

X-RAY IDENTIFICATION OF ONE-LAYER ILLITE VARIETIES: APPLICATION TO THE STUDY OF ILLITES AROUND URANIUM DEPOSITS OF CANADA

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Abstract—Structural and diffraction criteria for distinguishing between t-1M, c-1M, m-1M, and 3T illite varieties are described. The t-1M illite corresponds to a one-layer monoclinic structure with vacant trans-sites. The c-1M illite has vacant cis-octahedra forming one of two symmetrically independent point systems; the other cis-octahedra as well as the trans-octahedra are occupied; and the m-1M illite corresponds to the structure in which cations are statistically distributed over available trans- and cis-sites. For t-1M, c-1M, and m-1M, the values of $|c \cos \beta/a|$ are equal to 0.39–0.41, 0.29–0.31, and 0.333, respectively. Application of these criteria demonstrates that illite samples described in the literature as the 3T polytype usually are c-1M instead. The relatively common occurrence of c-1M illite in association with t-1M and 2M₁ polytypes has been recognized in illite from hydrothermal alterations around uranium deposits located in the Athabasca basement (Saskatchewan, Canada). The c-1M illite from these deposits was previously described as 3T one.

Key Words—Hydrothermal alteration, Illite, Octahedral cation distribution, Polytype, Uranium deposits, Vacant cis-sites, Vacant trans-sites.

INTRODUCTION

The existence of polytype modifications is one of the remarkable features of phyllosilicate structures. In particular, 1M, 2M₁, 2M₂, and 3T mica polytypes occur in different types of rocks. A sample can contain a single polytype or a mixture of different polytypes (Środoń and Eberl, 1984; Guiddotti, 1984; Frey, 1987; Lonker and Gerald, 1990; Ey, 1984; Ey *et al.*, 1985).

Identification of mica polytypes is based on the comparison between experimental and calculated d-values and peak intensities for the corresponding polytype structural models and are reported in reference books (Bailey, 1984; Brindley and Brown, 1980). It is usually assumed that 2:1 layers in all dioctahedral mica polytypes have vacant trans-octahedra. This supposition is based on single-crystal X-ray structure refinements where octahedral cations in 2:1 layers of various polytypes of muscovites, paragonites, phengites, and margarites were shown to occupy only cis-sites (Bailey, 1984).

The existence of 2:1 phyllosilicates with different distributions of octahedral cations was first reported by Mering and Oberlin (1967) for a sample of Wyoming montmorillonite. Tsipursky and Drits (1984) have found that dioctahedral smectites have a wide variety of octahedral cation distributions over trans- and cis-sites. Drits *et al.* (1984) and Tsipursky and Drits (1984) have described the main structural and diffraction features of dioctahedral smectites and 1M mica polytypes having a given type of octahedral cation distribution.

Zvyagin *et al.* (1985) were the first to describe a monomineralic Al-rich 1M mica with non-symmetrical 2:1 layers. Trans-octahedra in such layers are occupied by Al, where one of the two symmetrically independent cis-octahedra is vacant. Gavrilov and Tsipursky (1987) have described 1M illite with an almost random distribution of Al cations over the available trans- and cis-sites.

Most of the 2:1 phyllosilicates with an “abnormal” octahedral cation distribution have been identified by oblique texture electron diffraction (OTED) (Tsipursky and Drits, 1984; Zvyagin *et al.*, 1985; Gavrilov and Tsipursky, 1987; Zhuklistov and Zvyagin, 1991). One advantage of this method for structural studies of clay minerals is that, since OTED patterns do not contain 00l reflections, OTED permits observation of the 022 reflection, which occurs at the same position as the 003 (Zvyagin, 1967; Drits, 1987). This facilitates comparison between the 11 $\bar{2}$, 022, 112, and 11 $\bar{3}$ reflections, which are most sensitive to variations in cation distribution (Tsipursky and Drits, 1984; Drits *et al.*, 1984).

All these data indicate that the conventional approach to the XRD identification of 1M and 3T mica polytypes needs to be modified. Analysis of literature concerning this problem (Warsaw, 1959; Ey, 1984; Halter, 1988) indicates that the identification of 3T illite polytype is commonly based on two criteria: first, d-values for reflections on experimental XRD curves that differ substantially from those observed for the 1M polytype with vacant trans-octahedra; and second,

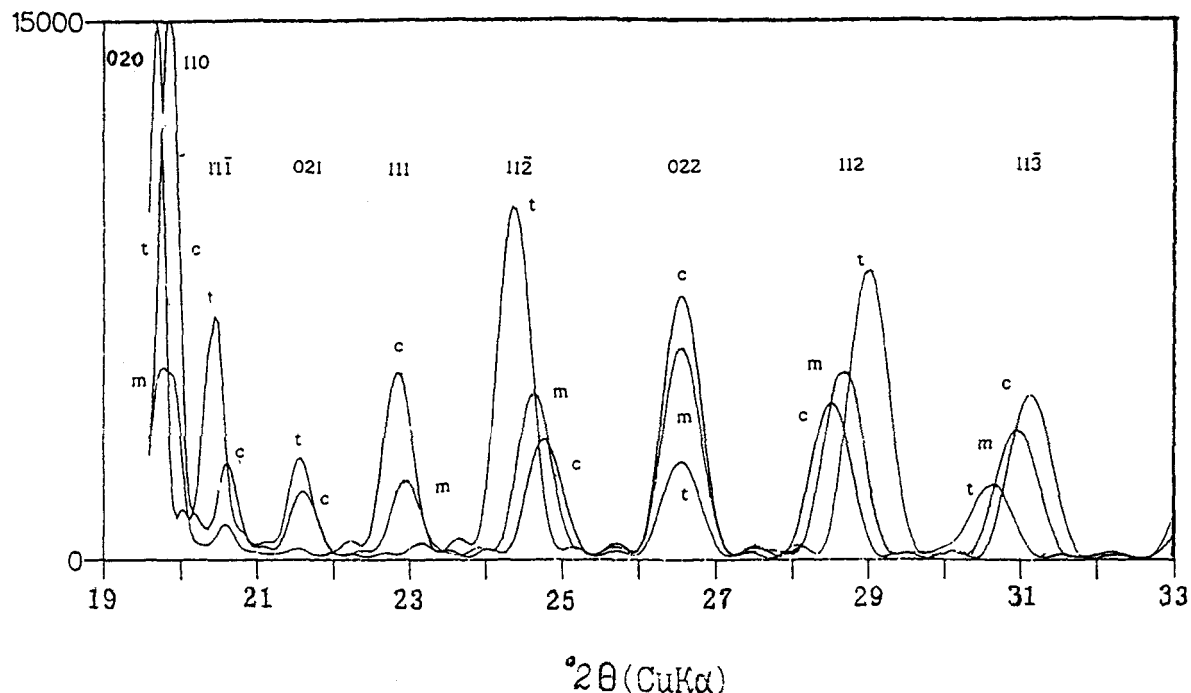


Figure 1. XRD curves calculated for t-1M, c-1M, and m-1M illite varieties. The letters t, m, and c denote the peaks corresponding to c-1M, m-1M, and c-1M structures, respectively; hkl indices are given above the corresponding triples of peaks.

intensity distribution and positions of the 111 and 021 reflections that are close to those for the 3T polytype.

Sometimes experimental d-values were compared with those for the 3T polytype, ignoring the possible difference in the unit cell parameters (Warshaw, 1959; Ey, 1984). In these cases, determination of the unit cell parameters and comparison between experimental and calculated d-values was not made, which can lead to a wrong conclusion. However, even if there is good agreement between calculated and experimental d-values, this fact alone cannot be considered as evidence for the 3T polytype identification. Illite with a 1M structure and a statistically random distribution of cations over cis- and trans-sites produces an XRD pattern with approximately the same peak positions as those on the XRD pattern for the 3T polytype. Therefore, in order to distinguish between these two varieties, d-values and peak intensities should be precisely measured and comparison with XRD curves simulated for the corresponding polytype structural models should be made.

The problem of interpretation of an illite XRD curve similar to that for 3T polytype will be discussed in a separate paper. Here we shall consider simpler cases in which unambiguous polytype identification can be made from the analysis of d-values. Structural and diffraction criteria for distinguishing between 1M illite varieties with different cation distributions will be presented in order to clarify the identification. These cri-

teria will be applied to coexisting illite varieties from a uranium hydrothermal system, one of the components of which was previously described as 3T (Ey *et al.*, 1985; Halter, 1988).

STRUCTURAL AND DIFFRACTION FEATURES OF t-1M, c-1M AND m-1M DIOCTAHEDRAL MICAS

Let us name the 1M mica structural varieties t-1M, c-1M, and m-1M, which have three extreme modes of octahedral cation distribution over trans- and cis-sites. In this scheme, t corresponds to vacant trans-octahedra; c refers to a structure in which cis-octahedra forming one of two symmetrically independent point systems are vacant while the other octahedra are occupied by cations; and m corresponds to a statistical distribution of cations over the available octahedral sites. XRD curves were simulated for these models (Figures 1 and 2), according to the technique described by Drits *et al.* (1984) (with the number of layers $N = 10$).

t-1M illite

Electrostatic interaction between octahedral cations leads to a distortion of the octahedral sheets in the 2:1 mica layers (Bailey, 1966). The sheets are flattened and shared edges in the octahedra occupied by cations are shorter than unshared edges. Besides flattening, cis-octahedra become distorted due to counter-rotation of their upper and lower triangular roofs. As a result,

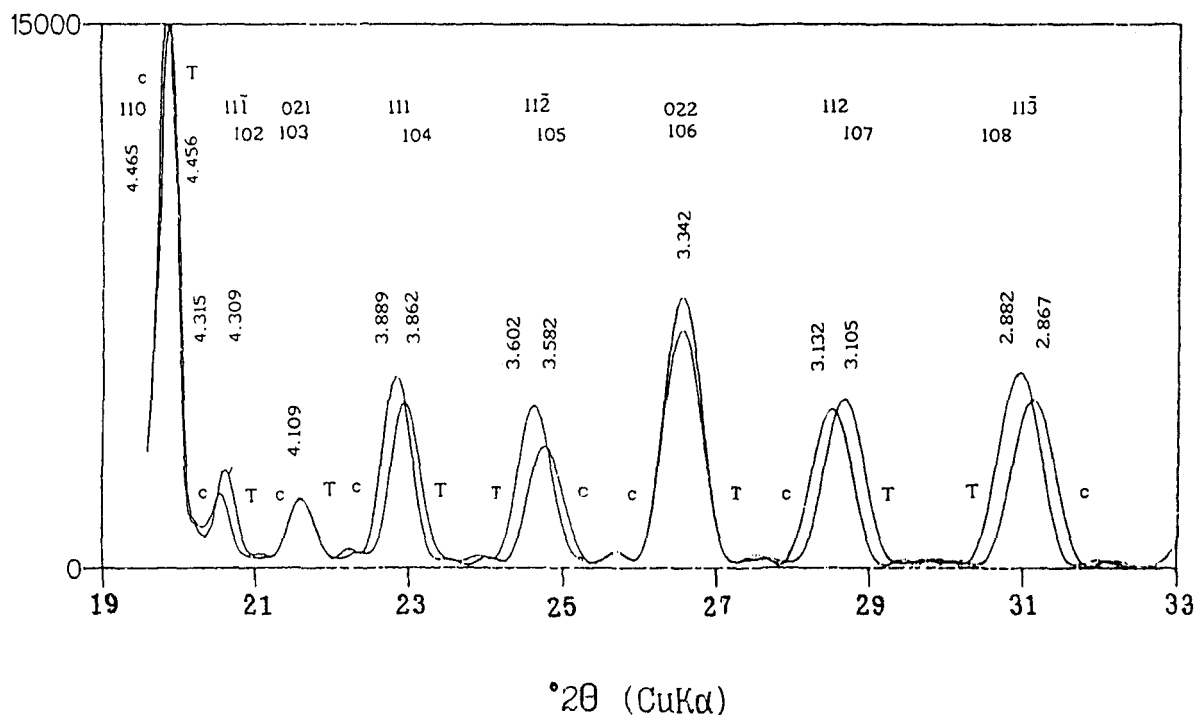


Figure 2. XRD curves calculated for c-1M and 3T illite varieties. The letters c and T stand for the peaks corresponding to c-1M and 3T polytypes, respectively; d-values and hkl indices are given above the corresponding peaks.

vacant trans-octahedra become larger but keep their relatively regular shape. Such a distortion of 2:1 mica layers leads to a peculiar relationship between the unit cell parameters (Bailey, 1966; Tshipursky and Drits, 1984):

$$|c \cos \beta/a| > 1/3$$

Usually, this quantity for K-containing t-1M micas ranges from 0.38 to 0.41 (Bailey, 1984; Sakharov *et al.*, 1990).

Experimental and simulated XRD curves for t-1M micas, where the most informative reflections have 021 and 111 indices, contain three strong reflections: 020, 112 and 112 (Figure 1). The relatively weaker 111 peak is sensitive to the presence of stacking faults, and its intensity decreases rapidly even in samples containing a small number of rotational stacking faults (Sakharov *et al.*, 1990; Drits and Tchoubar, 1990).

c-1M illite

The cation distribution results in specific distortions of cis- and trans-octahedra within the 2:1 layers. Counter-rotations of upper and lower oxygen triads in octahedra lead to a distortion of occupied trans- and cis-octahedra similar to that of the occupied cis-octahedra in the t-1M structure. On the other hand, vacant cis-octahedra have a more regular shape due to similar edge lengths common for six occupied neighbors. Such

a distortion in non-centrosymmetrical 2:1 layers results in new unit cell parameters for the c-1M structure (Tshipursky and Drits, 1984):

$$|c \cos \beta/a| < 1/3$$

For Al-rich mica, these values are 0.29–0.31 (Drits *et al.*, 1984; Zvyagin *et al.*, 1985).

The characteristic feature of XRD curves for the c-1M structure is the presence of the strong 022 reflection at 3.34 Å (26.6° 2θ), which overlaps with the basal 003 peak (not shown in Figure 1). The 111 and 113 peak intensities are greater for the c-1M species than they are for the t-1M polytype. The characteristic difference between XRD curves for t-1M and c-1M illites is that the strongest reflection for the t-1M is the 020 located at approximately 4.50 Å (19.7° 2θ), whereas the strongest reflection for the c-1M is the 110 located at 4.46 Å (20.0° 2θ) (Figure 1). However, the main criteria by which these polytypes can be distinguished are unit cell parameters based on precise measurements of d-values.

m-1M illite

A random distribution of octahedral cations over cis- and trans-sites should lead to the same shape for all octahedra in the average unit cell. Therefore, the unit cell parameters should be related by the equation:

$$|c \cos \beta| = a/3$$

Gavrilov and Tsipursky (1987) described 1M illite having $|c \cos \beta/a| = 0.345$. This value shows a strong tendency to a random distribution of Al over available octahedral sites.

Diffraction curves calculated for the m-1M illite contain 111, $11\bar{2}$, 022, 112, and $11\bar{3}$ reflections with nearly equal intensities (Figure 1). The overlapping of the 020 and 110 reflections at 4.50 and 4.46 Å, respectively, with nearly equal intensities leading to a noticeable decrease in intensity and broadening of the diffraction maximum at about 4.48 Å ($19.8^\circ 2\theta$) (Figure 1).

Conclusions based on structural considerations

In order to identify these illite varieties using XRD data, it is very important to determine precisely the unit cell parameters. The transition from t-1M to m-1M as well as from m-1M to c-1M could be gradual, and the deviation of $|c \cos \beta/a|$ from $1/3$ can be used to distinguish the different illite varieties. It is quite possible that $|c \cos \beta/a|$ can be slightly greater or less than $1/3$. When $|c \cos \beta/a| = 1/3$, the 1M polytype can be identified if $b \neq a\sqrt{3}$. However, if $b = a\sqrt{3}$, then it is not possible to distinguish between the m-1M and 3T structures; and registration of d-values and intensities, as well as simulation of the XRD curves for the samples under study, are required.

A useful diagnostic criterion for distinguishing between the 1M and 3T varieties is systematic deviation of experimental d-values (d_{exp}) from those calculated on the basis of the 3T unit cell parameters (d_{calc}). The meaning of this criterion becomes clear from comparison of the peak positions in the XRD curves calculated for c-1M and 3T varieties and shown in Figure 2. While the distribution of peak intensities is practically the same in both curves, peak positions differ such that: $d(104) < d(111)$; $d(105) > d(11\bar{2})$; $d(107) < d(112)$; $d(108) > d(11\bar{3})$, where 101 and 111 indices correspond to the 3T and c-1M varieties, respectively.

If, after indexing and calculating the d-values in terms of the 3T unit cell, the following relationships are valid:

$$\begin{aligned} d_{\text{calc}}(104) < d_{\text{exp}}(104); & \quad d_{\text{calc}}(105) > d_{\text{exp}}(105); \\ d_{\text{calc}}(107) < d_{\text{exp}}(107); & \quad d_{\text{calc}}(108) > d_{\text{exp}}(108), \end{aligned}$$

then the sample under study does not have a 3T structure but is a m-1M illite with some tendency toward c-1M. The difference between d_{calc} and d_{exp} depends on the deviation of $|c \cos \beta/a|$ from 0.333.

If $|c \cos \beta/a|$ is slightly greater than 0.333, the following relationships should be valid after indexing according to the 3T unit cell:

$$\begin{aligned} d_{\text{calc}}(104) > d_{\text{exp}}(104); & \quad d_{\text{calc}}(105) < d_{\text{exp}}(105); \\ d_{\text{calc}}(107) > d_{\text{exp}}(107); & \quad d_{\text{calc}}(108) < d_{\text{exp}}(108). \end{aligned}$$

In this case, the structure is not 3T but is m-1M with some tendency toward t-1M.

Application of the above criteria to the experimental

XRD data obtained by Yoder and Eugster (1955) for an illite sample, which they described as 3T, has shown that it may be described in terms of a one-layer monoclinic unit cell with the parameters: $a = 5.203 \text{ \AA}$, $b = 9.012 \text{ \AA}$, $c = 10.138 \text{ \AA}$, $\beta = 99.6^\circ$; $c \cos \beta/a = -0.325$. In this case, the discrepancies between d_{exp} and d_{calc} are smaller than those in terms of the 3T unit cell determined by Yoder and Eugster (1955).

Additional complications should be expected in the case of 1M and 3T polytypes that contain stacking faults because the presence of these defects may strongly modify both peak intensities and positions.

DESCRIPTION OF SAMPLES

The samples used in this study were collected from zones of hydrothermal alteration around uranium deposits. The structural, petrographic, and metallogenic characteristics of these deposits were described in detail by Ey (1984) and Halter (1988). Because of the peculiar illite polytype associations, we shall give a short description of the uranium deposits where the samples occur. The deposits are located in the Athabasca basement (Saskatchewan, Canada) and are spatially related to a major middle-Proterozoic unconformity between the Archean basement and the Helikian cover (Beck, 1977; Pagel and Svab, 1985).

Uranium ore deposits of this type are known in the Eastern edge and in the Western part of the Athabasca basin, which is located in the circular Carswell structure. Uranium mineralization occurs at the intersection between faults or shear zones and is associated with the weathered paleosurface. Around the uranium ore bodies, there is an intense hydrothermal alteration consisting of a complete argillitization of sandstones and basement rocks.

In the sediments, the clay mineral assemblage is mainly illite, kaolinite, and dickite with minor chlorite. In the hydrothermally altered basement rocks, kaolinite and illite are present; whereas, in zones of hydrothermal alteration, illite and di/trioctahedral chlorite (sудоite) dominate. The polytypes of diagenetic illite from the Athabasca sediments are $2M_1$ in most of the basin (Halter, 1988) but in certain areas, such as in the Carswell structure, the main polytype is t-1M (Ey, 1984). Illite from zones of hydrothermal alteration around the uranium deposits is represented mainly by t-1M structure but is sometimes mixed with $2M_1$. Ey (1984), Ey *et al.* (1985) and Halter (1988) also described 3T and coexisting t-1M and 3T polytypes (with occasional $2M_1$) in illites occurring close to "D" and "OP" ore bodies in the uranium deposits at Claff Lake and in the U-deposit at Cigar Lake in the Carswell structure. The samples were discovered in shear zones affected by hydrothermal alteration. Figure 3 shows the distribution of illite varieties in different zones of alteration within the D ore deposit (Ey, 1984). According to Ey (1984), 3T

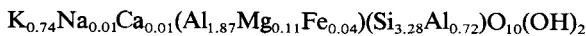
illite is located in a "zone a boules" that represents extensively argillized sandstones.

Here we shall describe only three of these samples because they differ mainly in the abundances of the coexisting illite varieties. The first (sample 91422) occurred in the altered (hematized) basement of the D ore body; the second (sample 90488) occurred in altered sandstones of the OP ore body; and the third (sample 10564) in altered sandstones of the Cigar Lake U ore body. The $<2 \mu\text{m}$ size fractions were extracted by centrifugation.

The chemical analysis of samples 91422 and 90488 (fraction $<2 \mu\text{m}$) gives the following results:

Sample	SiO ₂	Al ₂ O ₃	MgO	CaO	Fe ₂ O ₃	TiO ₂	Na ₂ O	K ₂ O	H ₂ O
91422	49.6	33.2	1.1	0.2	0.8	0.11	0.06	8.79	5.19%
90488	50.2	33.7	1.5	0.2	0.8	0.08	0.11	8.59	5.11%

These samples have a typical illite-like composition and can be characterized by the structural formulae:



(samples 91422 and 90488, respectively).

METHODS AND ANALYTICAL PROCEDURES

XRD patterns of the samples were obtained using CuK α radiation with the DRON-4 and Philips, PW 1050 automatic powder diffractometers supplied with graphite monochromators. Intensities were measured at an interval of $0.05^\circ 2\theta$ and a count time of 100 s per step. The diffractometers were supplied with a set of fine antiscatter slits (0.1–0.25 mm) to limit the horizontal beam divergence, along with Söller slits having an angular aperture of 1.5° to limit the vertical beam divergence. The XRD curves for the samples are shown in Figures 4 and 5.

Figure 4 shows partial overlapping of some of the hkl reflections, making it difficult to measure the peak positions precisely. This problem was solved by decomposition of the XRD profile into individual maxima by the procedure proposed by Salyn (1988). Each reflection was approximated by a bell-shaped function that is the sum of two Gaussian functions. One of these described the profile of the upper part of the reflection and the other, which was twice as wide, described the lower part. The quality of the approximation provided by this function was tested by analyzing profiles of individual reflections from standard samples. Application of this function combined with least-squares refinement allowed minimization of the difference between the experimental XRD profile and that simulated after summation of individual reflections. The results of such a decomposition for the XRD curve of sample 90488 are shown in Figure 5 and Tables 1 and

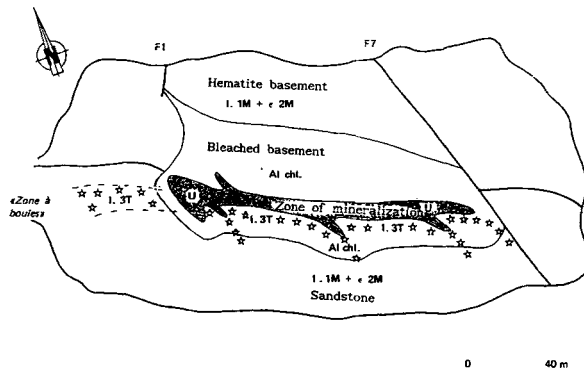


Figure 3. Location of illite polytype forms within the D ore deposit (from Ey, 1984). I.1M + 2M and I.3T stand for t-1M and 2M₁ illite association and 3T illite, respectively; Al chl stands for di-trioctahedral chlorite.

2. This procedure provides an increase in the precision of determining the position, height, width at half height, and area of an individual reflection. An XRD profile synthesized by summation of individual peaks practically coincides with the experimental one ($R = 0.14\%$).

RESULTS

The comparison of the experimental XRD curves (Figures 4 and 5, Tables 1–3) with calculated patterns for t-1M, c-1M and m-1M varieties (Figure 1) shows the 111, $11\bar{2}$, and 112 reflections at 4.32 \AA , $3.660\text{--}3.646 \text{ \AA}$ and $3.073\text{--}3.053 \text{ \AA}$, respectively, which are characteristic of the t-1M illite. The two reflections at $3.48\text{--}3.50 \text{ \AA}$ and $3.19\text{--}3.23 \text{ \AA}$ can be attributed to 2M₁ illite and are indexed as $11\bar{4}$ and 114. The reflections from 111, $11\bar{2}$, 112, and $11\bar{3}$ at $3.880\text{--}3.887$, $3.576\text{--}3.581$, $3.123\text{--}3.132$, and $2.861\text{--}2.866 \text{ \AA}$, respectively, are characteristic of the c-1M illite. Samples 91422 and 90488 consist of three coexisting illite varieties: t-1M, c-1M and 2M₁ (Figures 4a and 4b). The reflections that are characteristic of the t-1M and 2M₁ illites are nearly absent on the XRD curve for sample 10564, which may be either the c-1M or 3T polytype (Figure 4c).

Using the d-values of the reflections that are diagnostic for each structural variety and taking into account d(001) and d(060) values, the unit cell parameters for the t-1M, c-1M, and 2M₁ varieties can be calculated (Table 4). The presence of t-1M illite in samples 91422 and 90488 is confirmed by the $|c \cos \beta/a|$ values from 0.390 to 0.400. Indexing the reflections on the XRD curve for sample 10564 in terms of the 3T unit cell showed no coincidence between d_{exp} and d_{calc} , but indexing on the basis of the one-layer monoclinic unit cell given in Table 3 showed good agreement. The value of $|c \cos \beta/a| = 0.301$ demonstrates that sample 10564 corresponds to c-1M illite. The d_{exp} and d_{calc} values for 11 \bar{l} and 02 \bar{l} reflections coincide within the accuracy of $\pm 0.002 \text{ \AA}$ (Table 3).

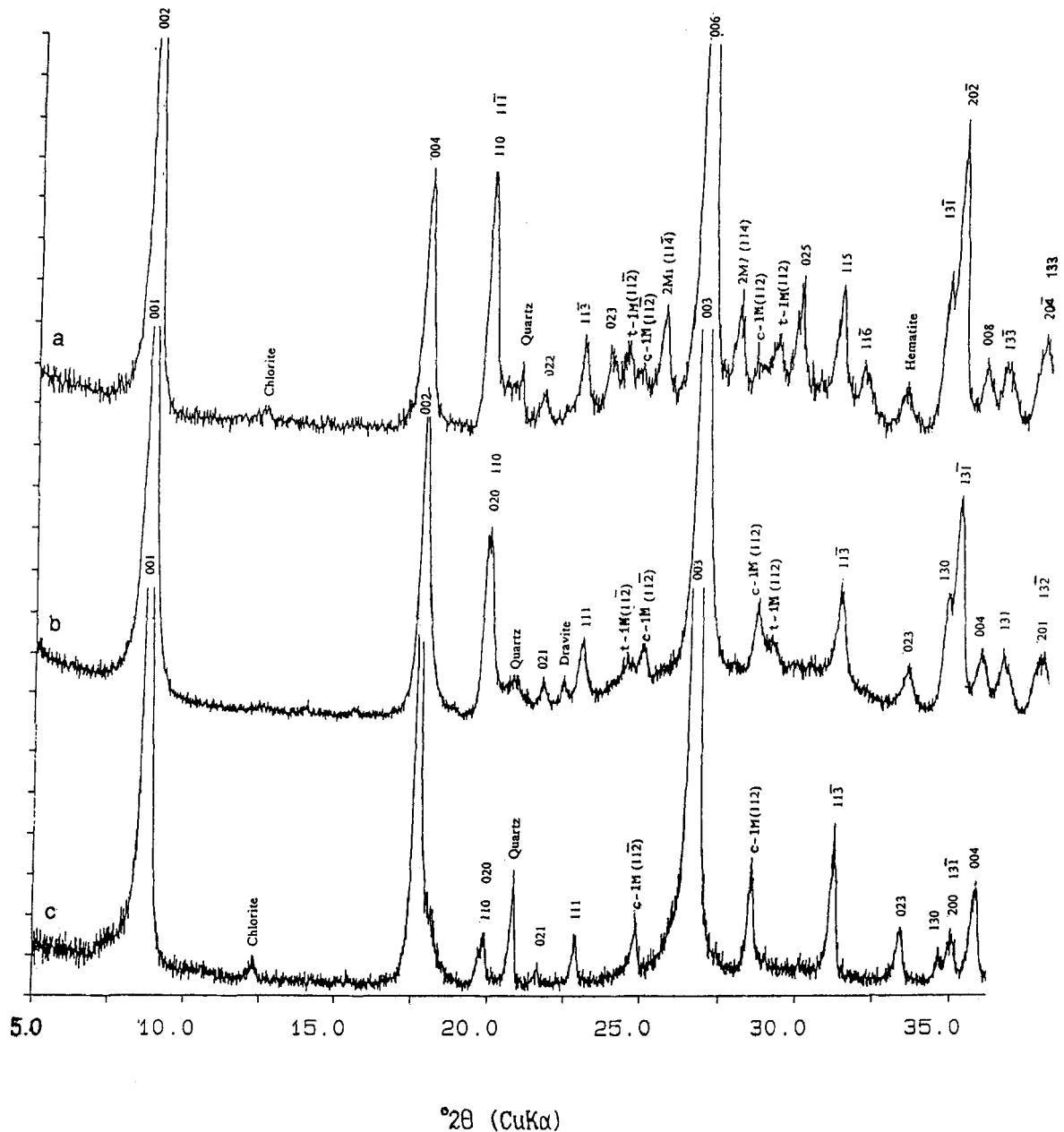


Figure 4. XRD powder curves for representative clay fraction $< 2 \mu\text{m}$; t-1M (112) and t-1M (112); c-1M (112) and c-1M (112). $2M_1$ (114) and $2M_1$ (114) correspond to the peaks that are characteristic for these illite varieties. a = sample 91422, presented mainly by $2M_1$ and t-1M, Cluff-Lake, the D ore body, altered basement; b = sample 90488, presented mainly by c-1M and t-1M polytypes, Cluff-Lake, the OP ore body, altered sandstone; and c = sample 10564, presented mainly by c-1M polytype, Cigar Lake (Waterbury), altered sandstone.

Indexing the reflections for sample 90488 after extraction of the peaks belonging to t-1M and $2M_1$ polytypes also yields unit cell parameters corresponding to the c-1M structure (Table 4). The experimental d-values and intensities of 11/ and 02/ reflections in comparison to those calculated for c-1M, t-1M, and $2M_1$ illites are given in Tables 1 and 2.

One of the important features of the polytype association is the fact that the abundance of every variety is different in different size fractions of the same sample. The intensity relationship shows that the content of c-1M illite is lower in the finer size fractions. Figure 6 shows that the ratio of 112 reflection intensities corresponding to the c-1M and t-1M illites is higher for the coarser size fraction.

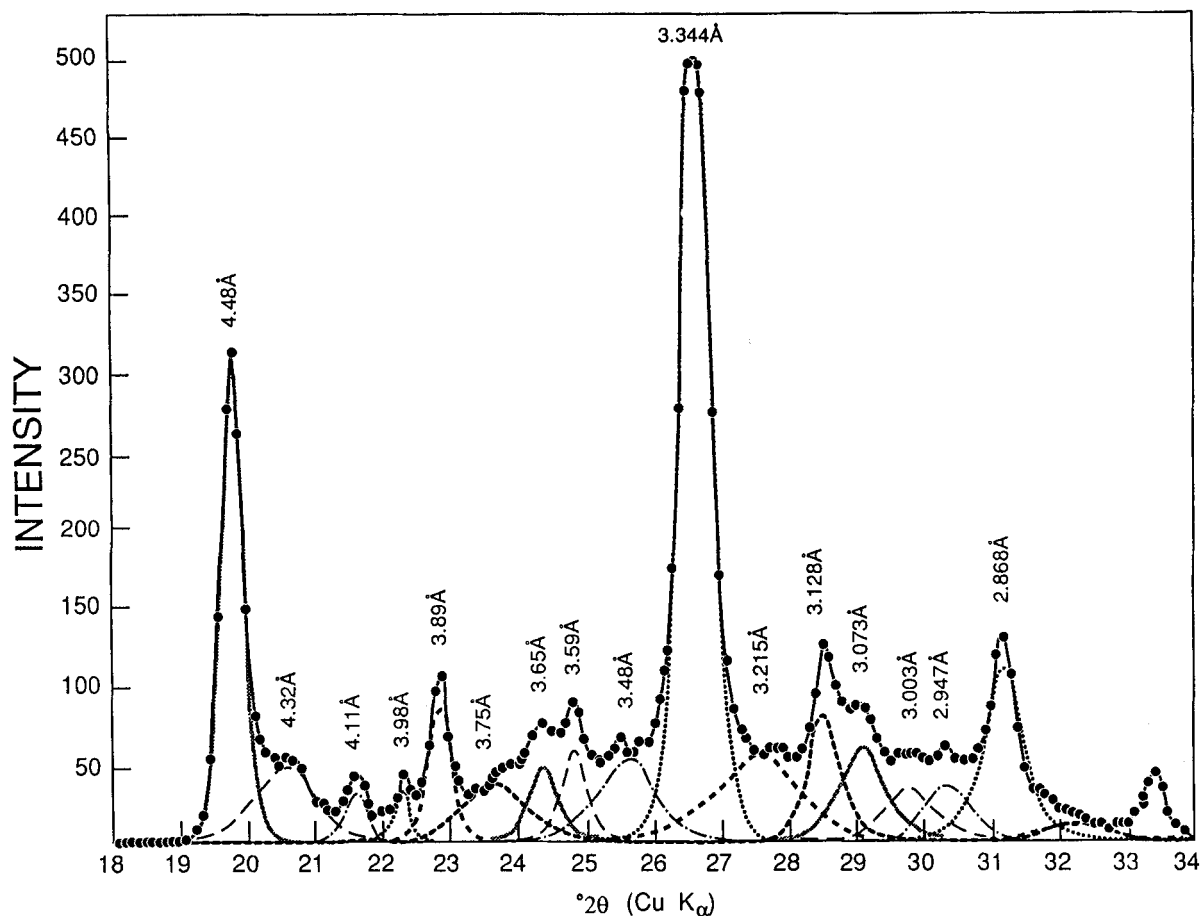


Figure 5. Decomposition of the experimental XRD curve (sample 90488) for the individual hkl maxima corresponding to c-1M, t-1M, and 2M₁ varieties. The data characterizing the maxima are given in Tables 1 and 2.

Table 1. d-values (d_{obs}) and heights (H) of the individual 111 and 021 peaks, obtained after the experimental XRD curve decomposition compared to (hkl), d-values (d_{cal}) and intensities (I) of 111 and 021 reflections for c-1M, t-1M, and 2M₁ illite polytypes found in sample 90488, fraction <2 μm , spacings in Å.

d_{obs}	H	c-1M		t-1M		2M ₁				
		hkl	d_{cal}	I_{cal}	hkl	d_{cal}	I_{cal}	hkl	d	I
4.485(5)	100	020	4.50	10	020	4.50	100	110	4.48	55
		110	4.47	100	110	4.44	10	11 $\bar{1}$	4.46	65
4.320(5)	15	$\bar{1}11$	4.309	20	$\bar{1}11$	4.351	45	—	—	—
4.110(5)	15	021	4.106	15	021	4.107	20	022	4.109	14
3.980(4)	10	—	—	—	—	—	—	112	3.973	12
3.890(4)	30	111	3.885	35	—	—	—	11 $\bar{3}$	3.889	37
3.751(4)	10	—	—	—	—	—	—	023	3.735	32
3.655(4)	15	—	—	—	$\bar{1}12$	3.655	65	—	—	—
3.588(4)	20	$\bar{1}12$	3.591	25	—	—	—	—	—	—
3.480(4)	15	—	—	—	—	—	—	$\bar{1}14$	3.500	44
3.344(4)	250	003	3.338	100	003	3.338	100	006	3.351	100
		022	3.348	50	022	3.350	20	024	—	—
3.215(4)	20	—	—	—	—	—	—	114	3.208	47
3.128(4)	30	112	3.126	30	—	—	—	—	—	—
3.073(4)	20	—	—	—	112	3.073	55	—	—	—
3.003(4)	10	—	—	—	—	—	—	025	2.999	47
2.947(3)	10	—	—	—	$\bar{1}13$	2.927	15	—	—	—
2.868(3)	35	$\bar{1}13$	2.873	30	—	—	—	115	2.87	35

Table 2. d-values (d_{obs}) and heights (H) for individual 131 and 201 diffraction maxima obtained after the experimental XRD curve decomposition together with hkl and d-spacings calculated for c-1M, t-1M, and 2M₁ illite polytypes found in sample 90488, fraction <2 μm , spacings in Å.

d_{obs}	H	c-1M		t-1M		2M ₁	
		hkl	d	hkl	d	hkl	d
2.590(3)	50	130 201	2.593	201 130	2.602 2.588	131	2.589
2.563(3)	130	200 131	2.573 2.560	131 200	2.569 2.555	202	2.562
2.507(3)	20	004	2.504			008	2.500
2.458(3)	35	131 202	2.454 2.462	131	2.447		
2.386(3)	35	132 201	2.386 2.402	201 132	2.365 2.400	133	2.380
2.244(3)	20	040	2.244	040	2.244	040	2.247
2.220(3)	5	203 132	2.217 2.230	132	2.211		
2.196(3)	10					221	2.201
2.153(3)	10	202	2.153	133	2.154		
2.132(3)	35	133	2.132			135	2.132
2.052(2)	5	042	2.051			044	2.051
2.002(2)	60	005	2.000	204	1.998	0010	2.000
1.973(2)	20	133	1.972			137	1.975
1.952(2)	10	204	1.958	133	1.954	206	1.950
1.500(1)	70	060	1.500	060	1.500	060	1.499

DISCUSSION

Accurate measurements of d-values corresponding to individual diffraction maxima and the determination of the unit cell parameters indicate that the illite in the samples studied, previously identified as 3T, is in fact c-1M. The existence of this variety emphasizes one of the problems with the one-layer dioctahedral mica nomenclature. As a matter of fact, c-1M and t-1M illite structures can be considered as polymorphs or polytypes depending on the choice of the independent structural units for the inference of different polytypes. If the 2:1 layer is chosen as an independent structural unit, these structures can be considered as polymorphs because the 2:1 layers for c-1M and t-1M have different structures. If the octahedral and tetrahedral sheets are chosen as independent structural units, the c-1M and t-1M structures can be considered as polytypes consisting of the two types of structural units (Zvyagin *et al.*, 1985).

The petrologic and geologic significance of c-1M illite is not known. This variety, as well as the association of t-1M and c-1M illite, are not restricted to areas of uranium deposits. Zvyagin *et al.*, (1985) found c-1M illite in the relicts of the buried weathering crust developed on the granodioritic basement south of the Siberian platform in the Careline area. Recently, Bloch *et al.* (1990) and Zhukhlistov and Zvyagin (1991) used OTED to describe samples bearing t-1M and c-1M sericitic micas, which formed as a result of hydrothermal metasomatic alterations of igneous rocks in the Upper Devonian of the Tuva trough. Gavrilov and

Table 3. Experimental and calculated XRD powder data for c-1M illite polytype, sample 10564, clay fraction <2 μm , spacings in Å.

hkl	d_{calc}	d_{obs}
001	10.035	10.038
002	5.018	5.018
110	4.465	4.465
021	4.109	4.105
111	3.889	3.887
112	3.582	3.581
003	3.345	3.348
112	3.132	3.132
113	2.867	2.866
023	2.685	2.686
130	2.587	2.590
131	2.559	2.561
004	2.509	2.506
131	2.464	2.462
132	2.380	2.378

Tsipursky (1987) have shown that an initial association of 2M₁ and t-1M illite plus kaolinite formed after hydrothermal alterations due to the presence of igneous intrusions can be transformed into the mineral pair: andalusite + m-1M. Therefore, 1M illites with different distributions of octahedral cations over trans- and cis-sites may be more common than is currently recognized.

Temperature may be one of the main factors controlling the occurrence of the different illite varieties. Experimental results on illite synthesis obtained by Warsaw (1959) seem to confirm this supposition. According to her data, at temperatures of 380°–500°C 3T illite was formed out of a gel of illite composition. An increase in temperature up to 500°–600°C leads to the formation of t-1M illite with the same composition as the initial gel. Warsaw must have synthesized the c-1M or m-1M illite and not 3T. Table 5 contains experimental d-values and peak intensities given by Warsaw (1959) as well as indices and d-values calculated on the basis of the unit cell parameters for the c-1M illite. Very good agreement between $d_{\text{exp}}(\text{hkl})$ and $d_{\text{calc}}(\text{hkl})$ confirms our interpretation. Indexing the reflections in question in terms of the 3T structure leads to strong and systematic deviations between the values of $d_{\text{calc}}(101)$ and d_{exp} mentioned above.

In the light of these results, the c-1M illite should have been formed at lower temperatures, and the t-1M illite, at higher temperatures. The location of the c-1M illite closer to the mineralization zone than t-1M shows that this assumption is not valid. In addition, an increase in the amount of c-1M illite in the coarser size fractions of the same sample indicated that there may be other factors controlling c-1M illite formation.

Another possibility for the formation of illites with abnormal octahedral cation distributions is a very fast illitization of montmorillonite having vacant cis-sites (Mering and Oberlin, 1967; Tsipursky and Drits, 1984;

Table 4. The unit cell parameters (in Å) determined for the illite polytype forms in the samples under study.

Sample fraction <math>< 2 \mu\text{m}</math>	Polytype	a	b	c	β	c cos β /a
10564	c-1M	5.202(5)	9.010(5)	10.157(10)	98.89	-0.302
90488	c-1M	5.213(5)	9.000(5)	10.150(10)	99.20	-0.311
	t-1M	5.21(1)	9.00(1)	10.23(1)	101.5	-0.390
	2M ₁	5.21(1)	9.00(1)	20.08(1)	95.8	-0.389
91422	c-1M	5.193(5)	8.994(5)	10.135(10)	99.28	-0.315
	t-1M	5.193(5)	8.994(5)	10.214(10)	101.76	-0.400
	2M ₁	5.193(5)	8.994(5)	20.10(10)	95.83	-0.393

Drits and Tchoubar, 1990). Therefore, occupied transites could be inherited by the illite structure if a solid-phase transformation of montmorillonite into illite takes place. This mechanism is not likely, however, because random distribution of 2:1 layer azimuthal orientations in montmorillonite should also be inherited by the illite and lead to the appearance of stacking faults in its structure if a transformation mechanism occurs. Narrow peak widths of the reflections belonging to the c-1M illite (Figure 4c) indicate very few of these type of defects. Additionally, the solid-state transformation mechanism does not explain the relationship of the c-1M component content to the size fraction of the clay separate since inheritance of the montmorillonite matrix should have led to greater abundance of c-1M illite in the finer size fraction.

The practically identical chemical compositions of samples 90488 and 91402, in spite of the different abundances of the t-1M, c-1M, and 2M₁ varieties in both samples, show that this factor also is not responsible for c-1M illite formation. Ey (1984) supposed that the prolonged high pressure in the compression zones around the uranium deposits had an effect on the hydrothermal fluids and that this was one of the possible factors responsible for the formation of 3T illite that turned to be actually c-1M. Zvyagin *et al.* (1985) also assumed that the prolonged, relatively high pressure in zones of hydrothermal activity, coupled with slow decrease in solution temperature, were favorable conditions for crystallization of c-1M illite. Therefore, c-1M illite may reflect hydrothermal alteration under a relatively high pressure, similar to 3T phengite, which reflects high pressure and relatively low temperature metamorphic conditions (Frey, 1987; Guiddotti, 1984). Also, the coexistence of c-1M and t-1M varieties as well as the increase in the abundance of c-1M illite in coarser size formations may be evidence that, under such hydrothermal conditions, the c-1M polytype is more stable than the t-1M structure.

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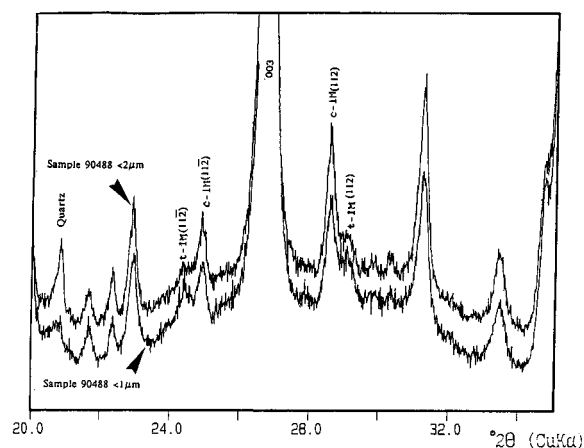


Figure 6. Comparison of XRD curves obtained for two different clay fractions <math>< 1 \mu\text{m}</math> and <math>< 2 \mu\text{m}</math> of sample 90488; t-1M (112) and t-1M (112), c-1M (112), and c-1M (112) stand for diagnostic reflections corresponding t-1M and c-1M.

Table 5. Comparison of d-values calculated (d_{cal}) from the unit cell parameters: $a = 5.179 \text{ \AA}$, $b = 8.970 \text{ \AA}$, $c = 10.138 \text{ \AA}$, and $\beta = 99.12^\circ$ with experimental values (d_{exp}) given by Warsaw (1959), spacings in Å.

Indices	d_{cal}	d_{exp}	I
001	10.0	10.1	75
002	5.01	5.01	35
020	4.485	4.48	65
110	4.442		
11 $\bar{1}$	4.277	4.27	10
021	4.093	4.10	10
111	3.872	3.87	20
11 $\bar{2}$	3.579	3.58	5
022	3.339	3.34	70
003	3.337		
112	3.119	3.12	15
11 $\bar{3}$	2.861	2.86	20
023	2.677	2.68	5
060	1.495	1.495	15

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