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## PREFERRED ORIENTATION EFFECTS IN THE CALCITE AND DOLOMITE QUANTITATIVE X-RAY DIFFRACTION ANALYSIS

**Abstract** — The preferred orientation effects on the quantitative x-Ray diffraction analysis of dolomite in rocks and sediments is last influenced in the 113 reflection.

In calcite the 113 intensity must be corrected by means of the 104 intensity measurement.

The estimated standard deviation in quantitative analysis of calcite and dolomite is respectively about 8% and about 4%.

**Riassunto** — *Effetti di orientazione nella analisi quantitativa della calcite e della dolomite in diffrattometria di polveri a raggi-X.* Nella determinazione quantitativa della dolomite contenuta in rocce o sedimenti, mediante la diffrattometria di polveri a raggi-X, il riflesso 113 è quello che risente in minor misura degli effetti di orientazione preferenziale ed è quindi il più idoneo per una analisi di questo tipo.

Nella analisi quantitativa della calcite, invece, l'intensità del riflesso 113 deve essere corretta, per gli effetti di orientazione preferenziale, mediante la misura di intensità del riflesso 104.

La deviazione standard nell'analisi diffrattometrica quantitativa della calcite e della dolomite è rispettivamente dell'8% e del 4%.

### INTRODUCTION

Quantitative mineralogical analysis of carbonate rocks by X-ray powder diffraction methods has been the object of considerable research in the past years.

From our present knowledge we can deduce that the accuracy of X-ray analysis is limited by a number of factors such as: absorption effects, isomorphous substitutions, intensity measurement

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techniques, interference among peaks, variation in particle sizes of the powder, preferred orientation. Sufficient attention does not seem to have been paid to the effects caused on the intensities by preferred orientation. These effects can be attenuated but they are very difficult to eliminate. For this purpose some authors WEBER and SMITH, 1969; NERI-BELLANCA *et al.*, 1975 have proposed some techniques to produce random orientation of the powders, but these methods are time consuming and are frequently unsatisfactory, due to the lack of reproducibility of the results. Preferred orientation is more evident in the case of analysis of carbonate rocks characterized by calcite and/or dolomite crystals of great dimensions. Therefore a unique calibration curve cannot be used to determine these minerals quantitatively in carbonate rocks with variant grain sizes as for example lithographic limestones and metamorphic limestones.

When the knowledge of the concentration ratio of calcite to dolomite is sufficient, the preferred orientation effects are reduced by using a calibration curve established by plotting the calcite/dolomite intensity ratio against calcite/dolomite concentration ratio. Of course, it is impossible to use this method to determine the absolute concentration of the afore mentioned minerals.

In this article we report the results obtained from a study on the influence of the preferred orientation of intense calcite and dolomite reflections. As a result of this study, we have found a useful relation for correcting the measured intensity of the 113 diffraction for effects of preferred orientation.

As a practical application we report on the quantitative mineralogical analysis of artificially prepared mixture of calcite and dolomite of different origin as well as the analyses of 4 international standards (400; 401; 402; 403;).

## EXPERIMENTAL

To study the preferred orientation effects we have utilized the following specimens:

Synthetic calcite C1 (Carlo Erba RPE) Title min. 99,5%.

Lithographic limestone C2 (« Maiolica » formation of Cretaceous age belonging to the Tuscan series).

Metamorphic limestone C3 (Marble formation of Hettangian age belonging to the metamorphic Tuscan series).

Spathic calcite C4 (Vein of calcite).

Sedimentary dolostone D1 (« Calcare Massiccio » formation of Hettangian age belonging to the non metamorphic Tuscan series).

Metamorphic dolostone D2 (Ejecta block of Somma-Vesuvio).

The sample were ground in a tungsten carbide disk mill; we obtained from each sample three powders of different granulometry, using grinding times of 15", 60", and 90".

The granulometry measurement of the powders are as follows:

Grinding Time	Particle Size
15"	~ 75 $\mu\text{m}$
60"	~ 63 $\mu\text{m}$
90"	~ 50 $\mu\text{m}$

The granulometry of the powders are chosen in accordance with the one suggested by different authors (KLUG and ALEXANDER, 1954, p. 290; MILLIMAN, 1973; GOLDSMITH *et al.*, 1955; TAFT and HARBAUGH, 1964).

In Table 1 the chemical analysis and lattice parameters ( $a$  and  $c$ ) are reported. Chemical analysis was performed using x-ray fluorescence following the analytical procedure developed by FRANZINI *et al.*, 1975. Lattice parameters were computed by least square refinement of x-ray powder patterns, calibrated with an internal standard ( $\text{CeO}_2$ ). Values of the parameters  $a$  and  $c$  show that the calcite of the limestone samples is substantially free from  $\text{Mg CO}_3$  in solid solution and that the dolostone samples contain stoichiometric dolomite (GOLDSMITH and GRAF, 1958).

Chemical analyses show that C1, C3, C4, D2 samples contain only calcite and dolomite, whereas the samples D1 and C2 contain respectively up to about 3% and 15% in weight of non carbonate fraction. This fraction is composed exclusively of quartz (3%) in the sample D1 and quartz (10%) together with some of clay minerals (5%) in sample C2.

In the Table 1 the calculated concentrations, obtained from the chemical analysis of the carbonate phases present in the analyzed samples are presented.

The diffracted intensity measurements were made on the following selected reflections (referred to hexagonal axes):

Calcite 102, 104, 110, 113, 202, 116, 212.

Dolomite 102, 104, 006, 015, 110, 113, 202, 211, 212, 214, 030.

The intense 108, 204 reflections of the calcite and 108, 116,

TABLE 1 - Chemical analyses, weight percent of the carbonate phases computed from chemical analyses, latitude parameters\*.

Sample	C1	C2	C3	C4	D1	D2
CaO		47.78	55.48	55.46	31.63	30.27
MgO		0.40	0.71	* 0.75	19.30	21.62
MnO		--	--	--	--	0.06
SiO <sub>2</sub>		11.76	<0.10	<0.10	3.04	0.14
Al <sub>2</sub> O <sub>3</sub>		1.57	<0.10	<0.10	0.10	0.08
TiO <sub>2</sub>		0.03	<0.01	<0.01	0.02	--
Fe <sub>2</sub> O <sub>3</sub> total		0.37	0.01	<0.01	0.04	0.06
Na <sub>2</sub> O		<0.01	<0.01	<0.01	<0.01	0.02
K <sub>2</sub> O		0.33	0.01	0.01	0.03	0.01
I.L.**		37.75	43.57	43.55	45.84	47.74
Wt% CaCO <sub>3</sub>		85.32	99.07	99.04	8.54	--
Wt% CaMg(CO <sub>3</sub> ) <sub>2</sub>		--	--	--	83.28	98.89
$\frac{a}{c}$	4.986(2)	4.988(2)	4.988(2)	4.989(1)	4.807(18)	4.810(1)
$\frac{c}{a}$	17.111(18)	17.042(13)	17.034(14)	17.061(11)	16.017(7)	16.038(4)

\*Parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left.

\*\*Ignition loss.

009 of the dolomite were not measured owing to interference between the peaks. The measurements were obtained by integrating the peak-area. As is well known, this is the correct procedure when samples of different origin have to be compared (MILLIMAN and BORNHOLD, 1973) although some authors (GAVISH and FRIEDMAN, 1973; ROYSE *et Al.*, 1971) have used peak height analysis.

The operating conditions of the diffractometer during the measurements were 38 Kv and 18 mA, using Cu  $K\alpha$  Ni filtered radiation,  $1^\circ$  divergence and scatter slits, 0.2 mm receiving slit, scanning speed  $1/2^\circ$  2 $\theta$  per minute, and a time constant of 4 seconds. The intensities of the reflections were measured by scanning the peak-area intensity through a fixed angular interval ( $1.66^\circ$  2 $\theta$ ). The measurements were corrected for background. The absolute intensity measurements performed on C2 and D1 samples were corrected taking into account the presence of impurities and the effect produced by those impurities on the intensities for the change of the absorption coefficient. This was carried out in order to compare all the intensity measurements.

Furthermore, the intensity of 113 reflection ( $d = 2.285 \text{ \AA}$ ) of the C2 sample was corrected (a small correction) for the overlap of the 102 reflection ( $d = 2.282 \text{ \AA}$ ) of the quartz. The intensity measurements were calibrated against an external standard of metallic silicon. The measured diffraction intensities are reported in Table 2 for the calcite and in Table 3 for the dolomite. The intensities of the specimens C2, C3, C4, D1 and D2 were measured on the three powders of different granulometry.

The resulting measurements are referred in the same tables as C2', C2'' and C2''' etc. to indicate a granulometry of 75, 63 and 50  $\mu\text{m}$  respectively. To check the reproducibility of slide preparations the intensities of some samples were measured several times repacking each time the powder.

These measurements are listed in Table 2 and 3. In the case of the C2 sample the integrated intensity measurements were also performed on a rock slab (see Table 2). Some sets of measurements repeated on the same slide show that the statistical counting error is the only instrumental error. This error was  $\pm 2\text{-}3\%$  for the 104 reflection and about  $\pm 2\text{-}4\%$  for the other peaks. To estimate the presence of preferred orientation effects on the measured intensities, were computed, for the selected reflections, the integrated intensities of the calcite and dolomite; these are shown respectively in Table 2 and Table 3.

TABLE 2 - Observed\* and calculated integrated intensities, of the limestones, for copper radiation.

Sample	012	104	110	113	113 <sup>●</sup>	202	116	212
C1	5.14	51.44	7.23	10.64	10.65	9.30	9.48	4.99
C2'	5.06	53.39	6.85	10.03	10.07	7.89	9.98	4.27
C2''	4.21	55.22	5.97	9.08	9.19	7.31	8.61	3.43
C2'''	4.36	56.05	5.52	8.55	8.71	7.19	8.18	3.41
C2 <sup>▲</sup>	4.47	54.41	5.52	8.86	8.98	7.09	7.93	2.85
C3'	4.68	53.58	6.76	10.13	--	7.93	10.72	4.29
C3''	3.37	124.80	4.31	7.15	8.36	7.15	8.38	2.89
C3'''	3.65	115.67	4.43	8.18	9.08	7.76	8.78	2.98
C3 <sup>▲</sup>	3.36	124.36	4.23	8.14	9.15	7.68	10.56	3.37
C4'	3.05	101.47	5.15	9.43	9.99	8.12	9.50	3.16
C4''	3.47	105.60	5.31	8.29	9.06	7.75	10.30	2.69
C4'''	4.00	91.80	5.19	8.17	8.79	7.75	10.06	2.81
C4 <sup>▲</sup>	3.88	125.13	4.92	8.08	9.11	7.53	9.62	3.22
C4 <sup>▲</sup>	3.79	113.59	4.95	8.41	9.25	7.31	9.51	2.79
C4 <sup>▲</sup>	3.53	101.53	5.42	7.89	8.67	6.95	9.28	2.79
C4 <sup>▲</sup>	2.86	201.45	4.20	7.20	9.45	8.55	8.23	2.68
C4 <sup>▲</sup>	3.59	205.86	5.69	8.77	10.58	8.69	10.56	2.71
CaCO <sub>3</sub>	20.77	217.67	31.88	44.29	--	35.16	51.37	25.72
$\bar{N}$ **	3.86	105.11	5.31	8.55	9.32	7.75	9.31	3.19
(esd)% <sup>†</sup>	16.88	45.29	16.38	10.76	7.18	8.39	9.34	19.75
E% <sup>‡</sup>	33.16	95.85	36.16	24.44	14.29	20.00	15.14	56.43

\*All the values of the observed intensities are divided by 1000

\*\*Calculated relative integrated intensities, all values divided by 2000 to facilitate comparison with Runmells (1970).

● Intensities corrected from equation (1) (see text).

† Average value of each reflection for the observed intensities.

‡ Estimated standard deviation % of the observed intensities.

▲ Max deviation %.

▲ Rocks slab (lithographic limestone).

TABLE 3 - Observed\* and calculated integrated intensities of the dolostone, for copper radiation.

Sample	012	104	006	015	110	113	202	211	212	214	030
D1'	2.43	107.68	4.39	3.93	5.56	16.75	10.05	1.29	3.76	3.81	3.26
D1''	2.29	106.30	3.50	3.73	5.56	16.63	8.56	1.19	3.52	3.50	3.72
D1'''	2.46	104.09	3.95	3.44	5.33	17.61	8.85	1.40	3.73	3.46	3.79
D2'	3.09	142.75	5.05	4.75	4.31	17.16	6.11	0.72	3.81	5.06	4.61
D2''	1.87	188.43	5.29	4.23	3.81	19.21	6.31	1.55	2.22	2.96	3.92
D2'''	2.41	108.85	5.38	3.47	5.13	17.26	9.40	1.23	3.26	3.15	2.86
D2''''	2.60	119.15	4.63	3.60	5.69	16.48	8.91	1.83	3.53	3.32	3.35
D2'''''	2.67	100.45	3.81	3.22	5.93	16.78	8.74	0.96	3.00	3.44	3.50
CaMg(CO <sub>3</sub> ) <sub>2</sub> **	6.63	136.00	6.38	7.68	15.34	39.40	20.61	5.99	14.23	10.05	12.66
$\bar{M}$ **	2.48	122.21	4.50	3.80	5.16	17.24	8.37	1.27	3.35	3.59	3.63
(esd)z*	13.97	24.47	15.73	13.07	14.15	5.10	16.84	26.77	15.82	18.10	14.32
E%#	24.72	54.18	22.22	25.12	26.16	11.43	27.00	44.09	33.73	40.95	26.99

\*All the values of the observed intensities are divided by 1000.

\*\*Calculated relative integrated intensities. All values divided by 2000 to facilitate comparison with Runmells (1970).

\*\*\*Average value of each reflection for the observed intensities.

#Estimated standard deviation % of the observed intensities.

\*Max deviation.

This calculation, for copper radiation, was made following the procedure indicated by RUNNELLS (1970). More recent values for the anomalous scattering (International Tables, volume 4, 1977, p. 148) were used and this is the reason for the small difference between Runnells values and ours.

## DISCUSSION

### *Calcite*

Table 3 shows two major features. First of all, it appears that the measured intensity is dependent on the original dimension of calcite crystals. In fact, synthetic calcite C1 and lithographic limestone C2 give essentially the same intensity values which are quite different from the one measured on the metamorphic limestone C3 and sphatic calcite C4. The second observation is that the set of measurements on C2 are much more self consistent than the ones obtained on C3 and C4. These observations are chiefly emphasized by the 104 reflection corresponding to the rhombohedral cleavage of carbonate minerals. The lack (samples C1 and C2) or the presence (samples C3 and C4) of preferred orientation effects on the diffracted intensities is revealed comparing the experimental and calculated values of intensities normalized to the 104 reflection.

It seems that the preferred orientation effects cannot be eliminated by prolonged grinding times when the examined sample is made from large calcite crystals. In the samples where the crystal sizes of the calcite are small enough, as is the case of the synthetic calcite and lithographic limestone, the intensity value are comparable in spite of the different grinding times. It seems that the granulometry of the powder of those limestones with very fine grain size are not very important for the intensity measurements. The slab of the lithographic limestone C2 has, in fact, yielded for the used reflections, intensities comparable with those obtained from the samples grounded with different times.

To analyze the preferred orientation effects, the correlation coefficients between all the measured reflections and the 104 reflection were computed, (neglecting the measurement performed on the slab of lithographic limestone C2).

The greatest correlation coefficient ( $-0.585$ ) was found between the 113 and 104 reflections.

To correct the intensity of the 113 reflection by means of the intensity measurement of the 104 reflection, the following experimental relation was applied:

$$I_c = I_m + m \Delta \quad (1)$$

where  $I_c$  is the 113 diffracted intensity corrected for the preferred orientation effect,  $I_m$  is the 113 measured diffracted intensity,  $m$  (97.71) is the angular coefficient of the straight line,  $\Delta = (I_{104}/I_{113})_{\text{obs}} - (I_{104}/I_{113})_{\text{calc.}}$  is the difference between the observed and the calculated values of the intensity ratios of the 104 reflection to the 113 reflection.

The intensity values of the 113 reflection corrected for preferred orientation effects by using the relation (1) are reported in Table 2.

The percentage standard deviation of the intensity values decreases from 10.8 for the uncorrected measurements to 7.2 for the corrected intensities of the 113 reflection; the maximum deviation decreases from 24.4 to 14.3.

### *Dolomite*

As far as dolomite is concerned we examined only two samples. The collected data show that the intensity measurements are influenced less by the original size of crystals than calcite measurements, provided that the powder consists of fine particles such as is obtained after 90" of grinding time. Nevertheless also in this case some preferred orientation effects are present. These are revealed comparing the experimental and calculated values of intensities normalized to the 104 reflection. From the values quoted in Table 3 we can deduce that the 113 reflection for dolomite has the smallest standard deviation (5%) of the intensities. This is the best reflection to use for a quantitative analysis of dolomite because, apart from the smaller influence of preferred orientation effects, it is practically independent of isomorphous substitutions (RUNNELLS, 1970).

## QUANTITATIVE X-RAY DIFFRACTION ANALYSIS

To check the full use of the above-stated relation and the validity of the 113 reflection to reduce the preferred orientation effects, we analyzed 4 international standards (400, 401, 402, 403) and prepared binary mixtures of limestone and dolostone. The binary mixtures were prepared mixing in various proportions powders with a 50  $\mu\text{m}$  granulometry, of the limestone C2, C3 and of the calcite C4 with the metamorphic dolostone D2. These mixtures are indicated respectively in the Table 4 with the M2, M3 and M4 abbreviations.

The mixtures were subsequently homogenized by mixing the components in alcohol with a ball mill for 40 minutes. The percentage weights of the calcite and of the dolomite in the mixtures are presented in Table 4. The analysis was made measuring the integrated intensities of the 104 and 113 reflections of calcite and dolomite in the instrumental conditions described above. These measurements are listed in Table 4. The concentrations of calcite and dolomite were computed by means of the relation:

$$X_i = I_i \mu k_i \quad (2)$$

where  $\mu$  is the total mass absorption coefficient of the sample at the diffracted wavelength,  $K_i$  is a constant which depends on the characteristics of the apparatus and on the structure of component  $i$ ,  $I_i$  is the diffracted intensity of a crystalline component ( $i$ ) contained in the sample, and  $X_i$  is its concentration (wt%). The mass absorption coefficient  $\mu$  of the standard and mixture samples was estimated following the procedure developed by BATTAGLIA and LEONI (1977). These coefficients are listed in Table 4. In Table 4 the concentrations of the calcite and dolomite calculated with the equation (2) are also summarized. To determine the concentrations of calcite the intensities of the 113 reflection were also used corrected by preferred orientation effects by means of the relations (1). The values of the  $k_i$  constants in (2) were obtained through a simple linear regression program utilizing all the measurements performed on the mixtures. These computed values of the  $k_i$  constants were then used to calculate the concentrations of calcite and dolomite in the international standards. We calculated the reference concentrations of calcite and dolomite of the stan-

TABLE 4 - Values of the computed and theoretical concentrations, diffracted intensities\*, values of  $\mu$  for  $\lambda = 1.50 \text{ \AA}$ , of the mixtures limestone-dolomite and international standard.

Sample	Wt%CaCO <sub>3</sub>		Wt%CaMg(CO <sub>3</sub> ) <sub>2</sub>		$\mu$ $\lambda=1.50$	I <sub>104</sub> calcite	I <sub>113</sub> dolomite					
M2	12.85*	6.11*	12.37**	11.72 <sup>■</sup>	84.97*	81.20*	82.62**	48.95	9.92	1.58	80.74	13.56
	42.66	22.77	46.52	41.65	50.11	50.98	47.36	56.04	32.29	5.19	44.28	6.79
	76.87	44.51	83.93	74.93	10.09	10.62	9.51	64.18	55.10	8.18	8.06	1.19
M3	10.15	8.07	9.47	12.16	89.85	81.85	92.38	48.33	13.27	1.22	82.42	15.35
	40.03	50.78	31.81	39.44	59.97	66.76	63.38	55.54	72.64	3.58	58.50	9.16
	80.00	120.52	81.39	83.49	20.00	20.84	20.89	65.18	146.90	7.81	15.56	2.57
M4	20.00	18.80	18.41	21.66	80.00	82.34	80.16	50.71	29.45	2.27	79.03	12.69
	30.14	24.88	28.02	29.10	69.86	68.12	68.00	53.16	37.19	3.30	62.37	10.27
	89.74	105.99	90.52	88.27	10.26	12.39	10.81	67.54	124.69	8.38	8.93	1.29
	(esd)%*	37.20	9.77	8.56	(esd)%*	9.49	4.49					
400					99.00	121.12	98.06	46.34			127.50	16.99
401	80.50	55.06	96.42	86.33	16.45	24.75	16.61	65.42	66.87	9.22	18.46	2.04
402	69.00	37.73	84.20	74.23	26.24	30.74	26.02	62.65	47.85	8.40	23.94	3.34
403	33.70	17.97	40.72	32.17	62.99	67.00	58.87	54.28	26.31	4.69	60.21	8.71
	(esd)%*	51.14	25.60	8.08	33.56	3.89						

\*Theoretical concentrations.

\* Concentrations computed from Eq(2) using experimental mass absorption coefficients and intensities of the reflection 104.

\* Concentrations computed from Eq(2) using experimental mass absorption coefficients and intensities of the reflection 113.

■ Concentrations computed from Eq(2) using experimental mass absorption coefficients and corrected intensities of the reflection 113.

♦ Estimated standard deviation %.

\*All the values of the diffracted intensities are divided by 1000.

dards, listed in Table 4 through a chemical analysis (INGAMELLS and SUHR, 1967).

In the calculation, all the content of MgO was given as dolomite. This procedure is justified because, in the international standards, calcite does not contain Mg and dolomite is stoichiometric.

This results from a previous analysis by x-ray diffractometry (GOLDSMITH and GRAF, 1958) of the molar composition of calcite and dolomite in the standards.

#### CONCLUSION AND IMPLICATIONS

It seem evident from the preceding discussion that in the analysis of calcite and dolomite by means of x-ray diffractometry, the preferred orientation effects can introduce appreciable error, chiefly on the 104 intensity measurement, in the case that we must analyzed carbonate rocks with very great crystal size (metamorphic limestone, spathic calcite, metamorphic dolostone etc.). The use of the 104 reflection permits one to obtain fair results when the analysis is made on very fine grain rocks.

If we analyze rocks with an original variant crystal size, the use of 104 reflection is ill-advised because the measured intensities are affected by preferred orientation effects. The analysis of calcite, for this kind of rock, can be performed utilizing directly the intensities of the 113 reflection or else correcting these intensities by means of the 104 intensity measurements.

As far as the quantitative analysis of dolomite is concerned, the better results are obtained by a direct measurement of the 113 reflection. In both cases, (analysis of calcite or dolomite) the use of the 113 reflection has the disadvantage to reduce the sensitivity in the determination of the minerals.

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