Disordering of the Cations, Ca²⁺, Mg²⁺, Fe²⁺ in Dolomite Lattice

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Abstract

Several specimens of dolomite covering those of hydrothermal origin as well as of sedimentary origin have been examined. Content of $FeCO_3$ in specimens of hydrothermal origin is usually high. In specimens which are hydrothermal origin and high in $FeCO_3$ content, hkl reflexions utterly disappear when $h+k+l=2n+1$ and $h=k$ or $k=l$ or $l=h$, showing that space group turns from $R\bar{3}$ to $R\bar{3}c$. The elevation of symmetry may be attributed to a disordering of cations, Ca^{2+}, Mg^{2+} and Fe^{2+}.

Introduction

GRAF and GOLDSMITH (1956) observed that synthetic dolomites formed under various experimental conditions went through a protodolomite stage. The protodolomite contains more than 50 mol per cent $CaCO_3$ in the structure and in X-ray diffraction photographs shows weak or no hkl reflexions when $h+k+l=2n+1$ and $h=k$ or $k=l$ or $l=h$, which they called "order reflexions". GOLDSMITH and GRAF (1958) say that dolomite, in which appreciable substitution of Fe^{2+}, Mn^{2+} for Mg^{2+} has taken place, might show the same phenomenon in an X-ray diffraction photograph due to the increased scattering from Mg^{2+} positions.

Recently the author examined several specimens of dolomite which cover those of hydrothermal origin as well as of sedimentary origin. In specimens which are sedimentary origin and high in $CaCO_3$ content, hkl reflexions appeared even when $h+k+l=2n+1$ and $h=k$ or $k=l$ or $l=h$, while in specimens which are hydrothermal origin and high in $FeCO_3$ content, hkl reflexions utterly disappeared when $h+k+l=2n+1$ and $h=k$ or $k=l$ or $l=h$. Calculating the structure factors of dolomite in which considerable amount of Fe^{2+} is substituted for Mg^{2+}, they were compared with the calculated structure factors of dolomite in which $CaCO_3$: $MgCO_3=1:1$. As a result it was recognized that even appreciable substitution of Fe^{2+} for Mg^{2+} did not highly affect the structure factors. Complete disappearance of hkl reflexions ($h+k+l=2n+1$ and $h=k$ or $k=l$ or $l=h$), therefore, must be

attributed to a disordering of cations in the structure.

Details will be given in the following.

Experimental

Specimens examined in the present investigation are from the localities as described below.

Hydrothermal origin

Igashima Mine, Mikawa-mura, Niigata Prefecture

Nakase Mine, Sekinomiya-chō, Hyogo Prefecture

Mikawa Mine, Mikawa-mura, Niigata Prefecture

Kadogami Mine, Miyako-shi, Iwate Prefecture

Sedimentary origin

Gyushinzan, Liaoning, South Manchuria

Mitsuka, Kasuga-mura, Gifu Prefecture

Kuzuu, Kuzuu-chō, Tochigi Prefecture

Tsunemi, Matsugae-mura, Fukuoka Prefecture

Specimen from Igashima Mine is coarse-granular, white in colour, mixed with calcite and quartz in small quantity. Specimen from Nakase Mine is coarse granular, grown around prismatic crystals of stibnite, mixed with calcite and quartz. Specimen from Mikawa Mine is coarse granular, white in colour, translucent, mixed with calcite and quartz, minute crystals of pyrite are scattered as an impurity. Specimen from Kadogami Mine is coarse granular, greyish white in colour, mixed with calcite in large quantity. Specimen from Gyushinzan is coarse granular, greyish in colour, mixed with calcite. Specimen from Mitsuka is coarse granular, white in colour, mixed with calcite in large quantity. Specimen from Kuzuu is fine granular, greyish white in colour, intruded by calcite veinlets. Specimen from Tsunemi is coarse granular, greyish white in colour, in fractures calcite is deposited.

Specimens were crushed into 60~80 mesh and first picked out impurities such as quartz, stibnite and pyrite by using the binocular microscope, then, dolomite was separated from calcite by using staining method devised by FRIEDMAN (1959). The procedure is that a mixture of dolomite and calcite grains is immersed for 3 minutes into 2% HCl solution in which alizarine red is dissolved. Stained grains are calcite. After washed with water, dried in air, picked up non-stained grains under the binocular microscope. Since specimen from Kuzuu is fine granular, it was crushed into 100~120 mesh.

Dolomites obtained by the above mentioned procedure were examined chemi-

cally and Röntgenographically. Chemical analysis was carried out to get Ca^{2+}, Mg^{2+}, Fe^{2+} ratio. However, silica was also determined in fear of mixing minute quartz grains in the specimens. Silica and ferric oxide were determined as usual. Judging from the colour of ferric oxide, it may more or less be contaminated by manganese. Calcium and magnesium were determined by chelatometric titration. Results obtained are shown in Table 1 and 2. As will be seen in Table 1 and 2, in the dolomites of hydrothermal origin are generally high in $FeCO_3$ content as compared with those of sedimentary origin.

Table 1. Weight percentages of chemical compositions of dolomite

	Locality	SiO_2	$CaCO_3$	$MgCO_3$	$FeCO_3$	Total
Hydrothermal origin	Igashima Mine	5.17	51.20	34.46	9.09	99.92
	Nakase Mine	10.97	47.08	34.12	7.49	99.66
	Mikawa Mine	12.79	46.60	34.90	5.80	100.09
	Kadogami Mine	0.70	55.40	42.30	2.02	100.42
Sedimentary origin	Gyushinzan	0.00	53.31	44.42	1.74	99.47
	Mitsuka	0.66	55.11	43.63	0.64	100.04
	Kuzuu	0.00	58.45	41.02	0.36	99.83
	Tsunemi	0.00	64.07	36.21	0.21	100.49

Table 2. Mol ratios of chemical compositions of dolomite

	Locality	$CaCO_3$	$MgCO_3$	$FeCO_3$
Hydrothermal origin	Igashima Mine	50.95	40.82	8.22
	Nakase Mine	49.81	42.98	7.20
	Mikawa Mine	49.86	44.46	5.64
	Kadogami Mine	51.47	46.78	1.71
Sedimentary origin	Gyushinzan	49.47	49.07	1.47
	Mitsuka	51.20	48.26	0.54
	Kuzuu	54.32	45.38	0.31
	Tsunemi	59.67	40.15	0.18

With these specimens X-ray powder diffraction patterns were taken by using Norelco X-ray diffractometer. The diffraction patterns are shown in Fig. 1. 2θ's of the diffractions were calibrated by silicon powder pattern. Values of $1/d^2_{(hkl)}$ are shown in Table 3. Indices of the diffractions were calculated by using following formula.

Fig. 1.   X-ray diffraction patterns of dolomite
A. Igashima Mine   B. Nakase Mine   C. Mikawa Mine   D. Kadogami Mine
E. Gyushinzan   F. Mitsuka   G. Kuzuu   H. Tsunemi

Table 3. $\dfrac{1}{d^2_{(hkl)}}$ and lattice constants of dolomite

	Locality	$\dfrac{1}{d^2(001)}$	$\dfrac{1}{d^2(110)}$	$\dfrac{1}{d^2(211)}$	$\dfrac{1}{d^2(222)}$	$\dfrac{1}{d^2(221)}$	$\dfrac{1}{d^2(\bar{1}10)}$	$\dfrac{1}{d^2(210)}$	$\dfrac{1}{d^2(\bar{1}11)}$	$\dfrac{1}{d^2(200)}$	$a(\text{Å})$	α
Hydrothermal origin	Igashima Mine	—	0.07315	0.1197	0.1392	—	0.1723	0.2074	—	0.2456	6.036	47°01′
	Nakase Mine	—	0.07283	0.1196	0.1389	—	0.1724	0.2068	—	0.2451	6.045	47°00′
	Mikawa Mine	—	0.07305	0.1204	0.1340	—	0.1730	0.2081	—	0.2463	6.080	46°29′
	Kadogami Mine	0.06135	0.07326	0.1206	0.1401	0.1550	0.1730	0.2079	0.2338	0.2461	6.019	47°08′
Sedimentary origin	Gyushinzan	0.06180	0.07353	0.1210	0.1408	0.1556	0.1736	0.2085	0.2352	0.2465	6.005	48°08′
	Mitsuka	0.06177	0.07331	0.1206	0.1403	0.1550	0.1733	0.2081	0.2345	0.2461	6.017	47°07′
	Kuzuu	0.06158	0.07315	0.1204	0.1402	0.1551	0.1730	0.2081	0.2341	0.2463	6.017	47°07′
	Tsunemi	0.06093	0.07257	0.1183	0.1390	0.1538	0.1717	0.2068	0.2343	0.2446	6.043	46°58′

$$1/d^2_{(hkl)} = (h^2+k^2+l^2)a^{*2}+2(hk+kl+lh)a^{*2}\cos\alpha^*$$

where, $a^*=0.2465$, $\alpha^*=113°45'$

From the values of $1/d^2_{(hkl)}$ lattice constants were calculated putting indices into the above formula by using the method of least squares. Lattice constants obtained are shown in Table 3. No relationship is observed between the chemical compositions and lattice constants. In the diffraction patterns of specimens from Igashima Mine, Nakase Mine and Mikawa Mine, hkl reflexions utterly disappear when $h+k+l=2n+1$ and $h=k$ or $k=l$ or $l=h$. In the following this phenomenon will be considered.

Consideration

Space group of dolomite is $R\bar{3}$ and dolomite contains $CaMg(CO_3)_2$ in a cell. In the space group $R\bar{3}$ there are no reflexions which disappear. Space group of calcite is $R\bar{3}c$ and calcite contains $2[CaCO_3]$ in a cell. In the space group $R\bar{3}c$ hkl reflexions disappear when $h+k+l=2n+1$ and $h=k$ or $k=l$ or $l=h$. In the present study it was observed that in dolomites from Igashima Mine, Nakase Mine and Mikawa Mine hkl reflexions disappeared when $h+k+l=2n+1$ and $h=k$ or $k=l$ or $l=h$. The dolomites from Igashima Mine, Nakase Mine and Mikawa Mine are high in $FeCO_3$ content. From the mol ratios shown in Table 2, it seems that Fe^{2+} is substituted for Mg^{2+}. May the disappearance be caused by such a substitution? Structure factor of space group $R\bar{3}$ runs as follows:

$$F_{hkl} = 2\,\Sigma f[\cos 2\pi(hx+ky+lz)+\cos 2\pi(kx+ly+hz)+\cos 2\pi(lx+hy+kz)]\,.$$

Coordinates of atoms in a cell of dolomite are as follows:

Ca	(0 0 0)	
Mg	(1/2 1/2 1/2)	
C	(1/4 1/4 1/4),	(3/4 3/4 3/4)
O	(1/2 0 1/4),	(0 1/4 1/2), (1/4 1/2 0)
	(1/2 0 3/4),	(0 3/4 1/2), (3/4 1/2 0).

Accordingly, the structure factor of dolomite runs as follows:

$$F_{hkl} = f_{Ca}+f_{Mg}\cos 2\pi\left(\frac{h+k+l}{2}\right)+2f_C\cos 2\pi\left(\frac{h+k+l}{2}\right)+6f_O\cos 2\pi\left(\frac{h}{2}+\frac{l}{4}\right).$$

As an example, dolomite from Nasakse Mine is taken into consideration. Basing on the mol ratio shown in Table 2, chemical formula of the dolomite is expressed as $CaMg_{6/7}Fe_{1/7}(CO_3)_2$. Assuming that Fe^{2+} occupies the (1/2 1/2 1/2)

position in a cell, being substituted for Mg^{2+}, structure factors were calculated by using the above formula.   These are shown in Table 4.

Table 4.   Structure factors

Composition \ hkl	001	110	211	222	221	$\bar{1}10$	210	$\bar{1}11$	200
$CaMg_{6/7}Fe_{1/7}(CO_3)_2$	5	−23	32	−17	4	−2	34	4	45
$CaMg(CO_3)_2$	7	−25	31	−18	5	−4	35	5	44

Structure factors calculated with $CaMg(CO_3)_2$ are also shown in Table 4. Comparing the structure factors of $CaMg_{6/7}Fe_{1/7}(CO_3)_2$ with those of $CaMg(CO_3)_2$ there is almost no difference between them.   In the present study it was observed that in dolomite whose chemical formula is $CaMg_{6/7}Fe_{1/7}(CO_3)_2$, hkl reflexions utterly disappeared when $h+k+l=2n+1$ and $h=k$ or $k=l$ or $l=h$.   This fact no longer be interpreted by the above assumption that Fe^{2+} occupies $(1/2\ 1/2\ 1/2)$ position in a cell, being substituted for Mg^{2+}.   Contrary to this, the fact can satisfactorily be interpreted by the acceptance that space group of dolomite whose chemical formula is $CaMg_{6/7}Fe_{1/7}(CO_3)_2$ has turned from $R\bar{3}$ to $R\bar{3}c$ due to a disordering of the cations Ca^{2+}, Mg^{2+} and Fe^{2+}.   The disordering may be caused either by the relatively high temperature at which the dolomite was formed or by the entering of Fe^{2+} in a considerable amount in the lattice.

References

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