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Massimo Nespolo, Hiroshi . Takeda. Inhomogeneous mica polytypes. 8-layer polytype of the 2M1 structural series determined by the Periodic Intensity Distribution (PID) analysis of the X-ray diffraction pattern.. Mineralogical Journal, 1999, 21 (3), pp.103 - 118. 10.2465/minerj.21.103 . hal-01715500

HAL Id: hal-01715500

<https://hal.univ-lorraine.fr/hal-01715500>

Submitted on 23 Feb 2018

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Inhomogeneous mica polytypes: 8-layer polytype of the $2M_1$ structural series determined by the Periodic Intensity Distribution (PID) analysis of the X-ray diffraction pattern

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Abstract

The stacking sequence of an 8-layer polytype of oxybiotite from Ruiz Peak (New Mexico) has been determined by analyzing the Periodic Intensity Distribution (PID) of the single-crystal X-ray diffraction pattern. The stacking sequence is described by Z symbols $(46)_342$ and by RTW symbols $(2\bar{2})_3\bar{2}2$. This polytype, represented by Ramsdell symbol $8A_2$, belongs to the so-called $2M_1$ structural series and consists of a 2-layer $2M_1$ unit repeated three times, with an additional 2-layer unit of the same kind in twin orientation (rotated by 120°). The choice of the proper axial setting has been effective for PID analysis. The cell dimensions, computed on the basis of the refined conventional cell of the $1M$ polytype from the same sample, are $a = 5.3\text{\AA}$, $b = 9.2\text{\AA}$, $c = 79.6\text{\AA}$, $\alpha = 90^\circ$, $\beta = 91.3^\circ$, $\gamma = 90^\circ$. The geometrical analysis of a previous report of the same polytype unambiguously shows that the original diffraction pattern corresponded to a 24-layer polytype and not to a twin of an 8-layer polytype, as previously reported. A plausible formation mechanism, involving lateral attachment of two small crystals, is proposed.

Introduction

The investigation of mica structure and polytypism has attracted the attention of mineralogists and crystallographers since the early times of the X-ray diffraction studies (Mauguin, 1928). Micaceous minerals consist of layers about $10\text{\AA}$ thick, built by two tetrahedral (*T*) sheets sandwiching an octahedral sheet (*O*), between which interlayer cations occur (Pauling, 1930). The interlayer region is where cleavage is developed (Kogure, 1997). In spite of the nearly trigonal symmetry of each sheet, because of the intralayer stagger [$l/3$ in (001) projection] between the two *T* sheets, the highest layer-symmetry is only monoclinic, namely

$C12/m(1)$ (Pabst, 1955) [layer-group notation after Dornberger-Schiff (1959); details in Merlino (1990)]. Successive layers stacked along c direction can be rotated by $n60^\circ$ ($0 \leq n \leq 5$). Of these, all but 0° rotations do not belong to the layer symmetry: they give thus rise to polytypism. The stacking of layers in polytypic structures often results in reduction of the layer-symmetry, a phenomenon known as *desymmetrization* (Đurovič, 1979). Desymmetrization in micas depends upon isomorphic substitutions and structural distortions (Güven, 1971; Takeda and Ross, 1975; Bailey, 1984).

Smith and Yoder (1956) theoretically derived the six simple polytypes in which successive layers are rotated always by the same angle. The term *simple polytypes*, introduced by Smith and Yoder (1956), has been replaced by the more precise definitions of *homogeneous polytypes* (Zvyagin, 1988) or *MDO* (Maximum Degree of Order) polytypes (Dornberger-Schiff *et al.*, 1982). Of these, only the five polytypes with up to 3 layers have been reported to date.

The remaining polytypes were called *complex* by Smith and Yoder (1956), a term then replaced by the more precise definitions of *inhomogeneous polytypes* (Zvyagin, 1988). Inhomogeneous polytypes have a rather complex structure. However, knowing the structure of the layer and the stacking sequence, a rather accurate structural model is obtained. The stacking sequence can be determined in a simple way by comparing the theoretical and experimental values of the *Periodic Intensity Distribution* (PID) function (Takeda, 1967; Sadanaga and Takeda, 1969; Takeda and Sadanaga, 1969; Takeda and Ross, 1995; Nespolo *et al.*, 1999). PID is the Fourier transform of the stacking sequence, obtained by removing the modulating effect of the single-layer transform from the structure factor:

$$S^N(hkl) \approx \frac{G^N(hkl)}{G_0(hkl)} \quad (1)$$

G^N is the Fourier transform of an N -layer polytype, G_0 is the Fourier transform of the single layer. In principle G_0 depends upon the layer orientation; however, in a subspace of the reciprocal space G_0 is almost identical for all the six possible layer orientations. Eq. (1) is always obeyed at least in the three planes $0kl$, hhl and $\bar{h}hl$ (for details see Nespolo *et al.*, 1999). The possible stacking sequences for a given number of layers are obtained as described in Takeda (1971), and from them the theoretical PID is computed (Takeda and Ross, 1995). The theoretical PID sequence that best matches the experimental one individuates the correct stacking sequence.

PID analysis permits to determine the stacking sequence even of very long-period inhomogeneous polytypes, such as the 36-layer polytype reported by Kogure and Nespolo (1999). However, since the origin of PID is not fixed *a priori*, $2N$ comparisons should be operated for an N -layer polytype, corresponding to the N permutations of the sequence of N values and, for each of them, the inverse sequence. The number of comparisons to be performed rapidly increases with the number of layers. A suitable choice of the axial setting fixes PID origin and thus drastically reduces that number (Nespolo *et al.*, 1998, 1999).

In this paper the determination of the stacking sequence of an 8-layer polytype in the most suitable axial setting is presented, showing the general criteria to be applied in PID

analysis. It is shown that Smith and Yoder's (1956) interpretation of the diffraction pattern of a biotite sample (Hendricks and Jefferson, 1939) as the twin of an 8-layer polytype is not compatible with the geometry of the pattern itself. Finally, the possible formation mechanism for the reported polytype is discussed.

Material and Methods

The sample investigated consists of oxybiotite crystals from Ruiz Peak (New Mexico). Several inhomogeneous polytypes were already reported from this sample (Ross *et al.*, 1966; Kogure and Nespolo, 1999). The main features of the sample are described in Ross and Wones (1965), Ross *et al.* (1966), Takeda and Ross (1975) and Ohta *et al.* (1982). Briefly, it was formed by vapor growth in the cavities of lava at high temperature. In it, Fe^{2+} is almost completely oxidized to Fe^{3+} and a considerable amount of Ti is also present in the O sheet (Ohta *et al.*, 1982). The presence of Ti is responsible of the brown-reddish color of the crystals (Robbins and Strens, 1972). Because of the large amount of high-charge cations, OH^- is largely oxidized to O^{2-} (Ohta *et al.*, 1982).

The sample, of about $0.4 \times 0.2 \times 0.05$ mm., has been selected by direct inspection of single crystals under polarizing microscope (Olympus BX60). Observation of the sample immersed in clove oil (refractive index 1.531) did not suggest the presence of twinning. This however cannot be excluded just by morphological analysis. In fact, micas give twins with composition plane either (001) or normal to (001) (Goldschmidt, 1918; Hurlbut, 1956). In the first case, if the uppermost crystal is larger, the presence of the other crystals may be missed under the microscopic observation. The absence of twinning has to be confirmed through the analysis of the geometry of the diffraction pattern.

The crystal has been mounted on glass fibers, so as to have the (001) plane perpendicular to the goniometer rotation axis. In this way diffraction photographs always contain c^* axis. The experimental diffraction study was performed by using a single-crystal X-ray Buerger precession camera (Charles Supper Co., model 3000, series 7426). Cu radiation was used, with a Ni thin foil as a filter to remove $K\beta$ peak. Operating voltage and current were 35kV and 15mA respectively.

Diffraction was recorded on Imaging Plate (IP) and transformed into digital image by a Rigaku R-Axis DS2 laser reader. Intensities were then measured by using the Rigaku R-Axis software package.

In case of precession motion, the Lorentz-Polarization effect is rather severe and cannot be ignored. The relative correction was calculated using the equations developed by Waser (1951). The linear absorption coefficient, calculated from the chemical composition given in Ohta *et al.* (1982) for the same sample and by employing the total photon interaction cross sections (Creagh, 1992), is 233.19 cm^{-1} . However, since the purpose of the present research is the determination of the stacking sequence and not the structure solution, no correction was tried for absorption, as well as for primary/secondary extinction. The PID function is computed in a $0.1 \text{ \AA}^{-1}$ repeat, within which the variation of the absorption is small.

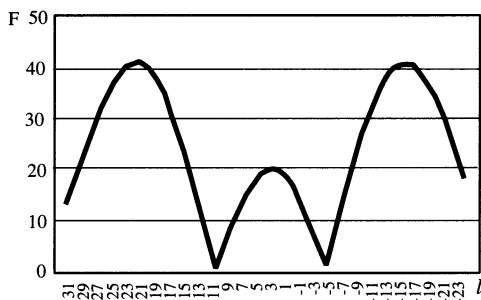


FIG. 1. The computed Fourier transform of the single layer of oxybiotite mica, on the basis of the atomic coordinates for the refined 1M polytype (Ohta *et al.*, 1982). F is the absolute value of the transform; the two sharp points where F is close to zero indicate a sign change of the transform.

Besides, PID computed along several repeats is finally weighted, so that possible uncertainties due to the absorption are further reduced. The single-layer Fourier transform (G_0 in Eq. 1) has been calculated by employing the atomic coordinates of the 1M polytype from the same sample (Ohta *et al.*, 1982), by using ORFLS program (Busing *et al.*, 1962) as modified by Takeda (1967). G_0 is shown in Fig.1, where l reciprocal lattice coordinate is referred to the period of 1M polytype. Since the Fourier transform is calculated for one-layer and not for a periodic structure, l is a continuous variable and not a discrete index.

The stacking sequences of all possible 8-layer polytypes have been generated by PTGR program (Takeda, 1971). The PID of all these 8-layer polytypes have been computed by PTST98 program (Nespolo *et al.*, 1999), a revised version of PTST (Takeda and Ross, 1995) in which proper axial setting and space group symmetry are taken into account (PTST98 is available on request).

Results

Geometry of the diffraction pattern

Fig. 2-3 show the diffraction patterns from two reciprocal lattice planes, which can be easily interpreted in the following way.

The (001) plane of mica layer consists of the basal oxygen atoms of the *T* sheets and has ideally hexagonal symmetry (Pauling, 1930). However, since the *b* parameters of the *T* and *O* sheets do not perfectly match, tetrahedra rotate around c^* and the basal oxygen atoms assume a trigonal configuration (Belov, 1949; Zvyagin, 1957; Takéuchi and Sadanaga, 1959). The rotation of the tetrahedra separates the six possible interlayer rotations into two groups: $2n60^\circ$, for which the coordination polyhedron is a trigonal antiprism, and $(2n+1)60^\circ$, for which it is a trigonal prism. Mica polytypes are thus divided into subfamily A (only $2n60^\circ$ rotations), subfamily B [only $(2n+1)60^\circ$ rotations] and mixed-rotation (both kinds of rotations) (Backhaus and Đurovič, 1984; Nespolo, 1999). Polytypes belonging to one of the two subfamilies are OD^{*1} structures, *i.e.* polytypes in which layer pairs are symmetrically equivalent (Dornberger-Schiff *et al.*, 1982).

In the diffraction pattern of an *N*-layer mica polytype, in principle *N* reflections appear

^{*1} OD stands for "Order-Disorder". However, OD phenomena are of completely different nature from the order-disorder phenomena in alloys.

in the $0.1\text{\AA}^{-1}$ repeat (the reciprocal lattice period of the one-layer polytype, hereafter called c^*_1 repeat) along reciprocal lattice rows parallel to c^* . However, because the symmetry of the sheets building the layer (trigonal) is higher than the symmetry of the whole layer (monoclinic), several systematic absences appear, which reveal the symmetry principles of the layer stacking. Reciprocal lattice rows are thus suitably classified as follows.

1. reflections with $h = 0 \pmod{3}$ and $k = 0 \pmod{3}$ always show only one reflection in the c^*_1 repeat: these reflections are common to all polytypes of the same mineral group (Zvyagin, 1967) and are thus not useful for polytype identification;
2. reflections with $h \neq 0 \pmod{3}$ and $k = 0 \pmod{3}$ show one (subfamily A), two equally spaced (subfamily B) or N (mixed-rotation) reflections in the c^*_1 repeat (Nespolo, 1999). For each of the two subfamilies these reflections are common to all polytypes of the same subfamily (Backhaus and Āuroviĉ, 1984).
3. Reciprocal lattice rows with $k \neq 0 \pmod{3}$ show N reflections in the c^*_1 repeat. These rows are typical of each polytype and are those to be used in polytype identification (Āuroviĉ *et al.*, 1984).

Reflections common to all polytypes built on the same symmetry principle are called family reflections (Backhaus and Āuroviĉ, 1984). Reflections with $h = 0 \pmod{3}$ and $k = 0 \pmod{3}$ are the only family reflections in absence of tetrahedral rotations (Pauling model). On the other hand, taking into account the tetrahedral rotation, reflections with $h \neq 0 \pmod{3}$ and $k = 0 \pmod{3}$ are family reflections for each of the two subfamilies, but not for the mixed-rotation polytypes (trigonal model) (for details, see Nespolo, 1999).

Fig. 2 is the diffraction pattern from the $h0l$ plane. The presence of only one reflection in the c^*_1 repeat along rows with $h \neq 0 \pmod{3}$ clearly shows the polytype under investigation belongs to subfamily A (only 0° , $\pm 120^\circ$ rotations between successive layers). Out of 9212 possible 8-layer polytypes, only 94 belong to subfamily A (Ross *et al.* 1966). Comparison of theoretically computed and experimentally recorded PID values has thus to be performed only for the 94 subfamily A polytypes. The choice of a consistent axial setting in both the computed and the measured pattern, as implemented in the new program PTST98 (Nespolo *et al.*, 1999), removes the necessity of repeating $2N$ (*i. e.* 16) times each comparison.

Fig. 3 shows the diffraction pattern from $\bar{h}hl$ plane, which contains non-family rows for $h \neq 0 \pmod{3}$. The geometry of the diffraction pattern clearly shows that the polytype is not orthogonal. Non-orthogonal polytypes may undergo twinning by reticular pseudo-merohedry. The diffraction pattern of non-orthogonal twinned micas can be mistaken for that of a polytype with a number of layers multiple of 3 (Sadanaga and Takéuchi, 1961; Nespolo *et al.*, 1997a, b; Nespolo and Kogure, 1998), a phenomenon known as *apparent polytypism* (Takano and Takano, 1958). Since the diffraction pattern of the sample under investigation shows eight reflections in the c^*_1 repeat, it follows that the crystal is not twinned.

PID analysis

The determination of the stacking sequence has been performed by comparison of measured and computed PID values. For subfamily A polytypes with a number of layers not

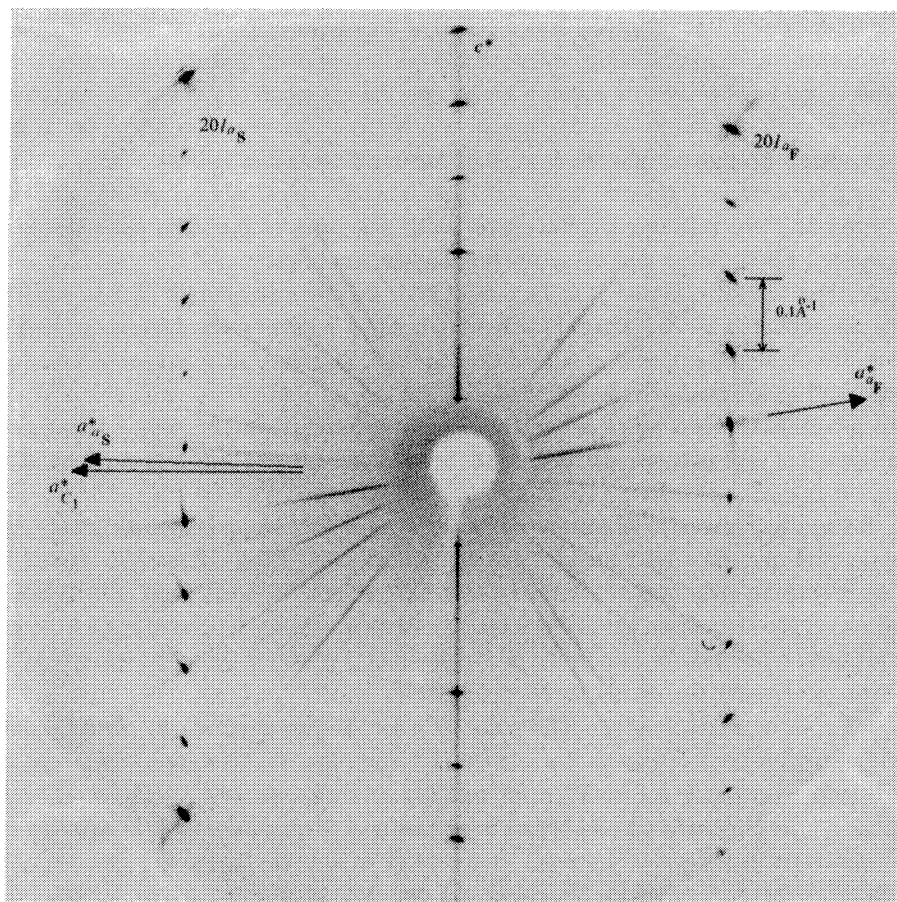


FIG. 2. Diffraction pattern from the family $h0l$ plane of $8A_2$ polytype (Cu $K\alpha$). The a^* axes of the three settings, C_1 , aS and aF , are traced according to the general theory of the axial settings for mica polytypes (Nespolo *et al.*, 1997a, 1998).

multiple of 3 the following symmetry relation holds (Nespolo *et al.*, 1999):

$$\begin{aligned} S^N(0, 2k, \hat{l}) &= S^N(\bar{k}, \bar{k}, \hat{l}) = S^N(\bar{k}, k, N - \hat{l}) \\ \hat{l} &= l \pmod{N} \end{aligned} \quad (2)$$

It is thus enough to compute PID from the measured intensities in one of the reciprocal lattice planes containing non-family reflections. Physical defects of the crystal result in broadening and doubling of the reflections. The plane containing reflections of the best quality has thus been selected, namely $\bar{h}hl$. Then, in order to minimize the effect of the experimental errors, PID has been calculated from five periods along the $\bar{1}1l$ reciprocal lattice row (Table 1) and a mean value has been obtained (Table 2). Two of the periods in the

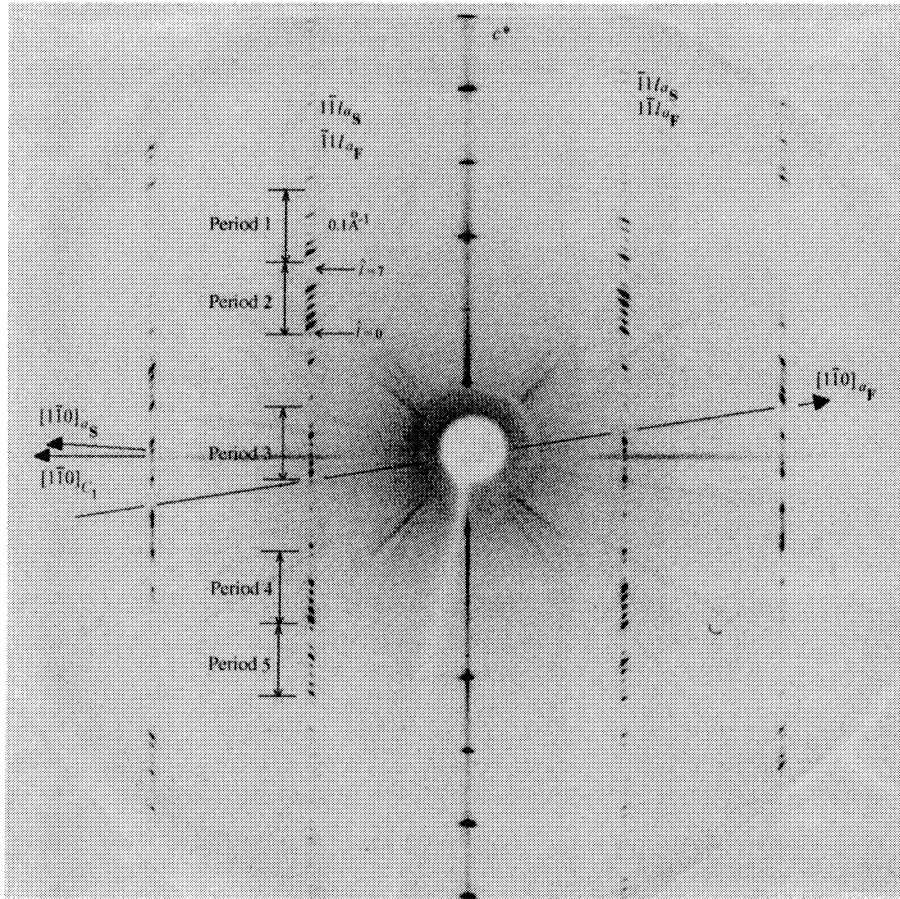


FIG. 3. Diffraction pattern from the non-family $\bar{h}hl$ plane of $8A_2$ polytype ($\text{Cu } K\alpha$). The $[1\bar{1}0]^*$ axes of the three settings C_1 , aS and aF are traced according to the general theory of the axial settings for mica polytypes (Nespolo *et al.*, 1997a, 1998). In aF setting the origin of PID is by definition in correspondence of $l = 0(\text{mod } N)$. PID has been obtained from the intensities measured along the five periods indicated in the figure.

diffraction pattern in Fig. 3 have not been used. They correspond to regions in which the Fourier transform of the single layer undergoes a sign change and where PID values are less reliable (Nespolo *et al.*, 1999). Finally PID has been normalized in order to have both computed and measured values expressed in the same scale:

$$\sum_{j=1}^N [S^N_f(hkl^{\hat{j}})]^2 = N^2 \quad (3)$$

The PID computed from the stacking sequence of the 94 different polytypes has been compared with the experimentally measured PID and the degree of matching has been evaluated

TABLE 1. Derivation of PID from measured intensities of 8A₂ polytype. Observed structure factors (Fo) have been obtained from the intensities measured in five periods along the 111 reciprocal lattice row of ^aF setting ($\bar{1}11$ of ^aS setting.). SLFT stands for Single Layer Fourier Transform. See Fig. 1 and Fig. 3.

Period	$l(C_1)$	$l(^a\mathbf{S})$	$l(^a\mathbf{F})$	$\hat{l}$	Fo	SLFT	Fo/SLFT	PID
1	85	28	31	7	.25	12.9925	.0192	.02
	82	27	30	6	.25	16.7667	.0149	.02
	79	26	29	5	83.33	20.6510	4.0352	4.44
	76	25	28	4	38.63	24.5330	1.5746	1.73
	73	24	27	3	47.01	28.2829	1.6621	1.83
	70	23	26	2	83.00	31.7709	2.6125	2.87
	67	22	25	1	168.75	34.8628	4.8404	5.32
	64	21	24	0	40.70	37.4274	1.0874	1.20
2	61	20	23	7	.22	39.3437	.0056	.00
	58	19	22	6	30.06	40.5091	.7421	.57
	55	18	21	5	183.05	40.8463	4.4814	3.47
	52	17	20	4	76.75	40.3088	1.9041	1.47
	49	16	19	3	91.39	38.8777	2.3507	1.82
	46	15	18	2	169.81	36.5677	4.6437	3.59
	43	14	17	1	246.62	33.4600	7.3706	5.70
	40	13	16	0	32.92	29.6496	1.1103	.86
3	13	4	7	7	24.77	12.4614	1.9877	1.46
	10	3	6	6	33.28	15.4120	2.1594	1.58
	7	2	5	5	111.86	17.6442	6.3398	4.65
	4	1	4	4	23.28	19.1113	1.2181	.89
	1	0	3	3	41.45	19.7841	2.0951	1.54
	-2	-1	2	2	60.84	19.6492	3.0963	2.27
	-5	-2	1	1	134.28	18.7094	7.1771	5.26
	-8	-3	0	0	30.39	16.9832	1.7894	1.31
4	-35	-12	-9	7	18.80	22.0798	.8515	.62
	-38	-13	-10	6	20.98	26.7785	.7835	.57
	-41	-14	-11	5	172.90	30.9908	5.5791	4.07
	-44	-15	-12	4	89.73	34.5793	2.5949	1.89
	-47	-16	-13	3	99.68	37.4301	2.6631	1.94
	-50	-17	-14	2	188.67	39.4573	4.7816	3.49
	-53	-18	-15	1	288.53	40.5866	7.1090	5.19
	-56	-19	-16	0	28.74	40.8295	.7039	.51
5	-59	-20	-17	7	.22	40.2094	.0055	.01
	-62	-21	-18	6	52.30	38.7837	1.3485	1.26
	-65	-22	-19	5	172.66	36.6389	4.7125	4.42
	-68	-23	-20	4	57.59	33.8844	1.6996	1.59
	-71	-24	-21	3	51.37	30.6456	1.6763	1.57
	-74	-25	-22	2	86.01	27.0555	3.1790	2.98
	-77	-26	-23	1	129.75	23.2475	5.5812	5.23
	-80	-27	-24	0	26.51	19.3487	1.3701	1.28

by means of an R factor defined exactly in the same way as for the structure factors, namely:

$$R_{PID} = \frac{\sum_{j=1}^N |S_j^N(hkl)_O - S_j^N(hkl)_C|}{\sum_{j=1}^N S_j^N(hkl)_O} \quad (4)$$

The best match corresponded to $R_{PID}=0.0424$ (computed PID values for this sequence are in Table 2); the second best match to $R_{PID}=0.3276$. This clearly shows that the stacking sequence has been uniquely identified. By employing the cell dimensions of the refined 1M

TABLE 2. Comparison of measured and computed PID of $8A_2$ polytype.

$\bar{l}$	Period 1	Period 2	Period 3	Period 4	Period 5	Mean	Calculated
7	.02	.00	1.46	.62	.01	.30	.23
6	.02	.57	1.58	.57	1.26	.89	.90
5	4.44	3.47	4.65	4.07	4.42	3.98	4.07
4	1.73	1.47	.89	1.89	1.59	1.52	1.73
3	1.83	1.82	1.54	1.94	1.57	1.74	1.78
2	2.87	3.59	2.27	3.49	2.98	2.98	3.35
1	5.32	5.70	5.26	5.19	5.23	5.13	5.31
0	1.20	.86	1.31	.51	1.28	1.04	1.00

TABLE 3. Z symbols (Zhukhlistov *et al.*, 1990), RTW symbols (Ross *et al.*, 1966) and TS symbols (Sadanaga and Takeda, 1969; Takeda and Sadanaga, 1969; Nespolo *et al.*, 1999) describing the stacking sequence of $8A_2$ polytype.

n	Z	RTW	TS
1	4	2	D(0,-1)
2	6	-2	D(0,-1)
3	4	2	D(0,1)
4	6	-2	D(0,1)
5	4	2	D(0,0)
6	6	-2	D(0,0)
7	4	-2	D(0,-1)
8	2	2	D(0,0)

polytype from the same sample (Ohta *et al.*, 1982), the approximate cell parameters of this polytype have been calculated through the axial transformations given in Nespolo *et al.* (1997a, 1998) and results are: $a = 5.3\text{\AA}$, $b = 9.2\text{\AA}$, $c = 79.6\text{\AA}$, $\alpha = 90^\circ$, $\beta = 91.3^\circ$, $\gamma = 90^\circ$.

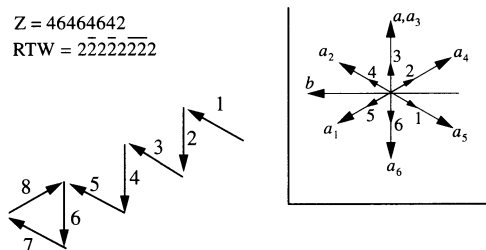
Three kinds of symbols describing the identified stacking sequence are given in Table 3. Z symbols give the absolute orientation of the layers in a space-fixed reference (Zvyagin *et al.*, 1979; Zhukhlistov *et al.*, 1990). RTW symbols give the relative rotations between layers and correspond to

the difference between pairs of Z symbols (Ross *et al.*, 1966). TS symbols give the (approximate) positions of the layers and are the most suitable ones to calculate PID (Sadanaga and Takeda, 1969; Takeda and Sadanaga, 1969) (for details refer to Nespolo *et al.*, 1999). Symbols in Table 3 identify the polytype under study as the one corresponding to Ramsdell's (1947) symbol $8A_2$ (lattice symbols according to Guinier *et al.*, 1984). The space group is $C\bar{1}$, derived by applying the transformation rules for Z symbols (Zvyagin 1974, 1997; Nespolo *et al.*, 1999).

Discussion

Most of the inhomogeneous polytypes reported to date belong to subfamily A and their stacking sequences are related in a more or less complex way to those of the three corresponding MDO polytypes, namely $1M$, $2M_1$, and $3T$. These three polytypes are considered basic structures (Baronnet and Kang, 1989), *i. e.* a sort of intermediate between polymorphs and polytypes. From the three basic structures, three *structural series* arise (Baronnet, 1978; Takeda and Ross, 1995).

Looking at the stacking vector sequence (Fig. 4), we can easily recognize that $8A_2$ polytype belongs to the $2M_1$ structural series (Baronnet, 1978; Takeda and Ross, 1995). Other known examples of this structural series are $4M_3$ [$Z=3531$; RTW= $\bar{2}\bar{2}\bar{2}$ 2; Zhukhlistov



$Z = 46464642$
 $RTW = 22222222$

FIG. 4. The stacking sequence of $8A_2$ polytype, given by means of the stacking vectors (Z vectors) as defined in Zhukhlistov *et al.* (1990), namely the (001) projection of vectors connecting two interlayer cations and passing the cation site in which the origin of the *O* sheet is located (each stacking vector has length $2|a|/3$). Z and RTW symbols are indicated. Definition of Z vectors and Z symbols: *a*, *b* define *a* space-fixed reference (the one labelled C_1 in the text); a_1, a_6 are the *a* axes of the structure-related references, in the six possible orientations. Vectors 1-6 are the (001) projection of vectors connecting an interlayer cation with the origin of the *O* sheet (half Z vectors). A layer has orientation *i* ($i = 1, 6$) when its a_i axis is parallel to *a* (for details see Zvyagin, 1997).

et al. (1988, 1990, 1993)], $6A_1$ [$Z = (64)_2 62$; $RTW = 2\bar{2} \ 2\bar{2} \ 2\bar{2}$; Zhukhlistov *et al.* (1993)], $21A_1$ [$Z = (64)_4 (62)_6 4$; $RTW = (\bar{2}2)_4 (\bar{2}2)_5 222$; Bigi and Brigatti (1994)] and $22M_1$ [$Z = (51)_7 (15)_4$ or $(15)_7 (51)_4$; $RTW = (\bar{2}2)_6 20\bar{2} (\bar{2}2)_3$ or $(\bar{2}2)_6 20\bar{2} (\bar{2}2)_3$; Konishi and Akai (1990)]. $4M_3$ and $6A_1$ polytypes were identified by oblique-texture electron diffraction, whereas $21A_1$ and $22M_1$ polytypes by HRTEM observation. For details about the former technique refer to Zvyagin (1967) and Zvyagin *et al.* (1979). The $8A_2$ polytype has been identified by single crystal X-ray diffraction. It is thus neither a small region nor a defect included into a simpler (*e.g.* $2M_1$) matrix.

Hendricks and Jefferson (1939), on the basis of a Weissenberg diffraction pattern, reported a 24-layer triclinic polytype in biotite from Ambulawa,

Ceylon, without attempting to determine the stacking sequence. Smith and Yoder (1956) re-analyzed the Weissenberg photographs of that sample, concluding that it could be indexed on an 8-layer unit cell. Takeda (1969), adopting Smith and Yoder's (1956) twin interpretation, performed a PID analysis taking into account only one reflection out of 3. He derived a semi-quantitative intensity distribution from the sequence of *w*(weak), *m*(medium), *s*(strong) from Hendricks and Jefferson (1939). The best match with the PID values computed from the stacking sequences of all possible 8-layer polytypes corresponded to $8A_2$ polytype, the same polytype discovered in the present research. Actually, when the number of layers suggested by the diffraction pattern is a multiple of 3 the possible presence of twinning (*apparent polytypism*; Takano and Takano, 1958) has to be taken into account (Sadanaga and Takéuchi, 1961; Nespolo *et al.*, 1997a; Nespolo, 1999). In particular, when the number of reflections in the c^*_1 repeat is a multiple of 3 it is always possible to choose a larger reciprocal cell based on one reflection out of three; the other two reflections could come from twinned individuals (twinning by reticular pseudo-merohedry). However, this is not a proof of twinning, which must be confirmed or excluded by means of a geometrical analysis of the diffraction pattern.

Mica non-orthogonal polytypes are divided into *Class a* ($\alpha = 90^\circ$; $\beta \neq 90^\circ$) and *Class b* ($\alpha \neq 90^\circ$; $\beta = 90^\circ$) (Nespolo *et al.*, 1997a, 1998). In case of polytypes belonging to subfamily A, polytypes with a number of layers not multiple of 3 always belong to *Class a*, while polytypes with a number of layers multiple of 3 either are orthogonal or belong to *Class b*.

Of these, *Class a* polytypes have one orthogonal plane (*i. e.* a plane in which, along each reciprocal lattice row parallel to c^* , a reflection appears on the line perpendicular to c^* and passing through the origin: it is $0kl$ plane), whereas *Class b* polytypes have no orthogonal planes (Nespolo, 1999; Nespolo *et al.*, 1999). Hendricks and Jefferson (1939) reported for the 24-layer polytype the following data:

- 1) cell dimension: $a = 5.3\text{\AA}$, $b = 9.2\text{\AA}$, $c = n10\text{\AA}$, $\gamma = 90^\circ$, $\beta = 90^\circ$: it was thus a *Class b* polytype;
- 2) Reflections hkl with $k = 0(\text{mod } 3)$ same as for the single layer structure: it was thus a subfamily A polytype;
- 3) the heavy trace of continuous scattering from 060 on an over-exposed photograph did not pass through any $02l$ reflection but rather at a distance of about one-third the periodicity from the closest reflection; the $(0kl)$ plane was thus not orthogonal and the diffraction pattern is typical of a *Class b* polytype.

An 8-layer subfamily A polytype cannot belong to *Class b*; a twin of an orthogonal or *Class a* polytype cannot produce a diffraction pattern typical of *Class b* polytype. Therefore, the diffraction pattern reported by Hendricks and Jefferson was actually from a 24-layer polytype, whose stacking sequence has not been solved yet, and not an $8A_2$ polytype. However, on the basis of Takeda's (1969) analysis of a subset of reflections, it can be inferred that Hendricks and Jefferson's (1939) 24-layer polytype likely possesses a stacking sequence related to that of $8A_2$, belonging thus to the $2M_1$ structural series too^{*2}.

The Ruiz Peak sample gave several examples of inhomogeneous polytypes belonging to $1M$ and $3T$ structural series (Ross *et al.*, 1966). The $8A_2$ polytype discovered in the present research is the first example of inhomogeneous polytype belonging to the $2M_1$ structural series from that sample.

The occurrence of inhomogeneous polytypes on an X-ray scale prompts for a mechanism capable of explaining their formation. Inhomogeneous polytypes belonging to one of the three structural series are probably formed by perturbation of the normal growth of the corresponding basic structure. Besides, the stacking sequences of the inhomogeneous polytypes reported to date suggest that once the perturbation has been introduced, the successive stacking vector(s) return as quickly as possible close to the original direction of the basic structure from which the inhomogeneous polytype has been formed (Takeda and Ross, 1995).

The Faulted Matrix Model (FMM) (Pandey *et al.*, 1982) tries to explain the stacking sequence of inhomogeneous polytypes through the occurrence of a stacking fault. This stacking fault may appear in the exposed ledge of the growing spiral and can thus be inherited as part of a new, longer stacking sequence. This model can explain only stacking sequences related in a simple way to those of the basic structures, and it cannot give a general explanation of the recovery of the original direction of stacking. In principle FMM is applicable to the formation of the $8A_2$ polytype, since its stacking sequence is a modification of that of the $2M_1$ basic structure. However, it would require an exposed ledge made of 8-layers

^{*2} Takeda's (1969) derivation of the $8A_2$ polytype is quoted in several papers [*e.g.* Baronnet (1980); Baronnet and Kang (1989); Takeda and Ross (1995)]. Since $8A_2$ polytype has now been actually found in the present research, all the arguments in those papers related to this polytypes are correct.

(80Å), which is not very frequent. As a matter of fact, the occurrence frequency of screw dislocations rapidly decreases with the number of layers in the exposed ledge (Baronnet, 1980).

Takeda and Ross (1995) proposed that an external perturbation, in the form of a thin platelet deposited onto the surface of a growing crystal and covered by the subsequent spiral, may modify the stacking sequence of the growing crystal. The platelet model can explain the tendency to recover the original direction of stacking: such tendency is due to the existence of an active growing spiral that has to overcome the presence of a foreign small crystal. In the present case, the uppermost two layers of the $8A_2$ polytype might have been originated by the deposition of a 2-layer thick $2M_1$ platelet onto the surface of a $2M_1$ spirally-growing polytype: the platelet and the matrix are in twin relation, with composition plane (001). The layers of the platelet can substitute an equal number of layers of the ledge: since the total number of layers does not change, the original ledge necessarily consists of 8 layers. Alternatively, the layers of the platelet can be added to the original ledge, if the ledge itself is able of growing over the platelet through an elastic deformation. In this case the ledge can consist of less than 8 layers.

A further possible mechanism, which seems of more general applicability, involves a lateral attachment of two small crystals, which are again in twin orientation, but with composition plane normal to (001). A few layers from one of the crystals begin to grow onto the surface of the other crystal and vice versa, giving rise to a co-operative growth. If the two crystals have a different stacking sequence a rather complex stacking sequence can be obtained, where the tendency to recover the original stacking direction is partially hidden by the co-existence of two such directions. On the other hand, if the two crystals have the same stacking sequence they can still produce a new, longer-period polytype: since the layer symmetry is monoclinic but the surface symmetry is pseudo-hexagonal, it is enough that the two crystals have a different orientation to produce a new stacking sequence. In this case the tendency to recover the original stacking direction directly comes from the identity of the stacking sequence of the two crystals. The lateral oriented attachment of crystals is a well-known phenomenon (Sunagawa *et al.*, 1975; Penn and Banfield, 1998a) and it has been proposed as a mechanism to originate screw dislocations of high Burger vectors, polytypes and mixed-layer minerals (Penn and Banfield, 1998b). A structural adjustment at the boundary between the two crystals cooperatively growing can further modify the stacking sequence, resulting in a polytype whose stacking sequence is significantly modified with respect to that of the original basic structure (Nespolo, 1998).

The large predominance of subfamily A polytypes over subfamily B and mixed-rotation polytypes is explained by taking into account two effects:

- 1) because of the ditrigonal rotation of tetrahedra (Zvyagin, 1957; Takéuchi and Sadanaga, 1959), the coordination polyhedra for interlayer cations are more stable for (0° , $\pm 120^\circ$) rotations than for (180° , $\pm 60^\circ$) rotations (Belov, 1949; Radoslovich, 1959; Zvyagin *et al.*, 1972);
- 2) the lateral attachment of two mica crystals with (0° , $\pm 120^\circ$) rotations preserves the octahedral coordination, whereas for (180° , $\pm 60^\circ$) rotations this coordination is highly distorted (Nespolo, 1998); the same reason explains the predominance of the so-called *perfect*

screw dislocations, i. e. screw dislocations in which the number of layers in the exposed ledge is an integral multiple of the basic structure repeat (Baronnet and Amouric, 1986).

Both the platelet mechanism and the lateral attachment of crystals imply the interaction of two individuals in twin orientation, with composition plane parallel (platelet) or normal (lateral attachment) to (001). Twinning is a common phenomenon in micas and the occurrence of twinning in the early stages of crystal growth is a plausible mechanism for initiating a new stacking sequence from that of a basic structure. The predominance of subfamily A polytypes generated through early-stage twinning is rationalized by the two factors listed above. When an inhomogeneous polytype is formed through lateral attachment, the (0° , $\pm 120^\circ$) rotations are always by far more favorable, since the orienting force is the necessity of preserving the octahedral coordination. On the other hand, when an inhomogeneous polytype is formed through platelet deposition, the preference of (0° , $\pm 120^\circ$) rotations over (180° , $\pm 60^\circ$) rotations depends upon the degree of ditrigonal rotation, which in its turn depends upon the crystal chemistry (Takeda and Mori, 1970; Hazen and Wones, 1972) and the temperature (Takeda and Morosin, 1975; Catti *et al.*, 1989).

The diffraction pattern of inhomogeneous mica polytypes is rather complex, but it can be solved in a straightforward way by exploiting the following features:

- 1) geometry of the diffraction pattern (number and position of reflections), to confirm or exclude the presence of twinning;
- 2) family reflections, to recognize the general features of layer stackings (namely, whether a polytype belongs to subfamily A or subfamily B or it is a mixed-rotation polytype);
- 3) PID analysis of the non-family reflections.

Twinning is a common phenomenon in micas and the presence of twinning must be confirmed or excluded before PID analysis. This can be done by applying the geometrical criteria described in Nespolo (1999). The geometry of the diffraction pattern and the Periodic Intensity Distribution give thus mutually completing information, and none of them can be undervalued in the analysis of inhomogeneous mica polytypes.

Conclusions

The stacking sequence of an 8-layer inhomogeneous polytype ($8A_2$) of oxybiotite has been determined by PID analysis of the X-ray diffraction pattern. Twinning has been excluded by analysis of the geometry of the diffraction pattern. This polytype belongs to $2M_1$ structural series and was probably formed by coalescence of two $2M_1$ crystallites in the early stages of crystal growth.

A previous report of $8A_2$ polytype (Takeda, 1969) is no longer supported by the twin interpretation (Smith and Yoder, 1956) of the diffraction pattern of a 24-layer polytype (Hendricks and Jefferson, 1939).

Acknowledgements—This research has been partly developed at the Mineralogical Institute, University of Tokyo, during a Doctoral Program (MN, 1995-98) supported by the Japanese Ministry of Education, Science and Culture. The authors express their deep gratitude to Prof. Boris B. Zvyagin (IGEM, RAS, Moscow), Prof. Slavomil Ďurovič (Slovak

Academy of Sciences, Bratislava), Prof. Giovanni Ferraris (University of Torino), Dr. Toshihiro Kogure (University of Tokyo) and Prof. Jillian F. Banfield (University of Wisconsin-Madison) for several profitable discussions. The sample has been kindly provided by Dr. Malcom Ross (U. S. Geological Survey). MN is deeply indebted to Prof. Masamichi Miyamoto (University of Tokyo) and Prof. Yasunari Watanabe (Teikyo Heisei University) for constant encouragement.

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Received December 18, 1998; accepted June 7, 1999