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A STUDY OF THE OCCURRENCE OF MAGNESIUM OXIDE IN DIFFERENT PHASES OF LIMESTONE

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ABSTRACT

Distribution of MgO in dolomite, calcite and silicate phases in a magnesian limestone from a deposit of Orissa, India, was investigated. For estimation of MgO in calcite, selective dissolution of limestone in 20% (V/V) acetic acid (at around 25 deg.C for 20 hours) is found to be the most suitable method. The optimal requirement of acetic acid in the stated dissolution process is found to be 10 ml. per gram of limestone. In the examined limestone, calcite contains 1.3-1.9% MgO and thus contributes about 11 - 45% of the total MgO present in the limestone. Associated silicate and dolomite are found to contain 9-21% and 19-23% MgO respectively.

Introduction

The principal magnesia bearing phases in limestone are known to be dolomite ($CaCO_3.MgCO_3$), Ca-Mg-silicates of pyroxenes and amphiboles groups and their hydrated phases and phlogopite [$K\,Mg_3\,(Si_3AlO_{10})\,(F, OH)_2$]. However, calcite often contains some magnesia. The substitution of Ca by Mg in calcite structure has been reported by a number of researchers (1-5). Foote and Bradley (1) showed that calcite crystals which were grown on dolomite contained about 1 % MgO. Similarly Clarke and Wheeler (2) measured considerable amount of Mg in the inorganic calcite present in many marine invertibrates. Chave (3) found a correlation between chemical composition and peak shifts in the XRD pattern of the phase representing solid solution between calcite and dolomite and established that calcite structure can accommodate a reasonable amount of Mg in solid solution. Harker and Tuttle (4) studied the cell parameters of calcite due to substitution of Ca by Mg. Goldsmith and Joensu (5) reported about 0.3-4.1% of MgO in the structure of calcites.

Grain size and distribution of periclase (MgO) which depend on the source of Mg, play very important role in controlling the expansion of cement structure. Fine and well distributed periclase grains do not cause significant expansion. Limestone with coarsely crystallised dolomite results in clustering of periclase grains, with somewhat larger size of crystals in comparison to periclase grains developed from calcite after decarbonation (6). This emphasizes the importance of the nature of occurrence of MgO in magnesian limestone.

The objective of the present study is to estimate the MgO contents in different phases and particularly in calcite present in the Lanjiberna limestone deposits of Orissa, India. Patra (7) while conducting experiments on removal of MgO from the said limestone, examined the nature of occurrence of MgO and reported that about 16-64% of the total MgO was accounted by calcite-dolomite solid solution (C-Dss) and calcite with inclusion of dolomite (C-Di). In the present investigation presence of MgO in the C-Dss, dolomite and silicates has been investigated.

Materials and Methods

Cement grade limestones of the examined deposit are classified on the basis of MgO and CaO contents as follows:

	CaO %	MgO %
Grade I	+ 44	- 2.8
Grade II	+ 44	2.8-3.5
Grade III	+ 40	3.5-5.0
Grade IV	High TC and High MgO	

The deposit also contains some dolomitic and dolomite limestone bands. SiO_2 is found to be the major impurity ranging up to 13%. The mineral phase assembalages in the limestone samples are found to consist of calcite ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$), quartz(SiO_2), phlogopite[$KMg_3(Si_3AlO_{10})$ $(F.OH)_2$], a small amount of kaolinite [$Al_2(OH)_4$ Si_2O_5] and anorthite ($CaAl_2Si_2O_8$) and occasionally some metallic minerals like pyrite (FeS_2) (Fig.1).

Four limestone samples with different MgO contents were considered for the study. MgO and some other chemical constituents of the samples are shown in TABLE-1. Sample Nos.1 and 2 belong to grade I and grade II respectively. The other two samples belong to the high MgO grade. The examined limestone samples contain significantly high amounts of F in the form of phlogopite (8).

Qualitative and quantitative phase estimations were made by X-ray diffractometry (XRD) using a Philips PW1730 Cu-Kα radiation with Ni-filter at 40 kV, 2 θ mA. For quantitative

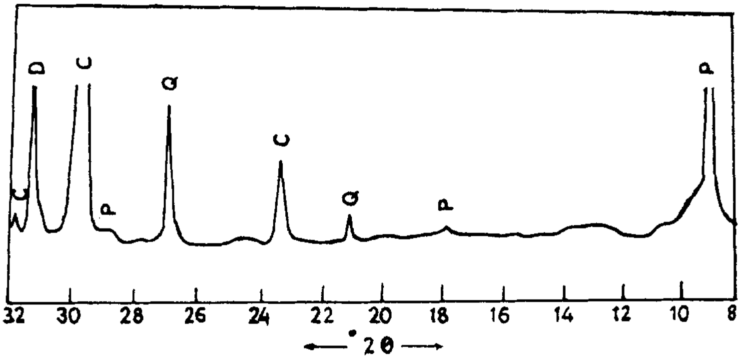

FIG. 1.

X-Ray Diffractogram (Cu-Kα) of the limestone sample No. 3 showing mineral phase assemblages (C = Calcite, D = Dolomite, P = Phlogopite, Q = Quartz).

TABLE 1
Chemical Analysis (Wt.%) of the Examined Limestone Samples

Sample No.	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	F
1	37.4	11.25	0.9	0.58	47.2	2.65	0.50	0.20
2	40.0	3.76	0.11	0.58	51.2	3.30	0.48	0.24
3	38.0	6.94	1.32	0.66	47.3	5.62	0.76	0.24
4	37.0	8.12	2.71	0.72	42.5	8.30	0.90	0.31

estimation (QXRD) constant quantity of 0.61 gm sample containing 10% CdO as internal standard was used. Calcite, dolomite and CdO intensities were measured at 29.5, 31.1 and 33.2, 2θ (Cu-Kα) respectively. An Icelandspar crystal representing pure calcite and a highly pure dolomite were taken as XRD standards.

A polished thin section of limestone was etched with 1M $Cu(NO_3)_2$ for 6 hrs. and then fixed with strong ammonia to distinguish calcite from dolomite (9).

Calcite and dolomite were separated by preferential leaching technique. Wolfe and Bartlett (10), reported that calcite on treatment with 0.5N acetic acid is dissolved in about 15 minutes, whereas dolomite requires more than 3 hours for complete dissolution. In the present case, the aforesaid conditions were not found to be optimal. The present combined study on the strength of the acid and corresponding dissolution time has established that by leaching 1 gm of magnesian limestone in 10 ml.of 20% (v/v) acetic acid for 24 hours at room temperature (25°C), it is possible to remove all the calcite without attacking dolomite and silicates. After leaching, complete removal of calcite was verified from XRD of the residue, which showed absence of calcite and increase of other phases (Fig.2). After leaching with acetic acid, CaO and MgO in the filtrate were estimated by complexometric titration with EDTA using calcein as the indicator. The residue was further treated with warm 1:3 HCl to dissolve the dolomite fraction.

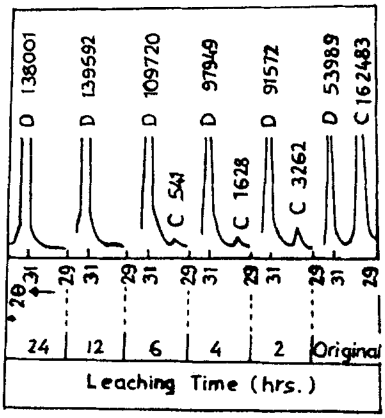

FIG. 2.
X-ray diffractogram (Cu-Kα) of the acetic acid leached residue. With increase of leaching time, Calcite (C) peak intensity decreases and dolomite (D) peak intensity increases.

TABLE 2

Estimation of Phases (Wt.%) in the Examined Limestones by QXRD and Selective Dissolution (SD Methods

Sample No.	MgO %	Calcite		Dolomite		Silicate
		XRD	SD	XRD	SD	SD
1	2.65	83	82.47	3.0	3.35	14.18
2	3.30	91	90.59	4.0	4.39	5.02
3	5.62	80	78.59	12.5	11.68	9.79
4	8.30	63	61.60	25.0	24.60	13.80

Then the filtrate as well as the silicate residues were analysed for CaO and MgO. The silicate residues were analyzed by XRD for determination of the phase assemblages.

Results

Calcite and dolomite contents of the samples as determined by QXRD and acetic acid leaching methods (SD) are shown in TABLE-2. The dolomite content of the samples range from 3 to 25% and calcite ranges from 60 to 90%. As expected, dolomite in general increases and calcite decreases with increase of MgO content, although in case of silicate, no such trend is noticeable.

Microscopic examination shows that besides as discrete grains, (Fig.3) dolomite also occurs occasionally as fine exsolved grains in calcite. Often dolomite grains occur surrounding the

FIG. 3.

Photomicrograph showing discrete dolomite grains (White) with calcite (Black). (Transmitted light, etched section, X 200).

FIG. 4.

Photomicrograph shwoing presence of dolomite (White grains with fine black spots) on the outer grain margin of calcite (Black). (Transmitted light, etched section, X 200).

calcite grains (Fig.4). However most of the calcite grains are free from exsolved dolomite grains.

In TABLE-3, MgO contents of calcite, dolomite and silicates present in different samples are shown. This also includes the calculated MgO contributions from different phases towards the total MgO content of the parent limestone. The MgO content in the calcite ranges from 1.30 to 1.93% and that in the silicate fraction it ranges from 9.26 to 20.5%. This wide variation in the silicate part is due to the fact that all the silicate phases are not MgO-bearing; only some particular phase/phases may contain MgO. Thus presence of non-magnesian phases in the IR fraction reduces the MgO% in the silicates. The only magnesia bearing phase in the studied limestones is phlogopite. The other major associated mineral is quartz only. Thus the MgO content of the silicates and consequently its contribution to the total MgO depends on the amount of phlogopite present in the sample and not on the total amount of silicates. Sample-1 with 14.18% and sample 3 with 9.79% silicates contribute 1.31 and 1.42% MgO respectively towards total MgO%. XRD patterns of the two samples (Fig.5) show that sample-3 contains noticeably more phlogopite than the sample-1.

MgO contents from the calcite and the silicate account for 11-45% and 22-42% respectively of the total MgO content of the parent rocks. Consequently dolomite contributes only 21-67% of the MgO present in the limestones examined.

Discussion

In the examined limestones, calcite contains 1.30 to 1.93% MgO (TABLE-3). Similar occurrence of MgO in calcite structure has been reported by some other researchers; varying from as low as 0.04% (11) to as high as 7.28% (12). Goldsmith and Graf (13) while investigating calcite formed in different environments reported that 0.3-4 Wt.% MgO substituted for CaO in

TABLE 3
MgO Distribution (Wt.%) in Different Phases of the Examined Limestones

Sample No.		Phase		MgO Contribution	
		Material %	MgO %	Actual %	% of the total
1.	Cal.**	82.47	1.30	1.07	36
	Dol.	3.35	18.80	0.63	21
	Sil.	14.18	9.26	1.31	44
	Total			3.01	
2.	Cal.	90.59	1.93	1.61	45
	Dol.	4.39	21.20	0.93	26
	Sil.	5.02	20.50	1.03	29
	Total			3.57	
3.	Cal.	78.59	1.66	1.30	24
	Dol.	11.68	23.30	2.72	50
	Sil.	9.79	14.50	1.42	26
	Total			5.44	
4.	Cal.	61.6	1.61	0.99	11
	Dol.	24.6	19.14	5.85	67
	Sil.	13.8	13.90	1.92	22
	Total			8.76	

** (Cal. = Calcite, Dol. = Dolomite, Sil. = Silicte)

calcite in association with dolomite. Chave (3) reported 1-7.6% MgO in calcite collected from marine organisms. Thus it can be stated that Mg substitution in the calcite of the examined limestone is noticeably in the low range.

The shift in 2θ peak position in the XRD spectrum of the calcite is generally due to presence of Mg in calcite (4, 5, 13, 14), though in the present samples no such discernible shift (2θ, 29.5-Cu-Kα) was detected. It may be due to the relatively low amount of Mg in calcite structure. The QXRD method for estimation of calcite and dolomite in magnesian limestone developed for the present investigation using CdO as internal standard is found to be quite a rapid one. From TABLE-2, it is observed that XRD estimation of these two phases does not vary much from the chemical method of estimation by selective dissolution.

Pure dolomites separated out by selective leaching of different limestone samples show different amounts of CaO (TABLE-4), which differ from the stoichiometric composition (CaO = 30.4%). Except sample-1, the other three limestone samples were found to contain excess CaO ranging from 0.03 to 7.02%. Hurlbut (15) reported 7.69% excess CaO in Zincian Plumbian dolomite samples from S.Africa. Goldsmith and Graf (16) reported up to 5 mole % excess structural $CaCO_3$ in dolomite samples. Thus the presence of excess CaO in dolomite, particularly in limestone is not unexpected.

The variation of MgO content in the silicate fraction is due to the presence of different Si bearing phases, and as shown in Fig.5, this is primarily determined by the amounts of phlogo-

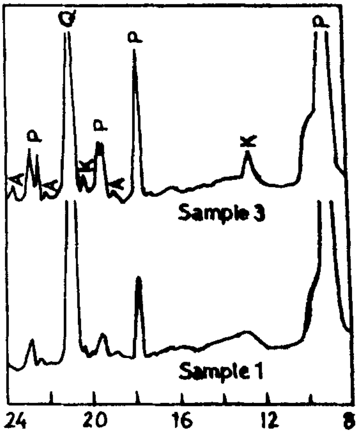

FIG. 5.

X-ray diffractogram (Cu-Kα) of the insoluble residue of the limestone sample-1 (MgO=9.26%) and sample-3 (MgO=14.5%) showing variation in phologopite contents.

pite and quartz present in the sample. In fact it is found that MgO content of the silicate increases with the increase of the ratio of XRD counts at 8.9 deg. 2 Θ and 26.7 deg. 2 Θ corresponding to phlogopite (001) and quartz (101), respectively.

From TABLE-3 it is also observed that calcite and silicate together contribute about 33-75% of the total MgO present in these limestone samples. In case of high MgO limestone samples (No. 3 and 4) dolomite contributes 50-67% of the total MgO. Interestingly with the increase in total MgO in the limestone, MgO contribution from dolomite fraction increases and that from calcite and silicate fraction decreases. Although the mechanism involved is not clear, it is possible that the process of dedolomitization is somewhat more active in the limestone with lower MgO content, than those with higher MgO content.

TABLE 4

CaO and MgO Contents (Wt.%) of Pure Dolomites Separated Out from Different Limestone Samples

	CaO % (A)	MgO % (B)	* CaO % (C)	CaO % (A-C)
Sample-1	22.6	18.8	26.32	-3.72
Sample-2	36.7	21.2	29.68	7.02
Sample-3	32.9	23.3	32.6	0.03
Sample-4	30.6	19.4	26.80	3.80

Conclusion

In magnesian limestone, although dolomite is generally regarded as the source of MgO, calcite coupled with silicate such as phlogopite may also provide a significant amount of MgO. In some dedolomatized limestone, calcite and silicate may contribute as high as 75% of the total MgO content. On the otherhand, dolomite in the examined limestones contains excess CaO, ranging from 0.03 to about 7.0%.

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