NATURAL ZEOLITES: OCCURRENCE, PROPERTIES, APPLICATIONS

Editors:

DAVID L. BISH
LOS ALAMOS NATIONAL LABORATORY
LOS ALAMOS, NEW MEXICO

DOUGLAS W. MING
NASA JOHNSON SPACE CENTER
HOUSTON, TEXAS

COVER: Representation of the crystal structure of heulandite viewed down the c-axis, with b vertical. Ten-membered and eight-membered tetrahedral rings form channels parallel to c. In the channels,
- small green spheres represent Na atoms,
- larger light-blue spheres represent K atoms,
- small yellow spheres represent Ca atoms,
- large blue spheres represent H₂O molecules.
[Figure courtesy of M.E. Gunter; cf. Fig. 16, p. 41, this volume.]

Series Editor for MSA: Paul H. Ribbe
Virginia Polytechnic Institute & State University
Blacksburg, Virginia

MINERALOGICAL SOCIETY OF AMERICA
# Reviews in Mineralogy and Geochemistry

## Volume 45

**NATURAL ZEOLITES: OCCURRENCE, PROPERTIES, APPLICATIONS**

### Table of Contents

1. Crystal Structures of Natural Zeolites  
   T. Armbruster, M. F. Gunter

**INTRODUCTION**

- General aspects .......................................................... 1
- Extended definition of a zeolite mineral .......................... 4
- Classification ............................................................ 5

**ZEOLITES WITH T(4)O_10 UNITS: THE PIRIFORM ZEOLITES**

- Natrolite group (NAT): natrolite, scolecite, mesolite, gonnardite, paranatrolite .................................................. 10
- Thomsonite (THO) and edingtonite (EDI) frameworks ............. 13

**ZEOLITES WITH CHAINS OF CORNER-SHARING FOUR-MEMBERED RINGS INCLUDING THOSE WITH FINITE UNITS OF EDGE-SHARING FOUR-MEMBERED RINGS AND RELATED STRUCTURES**

- Analcime, wairakite, pollicite, leucite, ammonioleucite, hsianghualite (ANA) ......................................................... 15
- Laumontite (LAU) .......................................................... 18
- Yugawaralite (YUG), Goosecreekite (GOO) .......................... 19
- Montesommaite (MON) .................................................... 20
- Roggianite (-RON) ......................................................... 21
- Partheite (-PAR) .......................................................... 21

**ZEOLITES WITH CHAINS OF EDGE-SHARING FOUR-MEMBERED RINGS**

- Gismondine, garsonite, amicite, gobbinsite (GIS) ................. 22
- Phillipsite (PHI) and merlinoite (MER) frameworks ............... 24
- Mazzite (MAZ) and perlialite (LTL) ................................ 25
- Baggosite (BOG) ........................................................... 27
- Paulingite (PAU) ........................................................... 27

**ZEOLITES WITH SIX-MEMBERED RINGS**

- Gmelinite (GME) .......................................................... 28
- Chabazite and willhendersonite (CHA) ................................ 28
- Levyne (LEV) ............................................................. 31
- Erionite (ERI) ............................................................. 31
- Bellbergite (BEB) ......................................................... 32
- Offretite (OFF) ............................................................ 32
- Faujasite (FAU) ............................................................ 32
- Pahasapaite (RHO) ....................................................... 34

**ZEOLITES OF THE MORDENITE GROUP**

- Heulandite and clinoptilolite (HEU) ................................ 39
- Stilbite, stellerite, barrerite (STI) .................................. 42
- Brewsterite (BRE) ......................................................... 44

**OTHER RARE OR STRUCTURALLY POORLY DEFINED ZEOLITES**

**APPENDIX IINDEX — TABLE I**

**REFERENCES** ............................................................. 57
The Crystal Chemistry of Zeolites
E. Passaglia, R. A. Sheppard

INTRODUCTION

Definition of zeolite
Classification
Chemistry
Symmetry and unit-cell parameters
Occurrence

DETAILED CRYSTAL CHEMISTRY

Structure Type: ANA

Analcime: Na₄[Al₆Si₁₄O₄₆]·16H₂O
Wairakite: Ca₆[Al₆Si₁₄O₄₆]·16H₂O

Structure Type: BAI

Tscherenpotite: Ca[Al₆Si₁₄O₄₆]·8H₂O
Bikitaite: Li₄[Al₆Si₁₄O₄₆]·2H₂O
Boggsite: Ca₆(Na,K)[Al₆Si₁₄O₄₆]·7H₂O

Structure Type: BRE

Brewsterite: (Sr,Ba)₄[Al₆Si₁₄O₄₆]·18H₂O

Structure Type: CHA

Chabazite: (Ca,K₄,Na₃[Al₆Si₁₄O₄₆]·12H₂O
Willhendersonite: Ca₄(Ca₃,K₄)[Al₆Si₁₄O₄₆]·10H₂O

Structure Type: DAC

Dachniardite: Ca₆(Na,K₄)[Al₆Si₁₄O₄₆]·18H₂O

Structure Type: EAI

Bellbergite: Ca₆(Sr,Ba)₄[Al₆Si₁₄O₄₆]·30H₂O

Structure Type: EPI

Epistilbite: Ca₄[Al₆Si₁₄O₄₆]·16H₂O

Structure Type: GME

Gmelinite: (Na,K,Mg₃,Na₄)[Al₆Si₁₄O₄₆]·22H₂O

Structure Type: GRI

Grismondite: Ca₆[Al₆Si₁₄O₄₆]·16H₂O
Garvontite: Ca₄Na₄[Al₆Si₁₄O₄₆]·13H₂O
Gobбинsite: Na₄Ca₄[Al₆Si₁₄O₄₆]·11H₂O
Amicite: Na₄K₄[Al₆Si₁₄O₄₆]·10H₂O

Structure Type: GME

Gmelinite: (Na,K,Mg₃,Na₄)[Al₆Si₁₄O₄₆]·22H₂O

Structure Type: GOO

Goosecrealkite: Ca₆[Al₆Si₁₄O₄₆]·10H₂O

Structure Type: HEU

Heulandite-Chimolite: (Na,K,Ca₄)[Al₆Si₁₄O₄₆]·22H₂O

Structure Type: LAU

Laumontite: Ca₆[Al₆Si₁₄O₄₆]·18-14H₂O

Structure Type: LEV

Levynite: (Ca₆Na₄)[Al₆Si₁₄O₄₆]·18H₂O

Structure Type: LOV

Lovdarite: Na₄K₄[B₁₂Al₆Si₁₄O₄₆]·20H₂O

Structure Type: LTL

Perfildite: K₆[Na₄Ca₄Mg₃Sr]Al₆Si₁₄O₄₆·16H₂O

Structure Type: MAZ
<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Chemical Formula</th>
<th>Structure Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mazzite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Mg₂,K₂Ca₁₅[Al₉Si₂₆O₆₉]·3₀H₂O              | MER            |
| Merlinoite              | K₂Ca₆Na[Al₁₀Si₅O₆]·2₂H₂O                  | MFI            |
| Mutinaite               | Na₃Ca₁₅[Al₁₀Si₂₆O₆₉]·6₉H₂O                | MON            |
| Montesommaite           | K₁₆[Al₇Si₅O₆]·1₀H₂O                      | MOR            |
| Maricopaite             | Pb₆[Ca₃Al₉Si₂₆(OH)₆]·₉(H₂O,OH)            | NAT            |
| Monticellite            | K₃Ca₂Na₆[Al₁₈Si₁₄O₆₃]·₂₈H₂O                | MON            |
| Mordenite               | Na₃Ca₉[Al₁₈Si₂₆O₆₉]·₂₈H₂O                  | MOR            |
| Maricopaite             | Pb₆[Ca₃Al₉Si₂₆(OH)₆]·₉(H₂O,OH)            | NAT            |
| Sciolite                | Ca₃[Al₁₈Si₂₆O₆₉]·₉₉H₂O                     | MFI            |
| Harkerite               | Ca₆[Al₁₈Si₂₆O₆]·₉₉H₂O                     | MFI            |
| Harmondite              | Ca₃[Al₁₈Si₂₆O₆]·₉₉H₂O                     | MFI            |
| Maricopaite             | Pb₆[Ca₃Al₉Si₂₆(OH)₆]·₉(H₂O,OH)            | NAT            |
| Stilbite                | Na₃Ca₂[Al₉Si₂₆O₆₉]·₃₀H₂O                   | TER            |
| Thomsonite              | Ca₆Na₃Al₁₈Si₂₆O₆₉·₈₉H₂O                   | YUG            |
| Thomasonite             | Ca₆Na₃Al₁₈Si₂₆O₆₉·₈₉H₂O                   | YUG            |
| Cowlesite               | Ca₆[Na₅K]Al₁₈Si₂₆O₆₉·₈₉H₂O                 | MOR            |
| Tschörnitzerite         | Ca₆Cu₄Sr[OH]₆Al₁₈Si₂₆O₆₉·₁₄H₂O             | S'T'I           |

**REFERENCES**

3 Geochemical Stability of Natural Zeolites
S. J. Chipera, J. A. Apps

INTRODUCTION

SOLUBILITY OF GLASS PRECURSORS

THERMODYNAMIC APPROACH TO EVALUATING

ZEOLITE STABILITY RELATIONS

Derivation of thermodynamic functions and databases

Estimation of thermodynamic data for zeolites

Thermodynamic stability calculations

CALCULATION OF ZEOLITE STABILITY FIELDS FOR VARIOUS GEOCHEMICAL ENVIRONMENTS

vii
6 Occurrence of Zeolites in Sedimentary Rocks: An Overview
R. L. Hay, R. A. Sheppard

INTRODUCTION
ZEOLITE MINERALOGY
ORIGIN OF NATURAL ZEOLITES
Zeolite-forming reactions
Role of water chemistry
Role of temperature
Role of pressure
Reaction rates
TYPES OF ZEOLITE OCCURRENCE
ZEOLITES IN DEPOSITS OF SALINE, ALKALINE LAKES
ZEOLITES IN SOILS AND SURFACE DEPOSITS
ZEOLITES IN DEEP-SEA SEDIMENTS
Distribution
Origin of zeolites
ZEOLITES IN LOW-TEMPERATURE, OPEN TO CLOSED TEPHRA SYSTEMS
Hydrogeology of tephra alteration
Open-system tephra alteration
Closed-system tephra alteration
BURIAL DIAGENESIS
HYDROTHERMAL ALTERATION
ZEOLITES IN LAVA FLOWS AND IGNEOUS ROCKS
FUTURE RESEARCH
ACKNOWLEDGMENTS
REFERENCES

7 Zeolites in Closed Hydrologic Systems
A. Langella, P. Cappelletti, M. de' Gennaro

INTRODUCTION
GEOLOGICAL SETTINGS OF SALINE, ALKALINE LAKES
Zeolite-bearing deposits of saline alkaline lakes
Chemical data
Questionable zeolitization systems
SOME GENERAL REMARKS
FINAL REMARKS AND CONCLUSIONS
ACKNOWLEDGMENTS
REFERENCES

8 Formation of Zeolites in Open Hydrologic Systems
R. A. Sheppard, R. L. Hay

INTRODUCTION
EXAMPLES OF ZEOLITE FORMATION IN SILICIC TEPHRA DEPOSITS
John Day Formation, Oregon
Yucca Mountain, Nevada
Southern Desatoya Mountains, Nevada
White River sequence in Wyoming and adjacent states
ZEOLITE FORMATION IN MAFIC TEPHRA DEPOSITS
ZEOLITE FORMATION IN ALKALIC TEPHRA DEPOSITS

ix
### Zeolites in Burial Diagenesis and Low-grade Metamorphic Rocks

**M. Utada**

**INTRODUCTION**

**TYPES OF ZEOLITIZATION**

- Burial zeolitization
- Zeolitization due to the thermal effects of an intrusive mass
- Zeolitization during uplift
- Miscellaneous zeolitization during burial diagenesis

**DISTRIBUTION OF ZEOLITES IN DIFFERENT GEOLOGIC PROVINCES**

- Precambrian and Paleozoic orogenic belts
- Late Paleozoic to Mesozoic orogenic belts
- Alpine orogenic belt of Mesozoic to Cenozoic age
- Himalayan orogenic belt of Mesozoic to Cenozoic age
- Circum Western-Pacific orogenic belt of Cretaceous to Holocene age
- Cordillera orogen of Mesozoic to Quaternary age
- Other areas

**MODE OF OCCURRENCE AND MINERAL REACTION**

**GENETIC CONSIDERATIONS**

- Bore-hole temperatures
- Homogenization temperature of fluid inclusions
- Inference of temperature from isotopic data
- P-T conditions as measured by hydrothermal experimentation
- Chemistry of reacting solutions

**SUMMARY AND FUTURE PROBLEMS**

**ACKNOWLEDGMENTS**

**REFERENCES**

---

### Zeolites in Hydrothermally Altered Rocks

**M. Utada**

**INTRODUCTION**

**TYPES OF HYDROTHERMAL ALTERATION**

- Calcium-silicate type
- Sodium-calcium-silicate type
- Sodium-silicate type

**PROVINCES OF HYDROTHERMAL ZEOLITIZATION**

- Geothermal areas in volcanic arcs of orogenic belts
- Active and fossil geothermal areas in intracontinental areas

**CONDITIONS OF HYDROTHERMAL ZEOLITIZATION**

- Homogenization temperatures of fluid inclusions
- Drill-hole temperatures
- Chemistry of solutions from drill holes
- Isotopic data
- Hydrothermal experiments

**SUMMARY AND EXISTING PROBLEMS**

**REFERENCES**
Zeolites in Soil Environments
D. W. Ming, J. L. Boettinger

INTRODUCTION.................................................................................................323
OCCURRENCES IN SOIL....................................................................................323
Pedogenic zeolites in saline, alkaline soils of non-volcanic parent materials........324
Pedogenic zeolites in saline, alkaline soils of volcanic parent materials............326
Lithogenic zeolites inherited in situ from volcanic parent materials...............327
Lithogenic zeolites inherited in situ from non-volcanic parent materials..........330
Lithogenic zeolites from eolian or alluvial deposition......................................332
Zeolites in other soil environments..............................................................335
IDENTIFICATION OF ZEOLITES IN SOILS....................................................335
Separation and quantification techniques.......................................................335
Identification and characterization methods..................................................338
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDY.........................340
ACKNOWLEDGMENTS......................................................................................343
REFERENCES..................................................................................................343

Zeolites in Petroleum and Natural Gas Reservoirs
Azuma Iijima

INTRODUCTION................................................................................................347
DIAGENETIC ZEOLITES IN HYDROCARBON RESERVOIRS...............................348
Burial-diagenetic zeolites in volcanogenic reservoirs.......................................348
Zeolite zones formed by burial diagenesis of silicic tuffs in marine sequences......352
Zeolites formed by a combination of burial diagenesis and saline, alkaline pore-fluid diagenesis in marine-freshwater sequences..............................365
Closed-system analcime (saline, alkaline-lake environments) in sandstone and conglomerate reservoirs..........................................................367
Open-system zeolites in hydrocarbon reservoirs..............................................369
HYDROTHERMAL ZEOLITES IN VOLCANIC RESERVOIRS..................................370
Occurrences of hydrothermal zeolites in volcanogenic reservoirs....................370
Relation of hydrothermal zeolites to reservoir properties..................................376
LAUMONTITE IN SANDSTONE RESERVOIRS..................................................382
Formation of laumontite in reservoir sandstones............................................383
Relation of laumontite to sandstone reservoir properties...................................390
LOG EVALUATION AND ENHANCED OIL-RECOVERY OF ZEOLITE-BEARING RESERVOIR ROCKS.........................................................393
Log evaluation................................................................................................393
Zeolites and enhanced oil-recovery projects....................................................394
SUMMARY AND CONCLUSIONS....................................................................396
ACKNOWLEDGMENTS......................................................................................398
REFERENCES..................................................................................................398

Thermal Behavior of Natural Zeolites
David L. Bish and J. William Carey

INTRODUCTION................................................................................................403
VOLUMETRIC AND STRUCTURAL CHANGES ON DEHYDRATION.......................405
Terminology....................................................................................................405
Category-1 transformations............................................................................407
Category-2 transformations............................................................................411
Category-3 transformations............................................................................415
Long-term transformations.............................................................................417
Cation-Exchange Properties of Natural Zeolites
R. T. Pabalan, F. P. Bertetti

INTRODUCTION........................................ 453
THERMODYNAMICS OF ION EXCHANGE.................. 456
Ion-exchange isotherm.................................. 456
Selectivity coefficient................................. 458
Concentration-valency effect.......................... 458
Equilibrium constant, Gibbs free energy, and Van't Hoff coefficient 458
Evaluation of $K_{A,B}$, $f_A$, $f_B$, and $\Delta G^\prime_{A,B}$............. 460
Triangle rule........................................... 461
Systems that exhibit incomplete exchange........... 461
Activity coefficients of aqueous ions................ 462
Activity coefficients of zeolite components........ 464
FACTORS TO CONSIDER IN EVALUATING ION-EXCHANGE DATA...... 465
ION-EXCHANGE STUDIES ON NATURAL ZEOLITES........... 467
Chabazite [Ca$_2$(Al$_4$Si$_7$O$_{24}$)·12H$_2$O]............. 467
Clinoptylllite [Na$_2$K$_2$(Al$_6$Si$_4$O$_{18}$)·20H$_2$O]........ 472
Eriolite [Na$_2$K$_2$Mg$_2$(Al$_6$Si$_4$O$_{18}$)·23H$_2$O]........ 476
Ferriemite [Na$_2$K$_2$Mg$_2$(Al$_6$Si$_4$O$_{18}$)·20H$_2$O]....... 479
Heulandite [Na$_2$K$_2$Si$_4$O$_{12}$]·24H$_2$O.................. 483
Laumontite [Ca$_2$(Al$_4$Si$_7$O$_{24}$)·16H$_2$O]............. 483
Mordenite [Na$_2$K$_2$Al$_6$(Si$_4$O$_{18}$)·28H$_2$O]........... 484
Phillipsite [K$_2$(Al$_4$Si$_4$O$_{12}$)·12H$_2$O]............... 488
APPLICATION OF THERMODYNAMIC MODELS.............. 489
Margules model parameters............................ 492
Isotherms as functions of solution composition and concentration 498
Aqueous composition calculated from zeolite analysis........ 500
ANION EXCHANGE ON SURFACTANT-MODIFIED ZEOLITES........ 509
RECOMMENDATIONS FOR FUTURE WORK.................. 510
ACKNOWLEDGMENTS..................................... 511
REFERENCES........................................... 511
APPENDIX............................................. 517
Equations for calculating $E_A$, $E_A$, $K_{A,B}$, and associated uncertainties from experimental data...... 517
Applications of Natural Zeolites in Water and Wastewater Treatment

Denes Kalló

INTRODUCTION

PRODUCTION OF DRINKING WATER

Removal of NH₄⁺ and other ions
Ion-exchange and filtration beds
Pilot plants and full-scale plants
Regeneration of NH₄⁺-zeolite

MUNICIPAL AND AGRICULTURAL WASTEWATER TREATMENT

Removal of NH₄⁺
Zeolite bed regeneration
Zeolites as coagulating agents
Complex treatment technologies

REMOVAL OF HARMFUL METAL CATIONS FROM WATER

Cesium and strontium
Heavy metals

INDUSTRIAL WASTEWATER TREATMENT

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

REFERENCES

Use of Zeolitic Tuff in the Building Industry

C. Colella, M. de' Gennaro, R. Aiello

INTRODUCTION

HISTORICAL DEVELOPMENT OF ZEOLITIC TUFF USE IN CONSTRUCTION

Historical use of zeolitic tuff in Italy
Uses of zeolitic tuff elsewhere
ZEOITIC TUFF AS DIMENSION STONE

Lithification of zeolitic tuff
Tuff lithology
Tuff mining techniques

MECHANICAL AND PHYSICAL PROPERTIES

Thermal behavior
Decay phenomena

ZEOLITIC TUFF AS A CONSTITUENT OF LIGHTWEIGHT BUILDING MATERIALS

Tuffs as lightweight aggregates
Tuffs for manufacturing foamed or cellular materials
ADOPTION OF ZEOLITIC TUFF TO BLENDED CEMENTS

Pozzolan and pozzolanic materials
Use of zeolitized tuff in pozzolanic cements
Use of zeolitized tuff in high-alumina cements

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

ACKNOWLEDGMENTS

REFERENCES
# Natural Zeolites in Solar Energy

*Heating, Cooling, and Energy Storage*

Dimiter I. Tchernev

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>589</td>
</tr>
<tr>
<td>HISTORY</td>
<td>589</td>
</tr>
<tr>
<td>STORAGE</td>
<td>589</td>
</tr>
<tr>
<td>COOLING</td>
<td>593</td>
</tr>
<tr>
<td>Open-cycle cooling</td>
<td>593</td>
</tr>
<tr>
<td>Closed-cycle cooling</td>
<td>596</td>
</tr>
<tr>
<td>Operating principle of the intermittent zeolite cycle</td>
<td>597</td>
</tr>
<tr>
<td>ZEOLITE HEATING/COOLING SYSTEMS</td>
<td>600</td>
</tr>
<tr>
<td>Intermittent solar heating/cooling systems</td>
<td>600</td>
</tr>
<tr>
<td>Heat pumps with energy regeneration</td>
<td>601</td>
</tr>
<tr>
<td>ENERGY CONSIDERATIONS</td>
<td>605</td>
</tr>
<tr>
<td>SUGGESTED FUTURE RESEARCH</td>
<td>611</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>612</td>
</tr>
</tbody>
</table>

# Use of Natural Zeolites in Agronomy, Horticulture, and Environmental Soil Remediation

Douglas W. Ming, Earl R. Allen

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>619</td>
</tr>
<tr>
<td>BACKGROUND</td>
<td>619</td>
</tr>
<tr>
<td>SOIL CONDITIONING FOR PLANT GROWTH</td>
<td>620</td>
</tr>
<tr>
<td>Chemical properties</td>
<td>620</td>
</tr>
<tr>
<td>Physical properties</td>
<td>622</td>
</tr>
<tr>
<td>FERTILIZER-USE EFFICIENCY AND PREVENTION OF NUTRIENT LEACHING</td>
<td>623</td>
</tr>
<tr>
<td>Fertilizer-use efficiency</td>
<td>627</td>
</tr>
<tr>
<td>Reduced nutrient leaching in coarse-textured soils</td>
<td>624</td>
</tr>
<tr>
<td>SLOW-RELEASE FERTILIZATION</td>
<td>626</td>
</tr>
<tr>
<td>Fertilization by ion exchange</td>
<td>628</td>
</tr>
<tr>
<td>Fertilization by mineral dissolution and ion exchange</td>
<td>630</td>
</tr>
<tr>
<td>ZEOPONIC PLANT-GROWTH SUBSTRATES</td>
<td>636</td>
</tr>
<tr>
<td>Zeoponic definition and background</td>
<td>636</td>
</tr>
<tr>
<td>Space applications</td>
<td>638</td>
</tr>
<tr>
<td>ZEOLITES AS CARRIERS FOR HERBICIDES, INSECTICIDES AND OTHER ORGANIC COMPOUNDS</td>
<td>639</td>
</tr>
<tr>
<td>ENVIRONMENTAL SOIL REMEDIATION</td>
<td>640</td>
</tr>
<tr>
<td>Remediation of soils contaminated with radioactive nuclides</td>
<td>640</td>
</tr>
<tr>
<td>Remediation of soils contaminated with heavy metals</td>
<td>643</td>
</tr>
<tr>
<td>COMMERCIAL APPLICATIONS FOR NATURAL ZEOLITES</td>
<td>647</td>
</tr>
<tr>
<td>CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK</td>
<td>648</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>649</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>649</td>
</tr>
</tbody>
</table>