, and they have grey and brownish colors Fig.4h. This limestone contains quartz intraclasts of varying sizes. Locally affected by karst erosion on the surface of the limestone bed. This limestone seems quite heterogeneous, and geochemical analysis results indicate that major oxide elemental concentration ratios show a wide range of variation as provided in Table 5, and the observed range in this region is CaO (27.80% to 31.7%), SiO_2 (11.60% to 19.60%), Al_2O_3 (5.32% to 8.48%), Fe_2O_3 (4.92% to 8.03%), MgO (6% to 9.79%), and LOI (27.99% to 34.79%). This limestone is most suitable for limestone due to its high CaO%. The detected XRD patterns are mainly calcite and quartz. The ratio factor analysis results confirm that the lime saturation factor and silica modulus are below the acceptable range, whereas the alumina modulus is near the acceptable range. Hence, this limestone was not suitable for cement manufacture according to Indian standard specifications.

4. Discussion

In order to evaluate the inaccessible and untested limestone resources of different locations of the Joldhal formation, which is rich in crystalline, banded, lime kankar, and dolomitic limestone deposits, the current research work is therefore planned for the utilization of raw materials from the cement industry. The present research wants to reveal the geochemical suitability of limestone from the Joldhal formation for cement making. Mineralogical, X-ray fluorescence, X-ray diffraction, Lime Saturation Factor, Silica Modulus, and Alumina Modulus were assessed. Mineralogical investigation demonstrates that, in varying amounts, calcite and quartz are the primary minerals that make up limestone. Similar mineralogical results were published by Rao et al. (2011), who analyzed the siliceous limestone sample from the Jayantipuram limestone deposit in order to incorporate this one into cement manufacture. The current study examines how significantly three parameters, viz., silica modulus (SM), lime saturation factor (LSF), and alumina modulus (AM), influence this various grade limestone sample from the Joldhal Formation of Shimoga schist belt for the cement making process by using the geochemical data. This investigation was carried out using appropriate methods. For this study, twenty-five representative limestone samples were collected from various locations, which consist of a greyish and brick red colour, and analyzed through the X-ray fluorescence (XRF) method. The results of major oxide concentrations are indicated (in wt%) as follows: SiO_2 (0.21 - 19.60), TiO_2 (0.00 - 0.45), Al_2O_3 (0.11 - 8.48), MnO (0.0178 - 0.92), Fe_2O_3 (0.23 - 9.28), CaO (27.80 - 55.50), MgO (1.35 - 9.79), Na_2O (0.00 - 0.49), K_2O (0.0053 - 2.20), P_2O_5 (0.00 - 0.21), LOI (27.99 - 42.82). Calcite is the main mineral, followed by quartz, chlorite, and traces of dolomite and kaolinite, which are present in limited samples, as determined by the X-ray diffraction studies.

Bandigudda, Joldhal, and Hanne area limestones have low MgO concentrations, whereas some of the other limestones have high MgO values. In the present investigation, limestone samples from various patches in the Bandigudda, Joldhal, and Hanne Formations meet the requirements to be used as raw materials in the cement production sector. Limestone from Vitalapura and Medugondanahalli is not feasible for cement production due to its impure nature. The lime saturation factor, silica modulus, and alumina modulus are the primary factors that determine the quality of limestone used in cement manufacture. The available limestone in the study area is of crystalline nature in the Bandigudda and Joldhal regions. Lime kankar were found in the Hanne region; the rest of the area was found with argillaceous varieties. Based on all these factors and the results of the present research, the high purity of limestone deposits in Bandigudda, Joldhal, and Hanne regions is recommended for cement manufacture. The studied limestone samples from different patches in the study area, Bandigudda, Joldhal, and Hanne Formations, fulfil the specifications for their use in the cement manufacturing industry as a raw mixture. Vitalapura and Medugondanahalli limestones are the nearest sources for the cement industry.

5. Conclusion

- This study has been geochemically investigated through the geochemical properties of limestone for cement manufacture in the study area.
- Based on the XRF studies, the pure and high-grade limestone (CaO-55.50%, SiO_2-0.21%) was observed in Bandigudda and Hanne regions (CaO-50.50%, SiO_2-5.03%) and next to Joldhal region (CaO-42.50%, SiO_2-10.40%).
- The present investigation shows that limestone deposits from Bandigudda, Joldhal, and Hanne regions are potentially high-grade and most suitable for cement, steel, and other minor industries. Other regions, such as Medugondanahalli and Vitalapura, are predominantly composed of quartz, magnesium, iron, and other impurities.
- The LSF, SM, and AM values of raw materials from Bandigudda, Hanne, and Joldhal areas are most suitable for cement manufacturing, with the remaining need to make some adjustments to raw mix design, which can be adjusted by using clays or other sources of low silica content, alumina, and iron as correcting combined materials.
- The suitability of limestone for cement production depends on its chemical composition, physical characteristics, geological origin, and other practical considerations. Cement manufacturers carefully select and blend raw materials to ensure the desired quality and performance of the final product. Regular testing and quality control measures are critical in the cement production process.
- The chemical composition of the limestone in the Bandigudda, Joldhal, and Hanne regions confirms its suitability for cement manufacture. Hence, we recommend the utilisation of this resource for cement production, which is based on very small deposits, and for sustainable development in terms of the utilisation of marginal and low-grade resources for future generations.
- The present research is helpful for natural mineral resource sustainable development for future India and country economic development

Compliance with ethical standards

Disclosure of conflict of interest

The authors declare that they have no known competing financial interests or personal relationships influenced by this work.

Authors contribution statement

Thippeswamy D R* - investigation, data interpretation, software, writing original draft, conceptualization, figures, and tables preparation, formal analysis and editing C Venkataiah - investigation, guided, validation, writing - Review, and editing Basavaraj Hatti - software, figures, and tables preparation, formal analysis and editing

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