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A New SiC Polytype, 45*Rb*

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Abstract

The stacking sequence of a new SiC polytype 45*Rb*, which was synthesized at room temperature is $(433212)_3$. This implies that the Zhdanov symbol 1 in the stacking sequence, except for the 2*H* polytype, might be a special characteristic of the structure of SiC grown at low temperatures. If this is true, the recently reported 5*H* polytype SiC found in limestone, dolomite and alluvial deposit, which can be deduced as (41) stacking, may be authigenic and might have grown at a low temperature. This idea may suggest the general distribution of SiC in limestone and in other low-temperature deposits. Unmetamorphosed limestones of about 20 localities were examined, and SiC was found in seven of those localities, although the 45*Rb* and 5*H* polytypes have not been found yet in these samples.

Introduction

Silicon carbide is a much studied substance, as an important industrial material, and academically from the viewpoint of polytypism (Verma & Krishna, 1966). SiC is usually synthesized at very high temperature (1570–3270 K). Natural silicon carbide (moissanite) was found in meteorites by Kunz in 1905 (Strunz, 1970), then in kimberlite (Bobrievitsch, Kalyuschny & Smirnov, 1957), and in the Green River formation (Regis & Sand, 1958). Gnoevaya & Grozdanov (1965) found SiC in a triassic limestone and dolomite from northwestern Bulgaria, and they reported the polytypes of these SiC as 4*H* and 5*H*. Then Gevorkyan, Gurkina & Kaminskii (1974) reported a new occurrence of the 5*H* polytype of SiC in alluvial deposits in the ophiolite zone in Armenia, USSR. All of these natural SiC have been explained by previous workers as being of high-temperature origin.

Description of SiC crystal

Since 1973, one of the authors (Fujii) has been trying to synthesize authigenic silicate minerals in colloidal silica solution at room temperature. In several runs of his systematic trials, small silicon carbide crystals were found among the precipitates of various kinds of silicate and oxide materials. These SiC crystals have glassy irregular shape and are approximately 0·1 mm in dimension with pale or dark bluish color. Quantitative chemical analysis was carried out using a computer controlled JEOL 50-A electron probe microanalyzer and showed that these SiC crystals are nearly pure in chemical composition except for a negligibly small amount of aluminum (maximum 0·02%). About fifteen crystals were examined by X-ray precession camera, and it was found that the polytypes of these SiC were 4*H*, 6*H* and 15*R*, except for a dark blue crystal which showed a 45*R*-type diffraction pattern (Fig. 1). The lattice constants of the 45*R* SiC are $a = 3{\cdot}08$ and $c = 2{\cdot}52$ Å × 45 (Sueno, Kojima, Nishio & Fujii, 1977).

Inoue, Inomata & Tanaka (1972) have reported the finding of 45*R* polytype SiC and have analyzed its stacking sequence. They have introduced a new assumption in the process of the analysis that an SiC crystal grown at high temperature may not include the

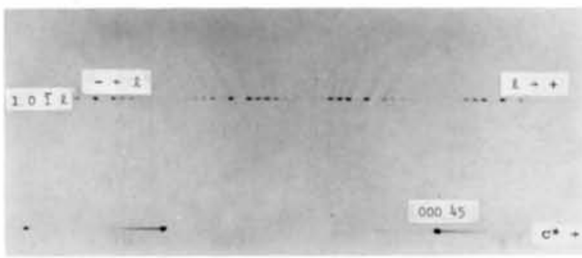

Fig. 1. Oscillation photography around the *c* axis of SiC type 45*Rb* ($r = 28{\cdot}7$ mm, $\lambda = 1{\cdot}54$ Å).

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stacking element represented by the Zhdanov symbol 1, for the purpose of reducing the number of possible stacking sequences of the 45*R* polytype. They found that only 22 models were possible for the 45*R* stacking sequence if Zhdanov symbol 1 was avoided, reduced from about 400 original models which were allowed to include Zhdanov symbol 1. They calculated F_c for all 22 models, and concluded that the calculated intensities of the stacking model $(3332232)_3$ were consistent with those of the observed ones. However, the 45*R* SiC of the present study showed a different intensity distribution from those of 45*R* SiC found by Inoue *et al.* In order to distinguish these two 45*R* SiC with the different stackings, it may be better to term them as 45*Ra* for the SiC reported by Inoue *et al.*, and 45*Rb* for the present one. The detailed comparison of intensities of 45*Ra*, 45*Rb* and a selected model among the 22 possible stackings of Inoue *et al.*, $(333222)_3$, which partly fit with 45*Rb* but is still violated at the points $l = -17$, -11 and 16. These results suggest that this 45*Rb* may include the stacking element represented by the Zhdanov symbol 1 in its structure.

Table 1. *Comparison of the intensity distribution along the* $10\bar{1}l$ *of* 45*Rb* *and other selected* 45*R* *type* SiC

l	45*Rb**	45*Ra*†	$(333222)_3$†
43	1·39	0·43	1·70
40	2·62	4·64	1·86
37	3·59	4·98	8·00
34	8·09	2·75	0·52
31	6·70	14·38	14·95
28	16·49	4·24	5·78
25	0·00	5·03	0·14
22	54·25	71·93	80·89
19	7·34	17·31	3·41
16	54·78	4·75	20·51
13	54·12	74·88	61·20
10	37·89	30·70	37·02
7	10·85	7·26	8·33
4	3·43	11·79	6·88
1	5·90	5·40	7·51
−2	4·34	1·74	6·96
−5	9·95	20·73	8·32
−8	13·83	23·48	37·71
−11	24·33	12·70	2·39
−14	23·27	57·20	59·47
−17	53.72	11·96	16·32
−20	0·00	8·42	0·23
−23	53·50	64·77	72·83
−26	3·88	8·55	1·68
−29	18·22	1·47	6·34
−32	12·27	17·55	14·35
−35	9·06	6·52	7·86
−38	2·58	1·56	1·79
−41	0·00	2·70	1·58
−44	1·61	1·36	1·89
$\frac{\sum \lvert I_o - I_c \rvert}{\sum I_o} \times 100$		70·00	61·10

* Present study.
† Inoue, Inomata & Tanaka (1972).

Stacking sequence analysis of the 45*Rb* polytype

The oscillation photographs of the 45*Rb* crystal around the c^* axis were taken using the multiple film method with Cu $K\alpha$ radiation. The intensity distribution along the $10\bar{1}l$ row for $l = -44$ to $+43$ was measured (Table 1) using a microphotometer with the aid of a standard exposure scale, and then Lorentz–polarization factor corrections were carried out.

Another long-exposure oscillation photograph has revealed that each reflection was accompanied by faint diffuse streaks along c^*. But we have concluded these diffuse streaks may not be essential and will not obstruct the analysis of the stacking sequence of the 45*Rb*.

Tokonami (1966) has derived a direct method for solving the stacking sequence of rhombohedral SiC, which was successfully applied to the determination of layer stacking of 96*R* SiC. His method stands basically on the rationalization of the vector set of the one-dimensional Patterson function, $V(z)$, with the aid of several properties of the Zhdanov symbol and those of the nearest-neighbor vector ($n.n$ vector). Here, an mth nearest-neighbor vector can be defined as a vector from a Si (or C) atom to the mth nearest-neighboring Si (or C) atom with the same x- and y-positional parameters, that is a vector among the atoms with the same layer stacking notation A, B or C (see Tokonami & Hosoya, 1965, for further explanation). As a general characteristic of a rhombohedral SiC polytype, the stacking of the first N layers repeat three times in the unit cell, and the coordinates of $3N$ Si atoms can be shown as

$$0,\ 0,\ Zn/3N;\ 2/3,\ 1/3,\ 1/3 + Zn/3N;$$
$$1/3,\ 2/3,\ 2/3 + Zn/3N$$
$$(n = 0, 1, 2, \cdots, N-1),$$

where Zn is an integer smaller than $3N$. The structure factor for the reflections with $-h + k + l \equiv 0 (\mathrm{mod}\ 3)$ can be expressed by the following simple equation based on the simple positional relationship between Si and C atoms.

$$F(hkl) = 3f(hkl) \sum_{n=0}^{N-1} \exp(2\pi lZj/3N) \qquad (1)$$

where $f(hkl) = f_{\mathrm{Si}} + f_{\mathrm{C}} \exp(2\pi ilc/3N)$.

Tokonami (1966) has derived the unitary structure factor, $U(l)$, in his stacking sequence analysis, which is

$$U(l) = \exp(2\pi ilZj/3N). \qquad (2)$$

The unitary structure factor is a function of l only, that is, $U(l)$ is equivalent to the structure factor of a one-dimensional crystal, which, in the case of SiC, corresponds to an array of N point atoms positioned on the layers of one of the three layer stacking notations within the periods of $3N$.

Here, the cosine transform of $|U(l)|^2$, which is given by

$$V(z) = 1/3N \sum_{l=0}^{3N-1} |U(l)|^2 \cos 2\pi lz, \quad (3)$$

behaves at $z = n/3N$ as the Patterson function of one-dimensional crystal consisting of point atoms, because $|U(l)|^2$ is a periodic function with the period of $3N$, where n is an integer (Tokonami, 1966). Accordingly, the vector set of the crystal, $\mathbf{V}(z)$, is

$$\mathbf{V}(z) = \sum_{n=-\infty}^{\infty} v_n \, \delta(z - n/3N), \quad (4)$$

where δ represents a delta function, v_n an appropriate positive integer including zero and should be equal to $V(n/3N)$. Therefore, $V(n/3N)$ is the number of vectors with the length of $n/3N$ derived from the observed data, and v_n is the number of vectors which really exist in the crystal structure.

However, direct application of his method upon the present study met some difficulties because of the existence of hypothetical Zhdanov symbol 1 in the stacking of $45Rb$, although the basic procedure is still useful. It may be appropriate here to summarize the properties of the Zhdanov symbol on the basis of Tokonami's paper for the convenience of the subsequent discussions.

(I) Each figure in the Zhdanov symbol represents a consecutive layer stacking block with the same orientational sign in SiC structure. Each figure also corresponds to a block of stacking layers represented by a straight line in Ramsdell's zigzag sequence diagram, and a period of the SiC stacking unit consists of pairs of these stacking blocks with two antiparallel orientations. Therefore, the Zhdanov symbol always consists of an even number of figures, such as (33) for the $6H$ polytype, except for the $3C$ polytype. In the case of the rhombohedral polytype, the symbol can be represented by the figures in parentheses with subscript 3, such as $(23)_3$ for $15R$, since N basal stackings repeat three times to complete a period. These N basal stacking layers are called an abbreviated symbol and also consist of an even number of figures. Namely,

$$\sum f_n \equiv 0 (\mathrm{mod}\ 2) \quad (5)$$

$$\sum n f_n = N \quad (6)$$

where f_n denotes the frequency of the figure n in the abbreviated symbol. For example, the abbreviated symbol of the polytype $15R$ is, therefore, $N = 2 + 3 = 5$.

Thus applying (5) and (6),

$$\sum f_n = f_2 + f_3 = 5,$$
$$\sum n f_n = 2 \times f_2 + 3 \times f_3 = 5.$$

(II) The number of figures, f_n, in an abbreviated Zhdanov symbol is equal to the total number of the junctions in the zigzag sequence of the N basal rhombohedral stacking. One junction, which is equivalent to one of ABA, ACA, BAB, BCB, CAC and CBC sequence of layers, corresponds to one $2/3N$ long vector. Therefore, the number of vectors with the length of $2/3N$, which is v_2, is also even and equal to the number of figures in the abbreviated symbol of rhombohedral structure, thus,

$$\sum f_n = v_2. \quad (7)$$

(III) The difference between the sum of even-ordered figures and that of odd-ordered ones in the Zhdanov symbol is a multiple of three. For instance, (3 + 3 + 3) − (2 + 2 + 2) = 3 can be deduced for the polytype $15R$ which has full Zhdanov symbol (232323). But in the abbreviated symbol of the rhombohedral polytype, the difference taken between these even-ordered figures and odd-ordered ones should not be a multiple of 3.

(IV) When the stacking includes one Zhdanov symbol 1, the one-dimensional vector set bears one first $n.n$ vector with a length longer than $4/3N$.

(V) When 2 is included in the symbol, the vector set bears one second $n.n$ vector with the length of $4/3N$ corresponding to each figure 2.

(VI) When 4 or a larger figure is included in the symbol, the vector set bears two second $n.n$ vectors $5/3N$ in length corresponding to each figure 4 or larger.

(VII) In the rhombohedral $3NR$ polytype, the number of first $n.n$ vectors within the period of $3N$ layers is equal to N, and the sum of their length is 1. Since the vector with length $1/3N$ is not allowed because of the nature of the stacking, the sum of the length of the first $n.n$ vectors can be represented by the following relation:

$$2v_2 + 3v_3 + 4(N - v_2 - v_3) \leq 3N,$$

namely,

$$v_3 \geq N - 2v_2. \quad (8)$$

Here, the equality can be applied only when there is no first $n.n$ vector longer than $4/3N$, that is, when 1 is included in the Zhdanov symbol the equality should not be applied (property IV).

In the first step of the analysis, we have calculated the one-dimensional Patterson function, $V(n/3N)$, following Tokonami's procedure on the basis of the observed intensities along the $10\bar{1}l$ row. The result is shown in Table 2.

Since our observed data can be trusted to be as high in accuracy as the film method from its careful handling, we have assumed the true v_2, which should be even number (property II), must be 4 or 6 based on the observed $V(2/3N)$ value 4·95. According to (8), v_3 should be larger than 3 when 6 was assigned for v_2, and the assignment of 4 for v_2 gives a v_3 value larger than 7.

Table 2. *Vector length* (z) *and observed number of one-dimensional vectors* [$V(z)$]

z	Observed $V(z)$	z	Observed $V(z)$
0/45	15·00	11/45	4·21
1/45	−0·04	12/45	4·70
2/45	4·95	13/45	4·40
3/45	5·12	14/45	8·38
4/45	6·31	15/45	0·00
5/45	3·06	16/45	6·66
6/45	7·89	17/45	5·66
7/45	1·01	18/45	5·18
8/45	9·20	19/45	4·48
9/45	1·96	20/45	5·02
10/45	6·92	21/45	5·14
		22/45	4·80

Then we have listed all the possible combinations of figures for these two possible cases, v_2 equal to 4 and 6, considering the property II and an assumption that the combination must include at least one Zhdanov symbol 1. Thus we have obtained 31 and 16 combinations for the cases v_2 equal to 4 and 6, respectively. However, about half of these combinations have been rejected for the reason that the combinations should not include two of figure 4 or larger because it gives a much larger v_5 value compared to the observed $V(5/45)$ of 3·06 (property VI). The remaining combinations are listed in Table 3.

Each of these remaining combinations was then arranged for the possible arrays of figures, that is the possible layer sequence, considering the property III. Then we have assumed that the true v_7 value may be 0 or 1 on the basis of the observed $V(7/45)$, 1·01. This is one of the conspicuous characters in this vector set. For utilizing this character to reduce the number of possible sequences, we have deduced the possible special short arrays of figures which bring about at least one $7/3N$ long vector into the vector set (Table 4). Each of the listed possible layer stackings was then examined to find if it included the above short arrays or not. Those which included more than two of these arrays in the stacking sequence were avoided because they would have larger $V(7/45)$ than the assumed true v_7 value, 0 or 1.

As a result of the application of the above new prohibition rule, the possible stacking sequences for 45*Rb* were brought down to only three, $(433212)_3$, $(432123)_3$ and $(433113)_3$. We then calculated the relative intensities for the three sequences. The resulting calculated and observed intensities are listed in Table 5. The stacking sequence for 45*Rb* has been successfully deduced to be $(433212)_3$ with the space group $R3m$. The R factor was 21% for this stacking sequence, much smaller than those for the others. The graphical comparison between the observed $V(n/45)$ and the calculated ones on the basis of the final $(433212)_3$ stacking also showed good consistency (Fig. 2). The difference between I_o and I_c. 1 in Table 5 for some comparatively weak reflections may be caused by the diffuse streaks detected on the long-exposure film.

Table 3. *Possible combinations of figures for* 45*Rb*

	Zhdanov symbol	12	11	10	9	8	7	6	5	4	3	2	1
Number of figures	$f_n = 4$	1	0	0	0	0	0	0	0	0	0	0	3
		0	1	0	0	0	0	0	0	0	0	1	2
		0	0	1	0	0	0	0	0	0	1	0	2
		0	0	1	0	0	0	0	0	0	0	2	1
		0	0	0	1	0	0	0	0	0	1	1	1
		0	0	0	0	1	0	0	0	0	2	0	1
	$f_n = 6$	0	0	1	0	0	0	0	0	0	0	0	5
		0	0	0	1	0	0	0	0	0	0	1	4
		0	0	0	0	1	0	0	0	0	1	0	4
		0	0	0	0	1	0	0	0	0	0	2	3
		0	0	0	0	0	1	0	0	0	1	1	3
		0	0	0	0	0	1	0	0	0	0	3	2
		0	0	0	0	0	0	1	0	0	2	0	3
		0	0	0	0	0	0	1	0	0	1	2	2
		0	0	0	0	0	0	1	0	0	0	4	1
		0	0	0	0	0	0	0	1	0	2	1	2
		0	0	0	0	0	0	0	1	0	1	3	1
		0	0	0	0	0	0	0	0	1	3	0	2
		0	0	0	0	0	0	0	0	1	2	2	1
		0	0	0	0	0	0	0	0	0	4	1	1

Table 4. *The special short arrays of figures which can arise from the vector with length* $7/3N$

The symbol ≤ means the maximum value of vectors. For example, $(m-1) \le 2$ means that there are at most two $7/3N$ vectors depending on m; when m is 2, we have one $7/3N$ vector, and when m is 3 or larger than 3, we have two $7/3N$ vectors depending on m.

v_7 (Number of $7/3N$ vectors)	Stacking sequence		Examples
one	$(n \ge 5)\,(n \ge 2)$		52, 62, 63
	$(n \ge 4)\ 11\ (n \ge 1)$		4111, 5111
	$(n \ge 3)\ 12\ (n \ge 1)$		3121, 4122
	$(n \ge 2)\ 13\ (n \ge 1)$		2131, 3132
	$(n \ge 1)\ 14\ (n \ge 1)$		1141, 2142
$(m-1)+n$	$m\ 131\ n$	one	11311, 151
$(m-1) \le 1$		two	21311, 251, 351
$n \le 2$	$m\ 5\ n$	three	21312, 252, 353
$(m-1)+(n-1)$	$m\ 121\ n$	one	11212
$(m-1) \le 2$		two	21212, 11213
$(n-1) \le 2$		three	21213, 21214
		four	31213, 41214
$(m-1)+(n-2)$			
$(m-1) \le 3$	$m\ 111\ n$	one	31111, 21112
$(n-1) \le 2$		two	41111, 31112
		three	41112, 31113
		four	41113, 51113
		five	41114, 51115
$(m-3)+(n-3)$	$m\ 2\ n$	one	421, 322
$(m-1) \le 4$		two	521, 422, 323
$(n-3) \le 2$		three	522, 423, 622
		four	523, 424, 623
		five	524, 624, 724
		six	525, 625, 626

After finishing the above-described theoretical stacking sequence analysis, we had a chance to calculate unitary structure factors of all the possible stacking sequences of $45Rb$ using the modified *SICAL* program originally written by Inoue *et al.* (1972). But even after exhaustive scanning of the computer output, $(433212)_3$ was the most probable model of them all.

Table 5. *Calculated relative intensities* I_c 1–3 *and observed intensity* I_o *for the* $10\bar{1}l$ *reflections*

l	I_o	I_c·1	I_c·2	I_c·3
43	1·39	2·38	1·45	0·38
40	2·62	6·65	1·24	6·41
37	3·59	5·67	0·00	1·78
34	8·09	2·84	16·02	8·01
31	6·70	3·14	0·63	0·34
28	16·49	18·71	14·39	23·32
25	0·00	6·92	4·10	2·41
22	54·25	59·41	62·61	53·23
19	7·34	1·24	0·46	3·31
16	54·78	47·37	75·49	77·58
13	54·12	47·60	20·29	23·26
10	37·89	37·89	1·90	11·84
7	10·85	9·06	44·89	32·68
4	3·43	1·68	18·31	9·48
1	5·90	0·74	1·31	5·14
−2	4·34	9·76	5·94	1·56
−5	9·95	29·73	5·52	28·63
−8	13·83	26·74	0·00	8·78
−11	24·33	14·45	74·15	37·04
−14	23·27	12·47	2·54	1·37
−17	53·72	52·80	40·61	65·81
−20	0·00	11·57	6·86	4·03
−23	53·50	53·49	56·38	47·92
−26	3·88	0·62	0·23	1·64
−29	18·22	14·65	23·35	24·00
−32	12·27	11·16	4·76	5·45
−35	9·06	8·04	0·40	2·51
−38	2·58	1·94	9·63	7·01
−41	0·00	0·39	4·20	2·18
−44	1·61	0·18	0·33	1·30
Zigzag sequence		$(433212)_3$	$(432123)_3$	$(433113)_3$
$\frac{\sum \lvert I_o - I_c \rvert}{\sum I_o} \times 100$		21·42	67·32	49·56

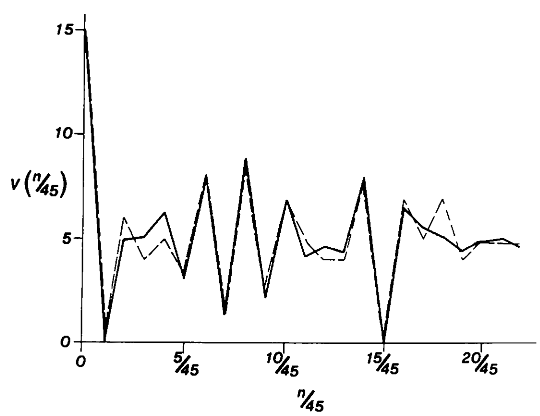

Fig. 2. A graphical comparison of observed and calculated $V(n/45)$ for $(433212)_3$ stacking.

SiC in limestone

Gnoevaya & Grozdanov (1965) have found SiC crystals in triassic limestone from northwestern Bulgaria and they concluded that these SiC crystals were formed by reaction of organic material with hydrothermal solution. But the condition of Fujii's synthesis indicates the possibility that these SiC may be authigenic and that there is a general distribution of SiC in limestone.

In order to test this hypothesis, limestone from about 20 localities, which were provided by Professor Igo of the University of Tsukuba, were dissolved in dilute acetic acid and the residua were examined under a microscope and by X-ray diffraction. A lot of SiC crystals which were quite similar to Fujii's low-temperature-grown SiC with reference to their size, color and glassy irregular shape were found in the residua of seven localities. Polytypes of SiC, the localities and the geological ages of these limestones are listed in Table 6. Judging from the common features among the residua containing SiC, these limestones are rich in iron hydroxide, titanium hydroxide and silica minerals, such as euhedral low quartz.

Summary and conclusion

1. The $45Rb$ SiC which was synthesized at room temperature (Fujii) was analyzed utilizing the special properties of the Zhdanov symbols and $n.n$ vector. The final result revealed that the stacking sequence of this SiC is expressed in abbreviated Zhdanov symbols as $(433212)_3$ and in Jagodzinski's notation as $hkkk(hkk)_2hkhhk$. This stacking sequence is quite unusual, since this contains the Zhdanov symbol 1 in its stacking. It has long been believed that the Zhdanov symbol 1 would not appear in the SiC stacking sequence, except for the $2H$ polytype,* on the basis of a number of previous data (Inoue *et al.*, 1972). This may be correct for the SiC grown at high temperature. We have arrived at a hypothesis that the Zhdanov symbol 1 in an SiC layer stacking sequence, except for the $2H$ polytype, may be a special characteristic of SiC formed under low-temperature conditions.

2. Gnoevaya & Grozdanov (1965) and Gevorkyan *et al.* (1974) have reported the finding and the

* Recently, Jepps, Smith & Page (1979) have reported a new $9R$ polytype SiC with $(21)_3$ stacking at a twin interface in $3C$ SiC based on their electron microscopic study. They did not affirm this $9R$ stacking to be a genuine $9R$ polytype, an unstable structure, or a moiré pattern between overlapping initial and twinned $3C$ orientation yielding a nine-layer repeat.

Table 6. SiC *in limestone: polytypes, localities and age of the country rocks*

Polytype	Locality	Age	References
6*H*	Kuzū, Tochigi, Japan	Middle Permian	Igo (1964)
6*H*	Langkawi Isl., Malaya	Upper Ordovician	Igo & Koike (1967)
6*H*	Ichinotani, Gifu, Japan	Middle Carboniferous	Igo (1956)
6*H*	Ichinotani, Gifu, Japan	Middle Carboniferous	Igo (1956)
6*H*	Ichinotani, Gifu, Japan	Middle Carboniferous	Igo (1956)
4*H*	Oxapampa, Peru	Lower Jurassic	Levin & Samaniego (1975)
6*H*			
15*R*			

occurrence of 5*H* polytype SiC in limestone, in dolomite and in alluvial deposits. Although neither group described its stacking sequence, it can be easily deduced as (41) in Zhdanov symbols as the only possible stacking of the 5*H* polytype. This may become another example of SiC which includes the Zhdanov symbol 1 in its stacking. According to the above hypothesis, this special characteristic of 5*H* SiC implies that the SiC found in limestone, dolomite and in other deposits, at least for the 5*H* polytype, may be an authigenic mineral and they might have grown at low temperature, although previous workers have suggested that these SiC were formed under the condition of hydrothermal alteration (Gnoevaya & Grozdanov, 1965; Gevorkyan *et al.*, 1974).

3. Based on Fujii's experimental condition, and on the reports by Gnoevaya & Grozdanov, and by Gevorkyan *et al.*, we have considered that SiC might have a general distribution in limestone, or in some low-temperature deposits. This consideration was tested using unmetamorphosed limestone of about 20 localities and, from our results, SiC was found from seven of these localities. Although our effort to find the SiC with Zhdanov symbol 1 from these crystals has not been successful, this result may support the hypothesis that SiC in limestone is authigenic.

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