

**CRYSTAL CHEMISTRY of a 2M<sub>1</sub> MUSCOVITE**

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05-13-90

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## ABSTRACT

The crystal chemistry and polytype of muscovite crystals picked from an intriguing sample were characterized using electron microprobe and single-crystal x-ray diffraction methods, respectively. The sample consisted of  $>2\ \mu\text{m}$  mica crystals and illite clay in intimate contact, with a continuous intermediate size gradation. X-ray powder diffraction of the clay indicated the polytype was 1M.

Electron microprobe analyses confirmed the  $>2\ \mu\text{m}$  crystals were muscovite:  $(\text{K}_{.902}\text{Na}_{.097}\text{Ba}_{.005})(\text{Al}_{1.692}\text{Mg}_{.126}\text{Fe}_{.092}\text{Ti}_{.072}\text{Cr}_{.002}\text{Mn}_{.001})(\text{Si}_{3.183}\text{Al}_{.817})\text{O}_{10}(\text{OH},\text{F})_2$ . X-ray precession h0l and 0kl photos were taken and indicated that the  $>2\ \mu\text{m}$  crystals were of polytype  $2\text{M}_1$  in contrast to 1M of the clay-size fraction. Three dimensional intensity data consistent with a C-centered unit cell was collected up to  $60^\circ$ ,  $2\theta$  and reduced with Lorentz, polarization and analytic absorption corrections. Both precession and four-circle x-ray analysis suggested that the crystal was not suitable for a detailed structure refinement.

The intimate juxtaposition of  $2\text{M}_1$  muscovite with 1M illite clay has not previously been documented. The author suggests that one of the phases may be metastable and transition from one polytype to the other may be occurring.

## INTRODUCTION

The basic T-O-T layered structure of the mica group was originally proposed by Pauling (1930) and first solved in detail on muscovite by Jackson and West (1931). Subsequently, many detailed crystal structure refinements of micas have been published.

The T-O-T layer consists of two negatively charged sheets of tetrahedrally coordinated cations arranged in hexagonal rings, and an interposed, positively charged cation sheet (figure 1). Cations of the positive interlayer are held in octahedral coordination by the apical oxygens and OH groups of the tetrahedral sheets. This coordination of the interlayer is the mechanism by which the tetrahedral sheets are tightly joined and charge balanced. The total thickness of the T-O-T layer is approximately 10 Å.

Within each T-O-T layer, the hexagonal rings of apical oxygens must be staggered relative to each other by a distance of  $a/3$  in order to accommodate regular octahedra in the interlayer (figure 2). This stagger can be directed in a positive or negative direction along  $a$  or either of the two pseudo- $a$  axes, and gives rise to structure subtypes, or polytypes (Smith and

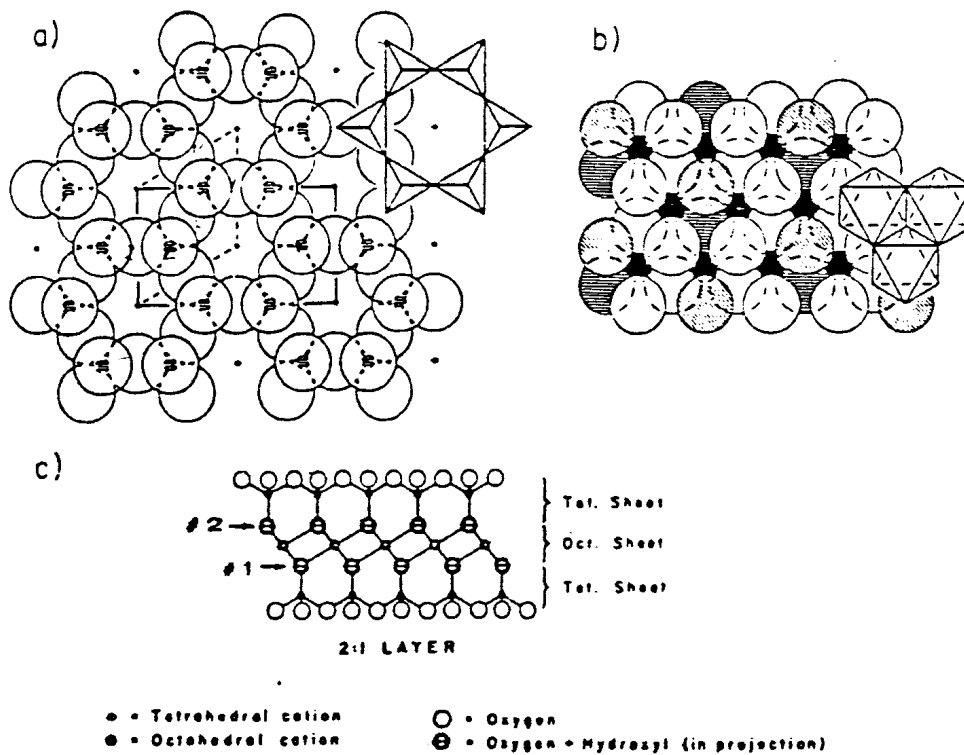


Figure 1. (a) Stylized tetrahedral sheet, fully extended laterally, with possible hexagonal (dashed line) and orthohexagonal (full line) cells shown. (b) Octahedral sheet with OH, F groups shaded. (c) T-O-T layer with #1 and #2 common planes of junction labeled. Modified from Bailey, 1984.

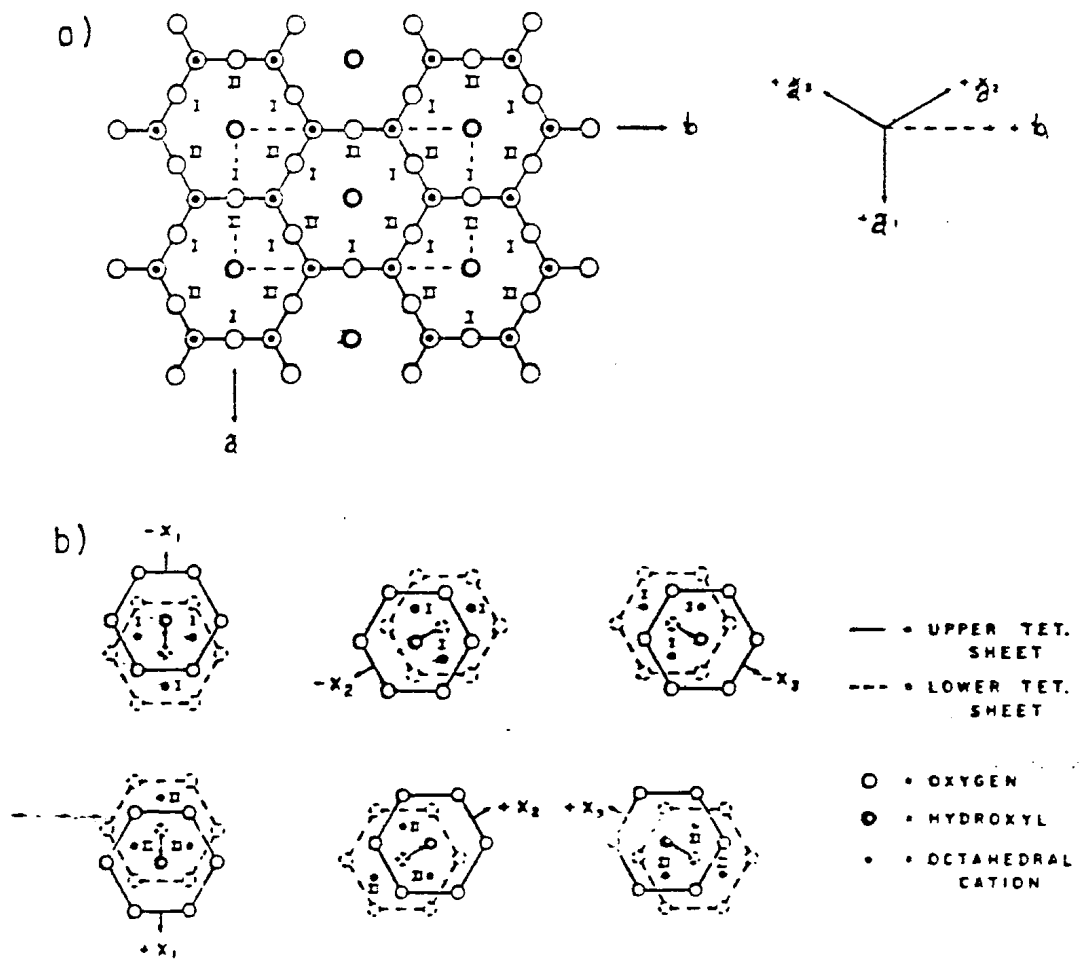


Figure 2. (a) Illustration of two possible sets of octahedral cation positions above a tetrahedral sheet relative to a fixed set hexagonal axes for a T-O-T layer. (b) Six directions of intralayer shifts of hexagonal rings of apical oxygens. Modified from Bailey, (1984).

Yoder, 1956).

The polytypes are divided into two groups on the basis of repetition of occupancy of cation sites of the octahedral layer. In group A polytypes, the same set of octahedral positions is occupied in each layer, and the octahedral layer repeat distance along  $c^*$  is 10 Å (figure 2). In group B, the occupied sites of adjacent octahedral layers alternate between the two possible sets of positions, producing a 20 Å octahedral layer repeat distance along  $c^*$ .

Partly due to this limited variability inherent to its structure, the mica group is diverse and significant gaps exist in our knowledge of it. Notable among these are details of the pressure, temperature, and chemical regimes under which different polytypes are stable. Yoder and Eugster (1955) demonstrated that transitions from one polytype to another could be effected in muscovite as pressure and temperature were increased. However, they were not able to accurately fix the polytype stability ranges, and subsequently these details have not been well characterized.

The focus of this project is centered on an unusual sample which has brought these questions to the forefront of our research. The sample consists of several kilograms of illite clay and muscovite crystals that were collected by from a suspected fault zone at Cap Rouge, Nova Scotia. Mica crystals are in intimate contact with the clay, with a continuous size gradation from several millimeters in diameter down through the

clay size fraction (Tettenhorst, personal communication).

Preliminary X-Ray powder diffraction studies indicated that the clay size fraction is of the 1M polytype (Tettenhorst, personal communication). Due to the complete size gradation exhibited by the sample, we assumed that the coarse fraction was of the same crystal structure. No 1M dioctahedral muscovite crystals of adequate size and quality for a detailed structure characterization have ever been found. All known 1M muscovite parameters are from powder diffraction studies on samples of poor crystallinity. We were excited by this discovery because our sample contained an abundance of crystals as large as several millimeters in diameter. The purpose of this study therefore was to complete a chemical analyses and detailed characterization of a presumed 1M muscovite single crystal.

## EXPERIMENTAL

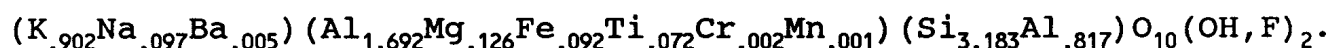
### Chemical Analysis

Crystal chemistry was characterized using a Cameca Camebax Electron Microprobe. Operating conditions were an accelerating voltage of 15 kV, sample current of 20 nA, and a defocused electron beam of approximately 125 to 150  $\mu\text{m}$  diameter. Standards were selected from various silicate minerals. Details of the analyses and recalculations are given in table 1.

Crystals were prepared in epoxy grain-mounts and each flake was probed several times at different locations. A total of

three points yielded acceptable analyses. Recalculation was based on 11 oxygens. The average composition was calculated by averaging the oxide weight percents and then recalculating the mean analysis. Results are listed in table 1. Note that the water and potassium in muscovite are easily volatilized under the electron beam and realistic totals should not exceed 94 or 95%.

The average analysis is acceptable and is therefore taken to be the mean chemistry for the coarse fraction of the cap rouge sample:



On this basis the mica is identified as muscovite.

#### Space Group Determination

Mica crystals were surveyed by x-ray precession photography to assess crystal quality and determine space group and polytype. h0l and Okl photos were taken with  $c^*$  parallel to the dial axis.

Space group and polytype were determined according to the criteria described by Bailey (1988). The first step in this process is the discrimination between group A and group B micas. In group A the same set of octahedral positions is occupied in every layer (which corresponds to a repeat of 10 Å along  $c^*$ ). The octahedral cations all repeat at  $b/3$  and thus contribute very strongly to all reflections of  $k=3n$ . Along  $c^*$  this octahedral contribution completely dominates these reflections. Therefore in group A, reflections along  $c^*$  of index  $k=3n$  repeat at 10 Å. In contrast to this, the group B octahedral layer occupies



Table 1. Muscovite Crystal Chemistry

Sample:	4-17-90			
	7	8	9	Mean
<u>Oxide</u>	<u>Weight percent</u>			
SiO <sub>2</sub>	46.267	45.525	45.378	45.723
Al <sub>2</sub> O <sub>3</sub>	31.666	31.169	28.806	30.547
TiO <sub>2</sub>	1.234	1.61	1.309	1.384
Cr <sub>2</sub> O <sub>3</sub>	0.000	0.039	0.103	0.047
FeO	2.305	1.036	1.416	1.586
Fe <sub>2</sub> O <sub>3</sub>	----	----	----	----
MnO	0.051	0.000	0.008	0.020
MgO	1.382	1.100	1.178	1.220
NiO	0.000	0.000	0.000	0.000
BaO	0.120	0.305	0.083	0.169
CaO	0.000	0.000	0.000	0.000
K <sub>2</sub> O	10.892	9.850	9.736	10.159
Na <sub>2</sub> O	0.503	1.021	0.627	0.717
FO	----	----	----	----
<u>Total:</u>	<u>94.419</u>	<u>91.655</u>	<u>88.645</u>	<u>91.572</u>
	<u>Tetrahedral Cations</u>			
Si	3.144	3.159	3.250	3.183
Al	<u>0.856</u>	<u>0.841</u>	<u>0.750</u>	<u>0.817</u>
<u>Total:</u>	<u>4.000</u>	<u>4.000</u>	<u>4.000</u>	<u>4.000</u>
	<u>Octahedral Cations</u>			
Al	1.680	1.708	1.682	1.692
Ti	0.063	0.084	0.071	0.072
Cr	0.000	0.002	0.006	0.002
Fe	0.131	0.060	0.085	0.092
Mn	0.003	0.000	0.000	0.001
Mg	0.140	0.114	0.126	0.126
Ni	0.000	0.000	0.000	0.000
<u>Total:</u>	<u>2.017</u>	<u>1.968</u>	<u>1.970</u>	<u>1.985</u>
	<u>Layer Charge</u>			
	-1.016	-1.029	-0.986	-1.011
	<u>Interlayer Cations</u>			
K	0.944	0.872	0.890	0.902
Na	0.066	0.137	0.087	0.097
Ba	0.003	0.008	0.002	0.005
Mg	0.000	0.000	0.000	0.000
Ca	0.000	0.000	0.000	0.000
<u>Total:</u>	<u>1.013</u>	<u>1.017</u>	<u>0.979</u>	<u>1.004</u>
	<u>Interlayer Charge</u>			
	1.016	1.025	0.981	1.009

Note: Cations calculated on basis of 11 oxygens. Values of zero = not detected  
dashes = not analyzed. Mean chemistry recalculated from weight percents averaged  
over points 7, 8, and 9.

alternating positions in adjacent layers, corresponding to a 20 Å repeat along  $c^*$ . Therefore, the group B reflections along  $c^*$  of index  $k=3n$  have a 20 Å repeat. In reciprocal space, the group B,  $k=3n$  reflections are repeated with twice the frequency as group A.

Reproductions of the  $h0l$  and  $0kl$  precession photos are given in figures 3 and 4. All of the reflections in the  $h0l$  photo are of index  $k=3n$ , and repeat at 10 Å intervals. Thus the crystals must be of group A polytypes:  $1M$ ,  $2M_1$ , or  $3T$ .

Discrimination between these polytypes can be made on the basis of unit cell axial angles and systematic absences. The polytypes  $1M$ ,  $2M_1$  and  $3T$  are of space groups  $C2/m$ ,  $C2/c$ , and  $P3_1,12$  respectively. The  $95.8^\circ$   $\beta$ -angle displayed on the  $h0l$  photo eliminates the possibility of  $P3_1,12$  symmetry of the  $3T$  polytype. Furthermore, the photos display systematic presence conditions  $hkl$ ;  $h+k=2n$ ,  $h0l$ ;  $h,l=2n$ , and  $00l$ ;  $l=2n$ . Of the two remaining group A space group possibilities, only  $C2/c$  is consistent with these observed conditions. The  $C2/m$  unit cell requires neither the  $h0l$ ;  $h,l=2n$  nor the  $00l$ ;  $l=2n$  reflections to be present. On this basis the crystal is assigned to space group  $C2/c$  and polytype  $2M_1$ . This is the most common polytype for muscovite.

### Data Collection

The slight but distinct annular streaking of diffraction spots on the precession photos suggests the crystal is of marginal quality for a detailed structure refinement. The  $060$

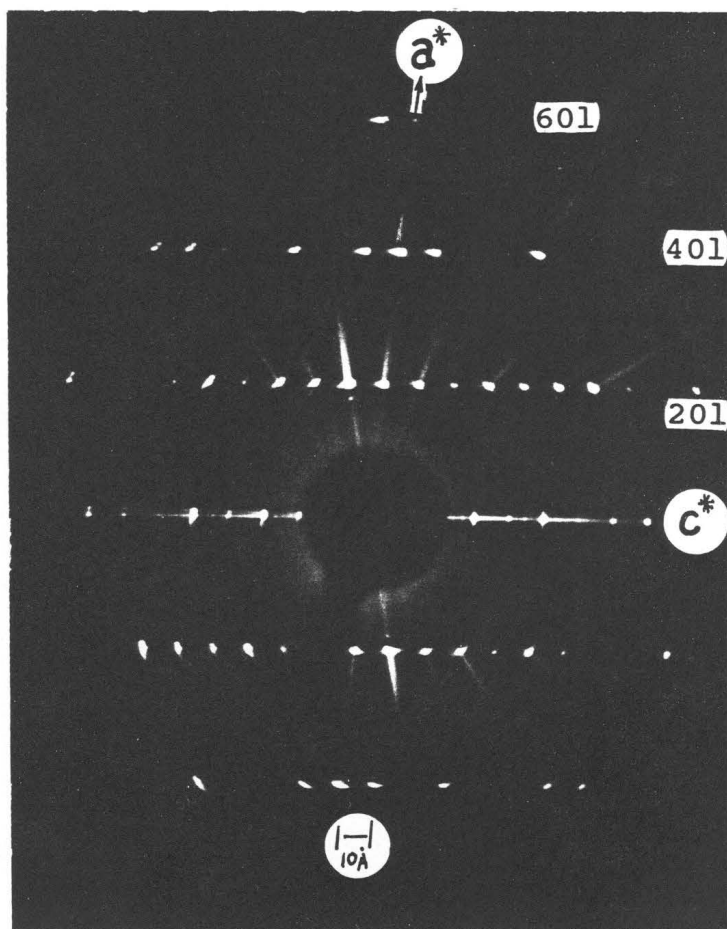


Figure 3. H01 Precession photograph for sample 3M. Mo. K radiation, 24 hour exposure, Precession angle of 25°.

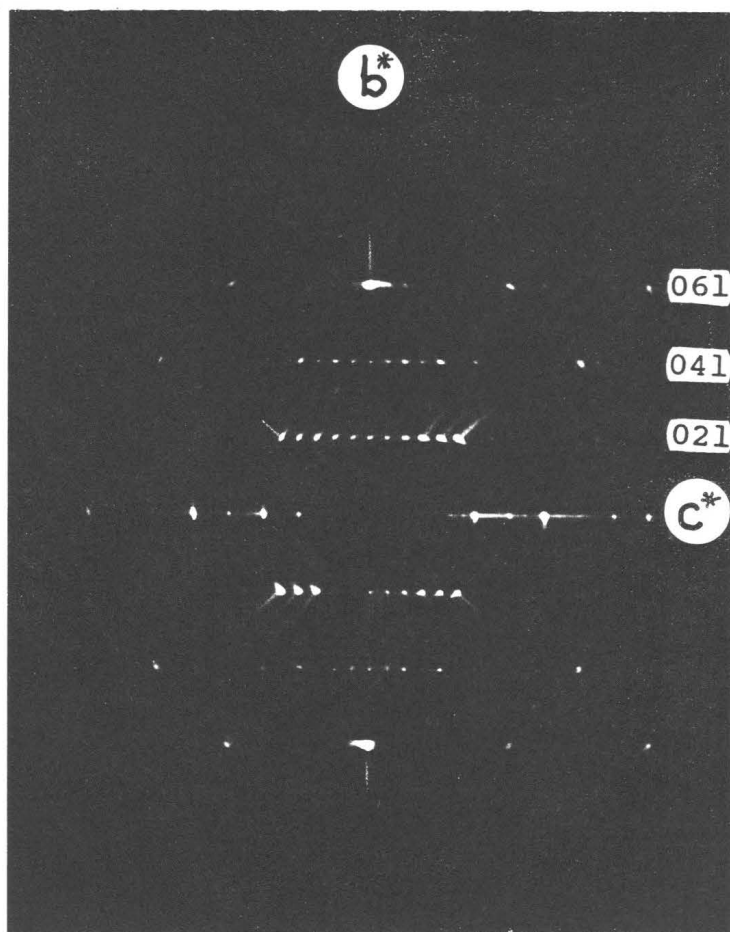


Figure 4. Ok1 Precession photograph for sample 3M. Mo. K radiation, 24 hour exposure, Precession angle of 25°.

reflection is most severely streaked with a spread of  $2^\circ \omega$  measurable from the photos. In the extreme case this streaking would constitute a complete circumference around the center of the photo, the equivalent of Debye-Scherrer rings.

To measure the full extent of streaking,  $2\theta$ - $\omega$  profile scans and two-dimensional profiles of distorted peaks were made on using a Rigaku RFC6-R rotating anode four-circle diffractometer. For reflections of  $2\theta > 15^\circ$   $\omega$ -streaking ranged from .5 to  $3^\circ$ . For peaks of  $2\theta < 15^\circ$ ,  $2\theta$ - $\omega$  scan widths were a maximum of  $1.6^\circ$ .

The slight doubling of spots on the photos was also inspected by these methods and was attributed to film bulge during exposure. Three dimensional intensity data was collected under operating conditions of 50 kV and 180 mA. The full sphere of reciprocal space was collected up to  $40^\circ$ ,  $2\theta$ , and the  $k > 0$  half-sphere was collected from  $40$  to  $60^\circ$ ,  $2\theta$ . Thus non-friedel symmetry-equivalent reflections in the high-angle data could be compared. Only reflections consistent with a C-centered cell were scanned.

Raw data was corrected for Lorentz and polarization effects, and then an analytical absorption correction was applied based on a cylindrical approximation of the crystal morphology. A total of 3,135 reflections with  $I > 3\sigma I$  were collected.

The annular streaking of peaks significantly affected data collection and reduction. Peaks were broad and could not be well centered. The resulting orientation matrix was not adequate for some high-angle regions of reciprocal space. Additionally, 135

forbidden reflections were observed. Two-dimensional profiles and centering operations were performed to check the validity of these reflections. Both tests indicated that the intensity collected at these points was attributable to  $\omega$ -streaking from nearby peaks.

Symmetry-equivalent reflections were averaged and yielded an R-factor of 12.1%. A significant detailed refinement of thermal and structural parameters of is realistically unfeasible for these conditions. However, cell parameters were refined from 23 intense reflections most of which were symmetry-equivalents of 20 to  $53^\circ$ ,  $2\theta$ . Unit cell and data collection parameters are given in Table 2.

### DISCUSSION

In our original estimation we assumed that both coarse and fine fractions had the same polytype because of the complete, uninterrupted particle size gradation between them. However, analysis indicates that they are disparate: the  $<2\mu\text{m}$  size fraction being of polytype  $1M$ , and the coarse fraction  $2M_1$ . Additionally, electron microprobe analyses of the  $<2\mu\text{m}$  fraction indicates it is phengitic in composition.

The occurrence of intimately juxtaposed  $>2\mu\text{m}$  muscovite and  $<2\mu\text{m}$  phengitic phases has previously not been documented. Therefore, our finding is somewhat startling and raises new questions. I suggest that one of the phases may be metastable

and that a transition from one polytype to the other is occurring. The question of crystal structure and chemistry as a function of particle size should be examined. Chemical analyses of the clay size fraction indicate a composition very similar to the muscovite, but somewhat enriched in calcium. This suggests the mobility of calcium may be important in alteration reactions.

### Acknowledgements

I am grateful to Dr James Downs, Dr. Rodney Tettenhorst, and Dr. Judith Gallucci for their support in this endeavor. Assistance with microprobe operation was provided by David Little. This research was supported by grants from The Honors Office of the OSU College of Arts and Sciences, NSF grant EAR-8618834 to J. Downs.

Table 2. Experimental Data

<u>Sample</u>	<u>M3</u>
Size (microns)	429x283x13
Least Squares	
Cell Parameters	
a(Å)	5.188(1)
b	9.005(4)
c	20.05(2)
Beta (°)	95.68(1)
Vol (Å <sup>3</sup> )	932(1)
Theta Range	0 -30°
Radiation	Mo-K $\alpha$
$\lambda$ (Å)	0.71069
	Graphite Monochromator
Absorption	
Correction	Analytical
Reflections with	
I>3 $\sigma$ I	3135
Symm. Equiv. R	0.144

Note: Cell parameters from least-squares refinement of 23 intense reflections.



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