

REVIEWS in MINERALOGY and GEOCHEMISTRY

Volume 46

2002

MICAS: CRYSTAL CHEMISTRY AND METAMORPHIC PETROLOGY

Editors

Annibale Mottana

Università degli Studi Roma Tre

Francesco Paolo Sassi

Università di Padova

James B. Thompson, Jr.

Harvard University

Stephen Guggenheim

University of Illinois at Chicago

FRONT COVER: Perspective view of TOT layers in biotite down [100] ([001] is vertical), produced by *CrystalMaker*. Red tetrahedra contain Si or Al, green and white octahedra contain Mg and Fe, respectively, and yellow spheres represent the K interlayer cations. Courtesy of Mickey Gunter, University of Idaho, Moscow. [Data: S.R. Bohlen et al. (1980) Crystal chemistry of a metamorphic biotite and its significance in water barometry. *Am Mineral* 65:55-62]

BACK COVER: A view down [001] of lepidolite- $2M_2$, showing tetrahedrally coordinated Si,Al (blue) joined with bridging oxygens (red thermal ellipsoids) in the T-layer and ordered, octahedrally coordinated Al (gray) and Li (yellow) in the O-layer. The interlayer cation is 12-coordinated K (green). Courtesy of Bob Downs, University of Arizona, Tucson. [Data: S. Guggenheim (1981) Cation ordering in lepidolite. *Am Mineral* 66:1221-1232]

Series Editor for MSA: Paul H. Ribbe
Virginia Polytechnic Institute and State University

MINERALOGICAL SOCIETY of AMERICA

Washington, D.C.

ACCADEMIA NAZIONALE dei LINCEI

Roma, Italia

SUB Göttingen
214 945 60X

7

LSA



2002 A 22027

MICAS: CRYSTAL CHEMISTRY and METAMORPHIC PETROLOGY

Editors: *A Mottana, F P Sassi, J B Thompson, Jr & S Guggenheim*

Table of Contents

1 Mica Crystal Chemistry and the Influence of Pressure, Temperature, and Solid Solution on Atomistic Models

Maria Franca Brigatti, Stephen Guggenheim

OVERVIEW.....	1
Treatment of the data and definition of the parameters used.....	3
End-member crystal chemistry: New end members and new data since 1984.....	4
Synthetic micas with unusual properties.....	11
EFFECT OF COMPOSITION ON STRUCTURE.....	11
Tetrahedral sheet.....	11
Tetrahedral rotation and interlayer region.....	19
Tetrahedral cation ordering.....	25
Octahedral coordination and long-range octahedral ordering.....	27
Crystal chemistry of micas in plutonic rocks.....	37
ATOMISTIC MODELS INVOLVING HIGH-TEMPERATURE STUDIES OF THE MICAS.....	39
Studies of samples having undergone heat treatment.....	39
Dehydroxylation process for dioctahedral phyllosilicates.....	41
Dehydroxylation models for <i>trans</i> -vacant 2:1 layers.....	43
Dehydroxylation models for <i>cis</i> -vacant 2:1 layers.....	44
Comparison of Na-rich vs. K-rich dioctahedral forms.....	49
Heat-treated trioctahedral samples: The O,OH,F site and <i>in situ</i> high-temperature studies.....	50
Heat-treated trioctahedral samples: Polytype comparisons.....	51
ACKNOWLEDGMENTS.....	51
APPENDIX I: DERIVATIONS.....	52
Derivation of "tetrahedral cation displacement", T_{disp}	52
Derivation of ΔE_1 , ΔE_2 , ΔE_3	52
Derivation of α	53
Explanation of ot_{cor}	54
Explanation of $E_{M-O(4)}$	54
APPENDIX II: TABLES 1-4.....	55
Table 1a. Structural details of trioctahedral true micas-1M, space group $C2/m$	55
Table 1b. Structural details of trioctahedral true micas-1M, space group $C2$	70
Table 1c. Structural details of trioctahedral true micas-2M ₁ , space group $C2/c$	72
Table 1d. Structural details of trioctahedral true micas-2M ₁ , space groups Cc , $C1$	74
Table 1e. Structural details of trioctahedral true micas-2M ₂ , space group $C2/c$	74
Table 1f. Structural details of trioctahedral true micas-3T, space group $P3_112$	74
Table 2a. Structural details of trioctahedral true micas-1M, Mspace groups $C2/m$ and $C2$	76
Table 2b. Structural details of trioctahedral true micas-1M, space group $C2/c$	78
Table 2c. Structural details of trioctahedral true micas-2M ₂ , space group $C2/c$	84
Table 2d. Structural details of trioctahedral true micas-3T, space group $P3_112$	84
Table 3a. Structural details of trioctahedral brittle micas.....	86
Table 3b. Structural details of dioctahedral brittle micas.....	88
Table 4. Structural details of boromuscovite-1M and -2M ₁ , calculated from the Rietveld structure refinement by Liang et al. (1995).....	88
REFERENCES.....	90

**2 Behavior of Micas at High Pressure
and High Temperature**
Pier Francesco Zanazzi, Alessandro Pavese

INTRODUCTION.....	99
Investigative techniques for the study of the thermoelastic behavior of micas.....	100
<i>P-V</i> and <i>P-V-T</i> equations of state.....	101
Diocahedral micas.....	103
Triocahedral micas.....	108
ACKNOWLEDGMENTS.....	114
REFERENCES.....	114

3 Structural Features of Micas
Giovanni Ferraris, Gabriella Ivaldi

INTRODUCTION.....	117
NOMENCLATURE AND NOTATION.....	117
MODULARITY OF MICA STRUCTURE.....	118
The mica module.....	118
CLOSEST-PACKING aspects.....	120
Closest-packing and polytypism.....	121
COMPOSITIONAL ASPECTS.....	122
SYMMETRY ASPECTS.....	124
Metric (lattice) symmetry.....	124
Structural symmetry.....	124
Symmetry and cation sites.....	125
Two kinds of mica layer: M1 and M2 layers.....	127
The interlayer configuration.....	128
Possible ordering schemes in the MDO polytypes.....	129
The phengite case.....	130
DISTORTIONS.....	130
The misfit.....	130
Geometric parameters describing distortions.....	131
Ditrigonal rotation.....	131
Other distortions.....	132
Effects of the distortions on the stacking mode.....	133
FURTHER STRUCTURAL MODIFICATION.....	135
Pressure, temperature and chemical influence.....	135
Thickness of the mica module.....	135
Ditrigonal rotation and interlayer coordination.....	137
Effective coordination number (ECoN).....	138
CONCLUSIONS.....	138
APPENDIX I: MICA STRUCTURE AND POLYSOMATIC SERIES.....	140
Layer silicates as members of modular series?.....	140
Mica modules in polysomatic series.....	140
The heterophyllosicate polysomatic series.....	140
The palysepiole polysomatic series.....	142
Conclusions.....	143
APPENDIX II: OBLIQUE TEXTURE ELECTRON DIFFRACTION (OTED).....	144
ACKNOWLEDGMENTS.....	148
REFERENCES.....	148

4 Crystallographic Basis of Polytypism and Twinning in Micas

Massimo Nespolo, Slavomil Āuroviĉ

INTRODUCTION	155
NOTATION AND DEFINITIONS.....	156
The mica layer and its constituents	157
Axial settings, indices and lattice parameters.....	158
Symbols.....	158
Symmetry and symmetry operations.....	159
THE UNIT LAYERS OF MICA	159
Alternative unit layers	160
MICA POLYTYPES AND THEIR CHARACTERIZATION.....	164
Micas as OD structures.....	164
SYMBOLIC DESCRIPTION OF MICA POLYTYPES	172
Orientational symbols.....	172
Rotational symbols	175
RETICULAR CLASSIFICATION OF POLYTYPES:.....	178
SPACE ORIENTATION AND SYMBOL DEFINITION	178
LOCAL AND GLOBAL SYMMETRY OF MICA POLYTYPES	
FROM THEIR STACKING SYMBOLS.....	180
Derivation of MDO polytypes.....	180
The symmetry analysis from a polytype symbol.....	184
RELATIONS OF HOMOMORPHY AND CLASSIFICATION OF MDO POLYTYPES	189
BASIC STRUCTURES AND POLYTYPOIDS. SIZE LIMIT FOR THE	
DEFINITION OF "POLYTYPE"	191
Abstract polytypes	192
Basic structures	193
HTREM observations and some implications	193
IDEAL SPACE-GROUP TYPES OF MICA POLYTYPES AND	
DESYMMETRIZATION OF LAYERS IN POLYTYPES	193
CHOICE OF THE AXIAL SETTING.....	204
GEOMETRICAL CLASSIFICATION OF RECIPROCAL LATTICE ROWS.....	206
SUPERPOSITION STRUCTURES,	
FAMILY STRUCTURE AND FAMILY REFLECTIONS	209
Family structure and family reflections of mica polytypes.....	212
REFLECTION CONDITIONS.....	213
NON-FAMILY REFLECTIONS AND ORTHOGONAL PLANES	214
HIDDEN SYMMETRY OF THE MICAS: THE RHOMBOHEDRAL LATTICE	216
TWINNING OF MICAS: THEORY	217
Choice of the twin elements	219
Effect of twinning by selective merohedry on the diffraction pattern	220
Diffraction patterns from twins	223
Allotwinning.....	224
Tessellation of the <i>hp</i> lattice.....	224
Plesiotwinning	230
TWINNING OF MICAS. ANALYSIS OF THE GEOMETRY OF	
THE DIFFRACTION PATTERN.....	233
Symbolic description of orientation of twinned mica individuals. Limiting symmetry.....	235
Derivation of twin diffraction patterns.....	237
Derivation of allotwin diffraction patterns	243
IDENTIFICATION OF MDO POLYTYPES FROM THEIR DIFFRACTION PATTERNS.....	244
Theoretical background.....	244
Identification procedure.....	245
IDENTIFICATION OF NON-MDO POLYTYPES:	
THE PERIODIC INTENSITY DISTRIBUTION FUNCTION.....	247
PID in terms of TS unit layers.....	249
Derivation of PID from the diffraction pattern.....	251

EXPERIMENTAL INVESTIGATION OF MICA SINGLE CRYSTALS FOR TWIN / POLYTYPE IDENTIFICATION	252
Morphological study	252
Surface microtopography	252
Two-dimensional XRD study	254
Diffractometer study	256
APPLICATIONS AND EXAMPLES	257
24-layer subfamily: A <i>Series 1 Class b</i> biotite from Ambulawa, Ceylon	257
8A ₂ (subfamily A <i>Series 0 Class a</i>) oxybiotite from Ruiz Peak, New Mexico	258
1M-2M ₁ oxybiotite allotwin $Z_T = \frac{3}{4}$ from Ruiz Peak, New Mexico	262
{3,6}[7{3,6}] biotite plesiotwin from Sambagawa, Japan	262
APPENDIX A. TWINNING: DEFINITION AND CLASSIFICATION	267
APPENDIX B. COMPUTATION OF THE PID FROM A STACKING SEQUENCE CANDIDATE	270
Symmetry of the PID	271
ACKNOWLEDGMENTS	272
REFERENCES	272

5 Investigations of Micras Using Advanced Transmission Electron Microscopy

Toshihiro Kogure

INTRODUCTION	281
TEMS AND RELATED TECHNIQUES FOR THE INVESTIGATION OF MICA	281
Transmission electron microscopy	281
New recording media for beam-sensitive specimens	286
Sample preparation techniques	287
Image processing and simulation	288
ANALYSES OF POLYTYPES	289
DEFECT STRUCTURES	299
CONCLUSION	310
ACKNOWLEDGMENTS	310
REFERENCES	310

6 Optical and Mössbauer Spectroscopy of Iron in Micras

M. Darby Dyar

INTRODUCTION	313
OPTICAL SPECTROSCOPY	315
Current instrumentation	315
Review of existing work	316
Summary	320
MÖSSBAUER SPECTROSCOPY (MS)	320
Current instrumentation	320
Recoil-free fraction effects	320
Thickness effects	321
Texture effects and other sources of error	322
Techniques for fitting Mössbauer spectra	323
Review of existing Mössbauer data	325
Summary	333
COMPARISON OF TECHNIQUES	334
CONCLUSIONS	336
ACKNOWLEDGMENTS	337
APPENDIX: Other techniques for measurement of Fe ³⁺ /ΣFe in Micras	337
X-ray ray photoelectron spectroscopy (XPS)	337
Electron energy-loss spectroscopy (EELS)	338
X-Ray absorption spectroscopy (XAS)	338
REFERENCES	340

INTRODUCTION.....	351
LATTICE VIBRATIONS.....	352
Far-IR region.....	352
Mid-IR region.....	353
OH STRETCHING VIBRATIONS.....	359
Polarized measurements.....	359
Quantitative water determination.....	360
Hydrogen bonding.....	360
Cation ordering.....	362
OH-F replacement.....	365
Dehydroxylation mechanisms.....	366
Excess hydroxyl.....	367
NH ₄ groups.....	367
ACKNOWLEDGMENTS.....	367
REFERENCES.....	367

8 X-Ray Absorption Spectroscopy of the Micas

Annibale Mottana, Augusto Marcelli,
Giannantonio Cibin, and M. Darby Dyar

INTRODUCTION.....	371
OVERVIEW OF THE XAS METHOD.....	373
EXAFS.....	375
XANES.....	376
Experimental spectra recording.....	384
Optimization of spectra.....	387
Systematics.....	395
ACKNOWLEDGMENTS.....	404
REFERENCES.....	405

9 Constraints on Studies of Metamorphic K-Na White Micas

Charles V. Guidotti, Francesco P. Sassi

INTRODUCTION.....	413
EFFECTS OF PETROLOGIC FACTORS ON WHITE MICA CHEMISTRY.....	414
Important compositional variations.....	414
Controls of mica composition by petrologic factors.....	418
MAXIMIZING INFORMATION FROM MICA STUDIES:	
SAMPLE SELECTION CONSTRAINTS.....	423
Petrologic studies.....	424
Mineralogic studies.....	428
DISCUSSION.....	440
Common failings in petrology studies.....	440
Common failings in mineralogy studies.....	441
"Standard starting points" for the compositional variations of rock-forming dioctahedral and trioctahedral micas.....	441
ACKNOWLEDGMENTS.....	443
REFERENCES.....	444

10 **Modal Spaces for Pelitic Schists**

James B. Thompson, Jr.

INTRODUCTION.....	449
NOTATIONS AND CONVENTIONS.....	450
THE ASSEMBLAGE QUARTZ-MUSCOVITE-BIOTITE-CHLORITE-GARNET.....	451
THE ASSEMBLAGE QUARTZ-MUSCOVITE-CHLORITE- GARNET-CHLORITOID.....	454
ASSEMBLAGES CONTAINING CHLORITOID AND BIOTITE.....	455
OTHER MODAL SPACES.....	458
ACKNOWLEDGMENTS.....	458
APPENDIX: INDEPENDENT NET-TRANSFER REACTIONS.....	460
REFERENCES.....	462

11 **Phyllosilicates in Very Low-Grade Metamorphism: Transformation to Micas**

Péter Árkai

INTRODUCTION.....	463
MAIN METHODS OF STUDYING LOW-TEMPERATURE TRANSFORMATIONS OF PHYLLOSILICATES.....	464
XRD techniques.....	465
TEM techniques.....	466
MAIN TRENDS OF PHYLLOSILICATE EVOLUTION AT LOW TEMPERATURE.....	467
CURRENT PROBLEMS IN STUDYING PHYLLOSILICATE EVOLUTION AT THE LOWER CRYSTALLITE-SIZE LIMITS OF MINERALS.....	469
REACTION PROGRESS OF PHYLLOSILICATES THROUGH SERIES OF METASTABLE STAGES.....	472
CONCLUDING REMARKS.....	473
ACKNOWLEDGMENTS.....	474
REFERENCES.....	474

12 **Micas: Historical Perspective**

Curzio Cipriani

INTRODUCTION.....	479
PRESCIENTIFIC ERA.....	479
THE EIGHTEENTH CENTURY.....	480
THE NINETEENTH CENTURY.....	483
Physical properties.....	483
Crystallography.....	485
Chemical composition.....	486
THE TWENTIETH CENTURY.....	491
Crystal chemistry.....	491
Synthesis.....	494
POLYTYPES.....	494
SYSTEMATICS.....	495
CONCLUSIONS.....	496
REFERENCES.....	497
APPENDIX I	
Present-day nomenclature of the mica group and its derivation.....	498
APPENDIX II	
Other works consulted in preparation of this historical review.....	499