

AMPHIBOLES: *Crystal Chemistry, Occurrence, and Health Issues*

67 *Reviews in Mineralogy and Geochemistry* 67

TABLE OF CONTENTS

1

Amphiboles: Crystal Chemistry

Frank C. Hawthorne, Roberta Oberti

INTRODUCTION	1
CHEMICAL FORMULA	1
SOME ASPECTS OF CHEMICAL ANALYSIS.....	1
Chemical composition	1
Summary	6
CALCULATION OF THE CHEMICAL FORMULA	7
24 (O, OH, F, Cl).....	7
23 (O).....	8
13 cations.....	8
15 cations.....	8
16 cations.....	8
Summary	8
AMPHIBOLES: CRYSTAL STRUCTURE.....	8
Space groups.....	9
Cell dimensions	9
Site nomenclature	9
The $C2/m$ amphibole structure	10
The $P2/m$ amphibole structure	12
The $P2/a$ amphibole structure	12
The $Pnma$ amphibole structure.....	12
The $Pnnm$ amphibole structure.....	14
The $C\bar{1}$ amphibole structure	17
STACKING SEQUENCES AND SPACE GROUPS.....	18
BOND LENGTHS AND BOND VALENCES IN $^{[4]}Al$ -FREE AMPHIBOLES.....	19
THE DOUBLE-CHAIN OF TETRAHEDRA IN $^{[4]}Al$ AMPHIBOLES.....	19
Variation in $\langle T-O \rangle$ bondlengths in $C2/m$ amphiboles.....	21
Variation in $\langle T-O \rangle$ bondlengths in $Pnma$ amphiboles	25
THE STEREOCHEMISTRY OF THE STRIP OF OCTAHEDRA.....	27
The $C2/m$ amphiboles: variation in mean bondlengths	27
The $Pnma$ amphiboles with $B(Mg,Fe,Mn)$: variation in mean bondlengths	30

The <i>Pnma</i> amphiboles with ⁸ Li: variation in mean bondlengths	32
THE STEREOCHEMISTRY OF THE M(4) SITE.....	34
The calcic, sodic-calcic and sodic amphiboles.....	35
Amphiboles with small B cations (magnesium-iron-manganese-lithium, magnesium-sodium and lithium-sodium)	36
The <i>C2/m</i> amphiboles: variation in <M(4)-O> bondlengths	36
The <i>Pnma</i> amphiboles: variation in <M4-O> bondlengths	36
THE STEREOCHEMISTRY OF THE A SITE	37
The <i>C2/m</i> amphiboles	37
The <i>P2/a</i> amphibole	40
The <i>Pnma</i> amphiboles	40
The <i>Pnmm</i> amphiboles	41
THE STEREOCHEMISTRY OF THE O(3) SITE	41
The <i>C2/m</i> amphiboles.....	41
UNIT-CELL PARAMETERS AND COMPOSITION IN <i>C2/m</i> AMPHIBOLES	42
SUMMARY	46
ACKNOWLEDGMENTS.....	46
REFERENCES	47
APPENDIX 1: CRYSTAL-STRUCTURE REFINEMENTS OF AMPHIBOLE	51

2

Classification of the Amphiboles

Frank C. Hawthorne, Roberta Oberti

INTRODUCTION	55
THE CURRENT CLASSIFICATION SCHEMES.....	55
HAND-SPECIMEN (FIELD) CLASSIFICATION OF AMPHIBOLES	55
AMPHIBOLE CLASSIFICATION BY CHEMICAL FORMULA	56
Prefixes	56
Adjectival modifiers	57
THE CURRENT CLASSIFICATION SCHEME (LEAKE ET AL. 1997, 2003)	57
The magnesium-iron-manganese-lithium amphiboles	58
The calcic amphiboles	58
The sodic-calcic amphiboles	58
The sodic amphiboles	62
The sodium-calcium-magnesium-iron-manganese-lithium amphiboles	62
Named amphiboles	62
SIGNIFICANT ISSUES INVOLVED IN THE CLASSIFICATION OF AMPHIBOLES....	62
The role of Fe, (OH) and Li.....	64
Root names	66
More on root names.....	66
Criteria for the recognition of distinct species	67
Prefixes	67
Synthetic amphiboles	68
THE PRINCIPAL VARIABLES USED IN THE CLASSIFICATION PROCEDURE.....	68
The T cations	69
The W anions	69

The B cations	69
The A and C cations	72
NEW SCHEMES FOR THE CLASSIFICATION OF AMPHIBOLES	73
AMPHIBOLES WITH (OH,F,Cl) DOMINANT AT W.....	73
The magnesium-iron-manganese amphiboles	73
The calcium amphiboles.....	74
The sodium-calcium amphiboles.....	77
The sodium amphiboles.....	78
The lithium amphiboles	79
The sodium-magnesium-iron-manganese amphiboles	79
AMPHIBOLES WITH O²⁻ DOMINANT AT W	80
MAJOR DIFFERENCES BETWEEN THE CURRENT CLASSIFICATION AND SCHEMES 1 AND 2	80
THE TWO SCHEMES: FOR AND AGAINST.....	82
Recognition of the sodium-calcium and lithium- (magnesium-iron-manganese) groups	82
Retention versus removal of intermediate amphibole compositions	82
SUMMARY	82
ACKNOWLEDGMENTS.....	83
REFERENCES	83
APPENDIX I: REJECTED, REDEFINED AND RENAMED END-MEMBERS	85

3

New Amphibole Compositions: Natural and Synthetic

Roberta Oberti, Giancarlo Della Ventura, Fernando Cámará

INTRODUCTION	89
NEW NATURAL-AMPHIBOLES COMPOSITIONS	89
Sadanagaites: how much ⁷ Al can occur in the amphibole structure?	90
Fluorocannilloite and joesmithite: constraints for divalent cations at the A site	95
Li in amphiboles: clinoholmquistites, leakeites and sodic-pedrizites	96
Other amphiboles with nearly equal amounts of large (Na, Ca) and small (Li, Mg, Mn, Fe) B cations: composition and symmetry	101
Anhydrous sodic amphiboles: ungarettiite, obertiite, dellaventuraite	102
NEW COMPOSITIONS FOR SYNTHETIC AMPHIBOLES.....	104
Synthetic amphiboles with cations other than Si and Al at the T sites.....	104
Synthetic amphiboles with uncommon C cations	110
Synthetic amphiboles with uncommon B cations	112
Synthetic amphiboles with uncommon A cations	114
Common and uncommon W anions	116
Synthesis of amphiboles in the system Na ₂ O-Li ₂ O-MgO-SiO ₂ -H ₂ O-HF (LNMSH)	116
CONCLUDING REMARKS.....	117
ACKNOWLEDGMENTS.....	117
REFERENCES	117

4

Long-Range Order in Amphiboles

*Roberta Oberti, Frank C. Hawthorne,
Elio Cannillo, Fernando Cámará*

INTRODUCTION	125
METHODS OF DERIVING SITE POPULATIONS	125
Single-crystal Structure REFinement	125
Mössbauer spectroscopy	129
Infrared spectroscopy	131
Other spectroscopic methods	134
SITE PREFERENCES OF THE MOST COMMON CATIONS	134
Aluminum	134
Beryllium	140
Boron	141
Calcium	141
Cobalt and nickel	141
Chromium, vanadium, scandium and indium	141
Gallium	142
Germanium	143
Ferrous iron	143
Ferric iron	146
Lithium	148
Magnesium	151
Manganese	151
Potassium	152
Sodium	152
Strontium	152
Titanium	152
Zinc	154
Zirconium	154
ANION INCORPORATION IN AMPHIBOLES	155
Chlorine	155
Fluorine	156
Hydrogen (as OH ⁻)	157
THE OXO COMPONENT: A DETAILED DISCUSSION	157
HYDROGEN IN EXCESS OF 2.0 APFU	162
FACTORS AFFECTING ORDERING OF CATIONS IN THE AMPHIBOLE STRUCTURE	163
ACKNOWLEDGMENTS	164
REFERENCES	164

5**Short-Range Order in Amphiboles***Frank C. Hawthorne, Giancarlo Della Ventura*

INTRODUCTION	173
LONG-RANGE ORDER	173
SHORT-RANGE ORDER	173
BOND-VALENCE ASPECTS OF SRO	175
SRO of heterovalent versus homovalent cations and anions	176
(OH) AS A PROBE OF LOCAL ORDER IN AMPHIBOLE	176
Mg-Fe ²⁺ order-disorder over <i>M</i> (1) and <i>M</i> (3) and its effect on the infrared spectrum	177
M ²⁺ -M ³⁺ order-disorder over <i>M</i> (1) and <i>M</i> (3) and its effect on the infrared spectrum	177
NEXT-NEAREST NEIGHBOR EFFECTS: SRO OF HETEROVALENT-CATIONS IN TREMOLITE	178
Infrared absorption in related amphiboles	179
The effect of next-nearest-neighbor (NNN) cations	180
Derivation of patterns of SRO	181
SRO of heterovalent cations in tremolite(56): application of bond-valence theory ..	181
NEAREST- AND NEXT-NEAREST-NEIGHBOR EFFECTS	182
Nearest-neighbor sites: configuration symbols and atom arrangements	182
NNN sites: the <i>T</i> sites	183
NNN sites: the <i>M</i> sites	183
The number of possible short-range arrangements of cations	184
SHORT-RANGE ORDER AND SHORT-RANGE DISORDER	184
SPECTRAL VARIATION IN THE INFRARED SPECTRA OF AMPHIBOLES	185
Peak width and band width	185
Band position (energy) as a function of composition	185
Resolution in infrared spectra	186
SHORT-RANGE DISORDER OF DIVALENT B CATIONS IN TREMOLITE	187
The infrared spectrum of synthetic tremolite	188
SRO IN RICHTERITE-PARGASITE SOLID-SOLUTIONS	190
The number of stable arrangements	190
Band assignment	191
SRO IN TREMOLITE-MAGNESIOHORNBLEDE SOLID-SOLUTIONS	192
SRO IN PARVO-MANGANO-EDENITE	197
SHORT-RANGE ORDER-DISORDER OF (OH) AND F IN AMPHIBOLES	198
One-mode and two-mode behavior	199
The stereochemistry of local coupling within the amphibole structure	200
Local arrangements in (OH,F)-bearing amphibole solid-solutions	201
Testing for SRO of (OH) and F in richterite	201
Testing for SRO of (OH) and F in pargasite	203
SHORT-RANGE DISORDER OF Ti ⁴⁺ AND Si	204
Band assignment	205
Local stereochemistry	205
SHORT-RANGE ORDER OF Ti ⁴⁺ AND O ²⁻	205
SHORT-RANGE ORDER OF CATIONS AROUND THE A SITE	207
C2/m amphiboles	207

Amphiboles – Table of Contents

The effects of variation in ^T (Al,Si) and ^C (M ²⁺ , M ³⁺)	210
The effects of variation in ^{O(3)} (OH,F).....	211
The relative stability of local arrangements	213
Assignment of local arrangements in structures.....	213
SUMMARY	216
ACKNOWLEDGMENTS.....	217
REFERENCES	217
APPENDIX I: (Mg,Fe ²⁺) ORDER-DISORDER AND BAND INTENSITIES IN THE IR SPECTRUM	222

6

Non-Ambient *in situ* Studies of Amphiboles

*Mark D. Welch, Fernando Cámara
Giancarlo Della Ventura, Gianluca Iezzi*

INTRODUCTION	223
TRANSITIONAL BEHAVIOR	224
The nature of the $P_{2_1}/m \leftrightarrow HT\text{-}C2/m$ transition in amphiboles	224
Application of the Landau Theory of phase transitions	226
Spectroscopy of structural phase transitions in amphibole:	
introductory comments.....	231
(Mg,Fe) cummingtonite: high- <i>T</i> studies.....	232
(Mg,Fe) cummingtonite: high- <i>P</i> studies of the $HT\text{-}C2/m \rightarrow P_{2_1}/m$ transition	232
Mn-Mg cummingtonite	238
$P_{2_1}/m \leftrightarrow HT\text{-}C2/m$ transition in synthetic amphiboles	239
Overall compositional trends and the $P_{2_1}/m \leftrightarrow HT\text{-}C2/m$ transition	243
Comparisons with the $P_{2_1}/c \leftrightarrow C2/c$ transitions in pyroxenes.....	243
A possible high-pressure $P_{2_1}/m \leftrightarrow "HP\text{-}C2/m"$ transition in amphibole:	
synthetic ^A Na ^B (NaMg) ^C Mg ₅ ^T Si ₈ O ₂₂ ^W (OH) ₂ and	
^A Na ^B (LiMg) ^C Mg ₅ ^T Si ₈ O ₂₂ ^W (OH) ₂	246
Other transitional behavior	247
IN SITU HIGH-TEMPERATURE STUDIES OF CATION ORDER-DISORDER	249
<i>In situ</i> high- <i>T</i> neutron diffraction studies of amphiboles	249
Mg-Mn and Fe-Mn ordering in mangan-manganocummingtonite and manganogruterite	249
^C (Ni-Mg) disorder in K-richterite	252
AMPHIBOLE COMPRESSIBILITIES	252
THERMAL EXPANSIVITIES	257
IDEAS FOR FUTURE STUDIES AND DIRECTIONS.....	257
REFERENCES	258

7 The Synthesis and Stability of Some End-Member Amphiboles

Bernard W. Evans

INTRODUCTION	261
TREMOLITE $\square \text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	262
FERRO-ACTINOLITE $\square \text{Ca}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	266
ANTHOPHYLLITE $\square \text{Mg}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	269
GRUNERITE $\square \text{Fe}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	271
GLAUCOPHANE $\square \text{Na}_2(\text{Mg}_3\text{Al}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$	271
RIEBECKITE-ARFVEDSONITE $\square \text{Na}_2(\text{Fe}^{2+}_3\text{Fe}^{3+}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2 - \text{NaNa}_2(\text{Fe}^{2+}_4\text{Fe}^{3+})\text{Si}_8\text{O}_{22}(\text{OH})_2$	272
MAGNESIORIEBECKITE-MAGNESIO-ARFVEDSONITE $\square \text{Na}_2(\text{Mg}_3\text{Fe}^{3+}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2 - \text{NaNa}_2(\text{Mg}_4\text{Fe}^{3+})\text{Si}_8\text{O}_{22}(\text{OH})_2$	278
RICHTERITE $\text{Na}(\text{CaNa})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	279
PARGASITE $\text{NaCa}_2(\text{Mg}_4\text{Al})\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$	280
TSCHERMAKITE $\square \text{Ca}_2(\text{Mg}_3\text{Al}_2)\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$	280
GENERAL CONCLUSIONS	281
ACKNOWLEDGMENTS	282
REFERENCES	282

8 The Significance of the Reaction Path in Synthesizing Single-Phase Amphibole of Defined Composition

Walter V. Maresch, Michael Czank

INTRODUCTION	287
INHERENT PROBLEMS ASSOCIATED WITH THE EXPERIMENTAL METHOD	289
POLYSOMATIC REACTION PATHS	289
Defect structures as a proxy for the reaction path	289
End-member synthetic tremolite	295
Amphibole solid solutions radiating from synthetic end-member tremolite	302
Synthetic amphiboles in the system $\text{MgO}-\text{FeO}-\text{MnO}-\text{SiO}_2-\text{H}_2\text{O}$	304
Is there a recipe?	312
AMPHIBOLE SOLID SOLUTIONS RADIATING FROM SYNTHETIC AMPHIBOLES IN THE SYSTEM $\text{MgO}-\text{FeO}-\text{MnO}-\text{SiO}_2-\text{H}_2\text{O}$	313
THE FLUID PHASE AND THE REACTION PATH	314
Synthesis with dissolved chlorides in the coexisting fluid	314
Synthesis with a saturated aqueous fluid	317
CONCLUSIONS	319
ACKNOWLEDGMENTS	319
REFERENCES	319

9

Amphiboles in the Igneous Environment

Robert F. Martin

INTRODUCTION	323
AMPHIBOLES IN IGNEOUS ROCKS ASSOCIATED WITH EXTENSION	
IN THE CRUST	324
Pargasite - hawaiitic magma as a pseudo-binary system?	324
The importance of pargasite in the fertilization of the upper mantle	325
The importance of pargasite in the generation of alkaline basic magma	327
basic magma in the mantle	327
The oxidation state of iron in mantle-derived amphiboles	329
in nodules and megacrysts	329
Amphibole minerals in derivatives of alkaline basic magmas	330
Amphiboles in juxtaposed SiO ₂ -undersaturated and SiO ₂ -oversaturated derivatives	335
Amphiboles in SiO ₂ -oversaturated anorogenic suites	335
THE AMPHIBOLE MINERALOGY OF OTHER MANTLE-DERIVED ROCKS	337
Amphiboles in kimberlites and lamproites	337
Amphiboles in carbonatites and associated metasomatic rocks	339
The amphibole mineralogy of “anatectic pseudocarbonatites”	341
AMPHIBOLES IN IGNEOUS ROCKS ASSOCIATED WITH COMPRESSION IN THE CRUST	
The amphibole mineralogy of arc-related rocks	343
Amphibole-rich clots in calc-alkaline granitic rocks	346
The question of appinites	348
Amphibole-dominant pegmatites in Alaskan-Uralian-type complexes	348
The occurrence of two-amphibole pairs	349
Metasomatic phenomena	351
AMPHIBOLE IN METEORITES	352
CONCLUDING STATEMENT	353
ACKNOWLEDGMENTS	353
REFERENCES	353

10

Metamorphic Amphiboles: Composition and Coexistence

John C. Schumacher

INTRODUCTION	359
CHEMICAL SUBSTITUTION IN METAMORPHIC AMPHIBOLES	
The amphibole formula	360
Formula basis and estimates of Fe ³⁺	361
Amphibole composition space used here	361
COMPOSITIONS OF METAMORPHIC AMPHIBOLES	364
Amphibole data	364
Edenite, tschermakite and glaucophane component vectors,	364

and X_{Mg} and X_{Ca} in calcic, sodic-calcic and sodic amphiboles.....	366
Edenite, tschermakite and glaucophane component vectors, and X_{Mg} and X_{Ca} in (Mg, Fe, Mn) amphiboles	370
Variations in Mg/(Mg + Fe ²⁺)	375
Compositional variations in Mg, Fe ²⁺ , Mn ²⁺ and total R ²⁺	375
Compositional variations at the A-site.....	381
COEXISTING METAMORPHIC AMPHIBOLES	384
Assemblages with multiple amphiboles	384
Evaluating equilibrium coexistence.....	384
The basic crystal chemistry of equilibrium coexistence.....	387
Cummingtonite-hornblende.....	389
Orthoamphibole-hornblende.....	393
Orthoamphibole-cummingtonite	396
Coexisting orthoamphiboles	396
Coexisting calcic amphiboles	398
Coexistence involving sodic and sodic-calcic amphiboles	400
Coexistence of three or more amphiboles	400
FINAL REMARKS.....	402
ACKNOWLEDGMENTS.....	403
REFERENCES	403
SOURCES OF AMPHIBOLE ANALYSES	406
APPENDIX I	413
Recalculating amphibole formulae from electron microprobe analyses	413

11

Trace-Element Partitioning Between Amphibole and Silicate Melt

*Massimo Tiepolo, Roberta Oberti, Alberto Zanetti
Riccardo Vannucci, Stephen F. Foley*

INTRODUCTION	417
PARTITION COEFFICIENTS	420
FACTORS AFFECTING SOLID/LIQUID PARTITION COEFFICIENTS	421
^{AMPH/L}D FOR THE LIGHT LITHOPHILE ELEMENTS (LLE)	422
Source of data	422
Overall values	422
Site preference	423
Factors affecting ^{Amph/L} D _{LLE}	423
^{AMPH/L}D FOR ALKALINE AND ALKALINE-EARTH LARGE ION LITHOPHILE ELEMENTS (LILE)	425
Source of data	425
Overall values	425
Site preference	425
Factors affecting ^{Amph/L} D _{LILE}	425
^{AMPH/L}D FOR RARE EARTH ELEMENTS (REE) AND Y	428
Source of data	428

Amphiboles – Table of Contents

Overall values	428
Site preference	428
Factors affecting $\text{Amph/LD}_{\text{REE}}$	432
AMPH/LD FOR HIGH FIELD STRENGTH ELEMENTS (HFSE).....	435
Source of data	435
Overall values	435
Site preference	438
Factors affecting $\text{Amph/LD}_{\text{HFSE}}$	439
AMPH/LD FOR ACTINIDES AND Pb.....	441
Source of data	441
Overall values	441
Site preference	442
Factors affecting $\text{Amph/LD}_{\text{U,Th,Pb}}$	442
AMPH/LD FOR TRANSITION METALS (Cr, V AND Sc).....	443
Source of data	443
Overall values	444
Site preference	444
Factors affecting $\text{Amph/LD}_{\text{Cr,V,Sc}}$	444
DIFFERENCES TO THE PARTITIONING BEHAVIOR OBSERVED IN POTASSIC-RICHTERITES	445
ON THE CORRECT CHOICE OF AMPH/LD	448
ACKNOWLEDGMENTS.....	449
REFERENCES	449

12

Amphiboles: Environmental and Health Concerns

Mickey E. Gunter, Elena Belluso, Annibale Mottana

INTRODUCTION	453
NOMENCLATURE AND BACKGROUND INFORMATION	454
Mineralogical.....	454
Medical	457
ANALYTICAL METHODS	460
Microscopic methods.....	460
DIFFRACTION METHODS	464
Chemical determination.....	466
MORPHOLOGY MATTERS	469
REGULATORY AND LEGAL ISSUES	472
Regulated mineral species.....	473
GEOLOGICAL OCCURRENCE	475
Association with rock type	475
Association with other fibrous minerals	477
Amphiboles in soils and unconsolidated material	478
OCCUPATIONAL VS. NONOCCUPATIONAL EXPOSURE	479
CURRENT EXAMPLES OF AMPHIBOLE EXPOSURE	483
Libby, Montana, USA.....	483
El Dorado Hills, California, USA.....	486

Biancavilla, Sicily, Italy.....	492
AMPHIBOLES IN BIOLOGICAL MATERIALS AND ASSOCIATED	
BIO-MARKERS	494
Amphibole in human lungs	495
Biomarkers	499
Amphiboles in animal lungs.....	501
Amphiboles in human urine	503
Conclusion for humans and animals.....	504
STABILITY OF AMPHIBOLES.....	504
Temperature conversions	505
In the lung.....	506
FUTURE AREAS OF RESEARCH.....	507
SUMMARY	508
ACKNOWLEDGMENTS.....	508
REFERENCES	509

13

Amphiboles: Historical Perspective

Curzio Cipriani

INTRODUCTION	517
ANTIQUITY.....	518
THE EIGHTEENTH CENTURY.....	518
THE NINETEENTH CENTURY.....	521
THE TWENTIETH CENTURY	535
PROBLEM OF WATER.....	541
NOMENCLATURE.....	542
CONCLUSIONS.....	544
REFERENCES	544