# FLUID-FLUID INTERACTIONS

65 Reviews in Mineralogy and Geochemistry 65

# TABLE OF CONTENTS

### Fluid–Fluid Interactions in the Earth's Lithosphere

Axel Liebscher, Christoph A. Heinrich

INTRODUCTION	1
GEOLOGIC ENVIRONMENTS OF TWO-PHASE FLUIDS	2
PRINCIPAL PHASE RELATIONS IN TWO-PHASE FLUID SYSTEMS	5
One-component systems	5
Binary fluid systems	5
TERMINOLOGY OF FLUID PHASES AND PROCESSES	8
Terms to describe fluid phases	8
Terms describing fluid processes involving one or two phases	9
A note on the term "supercritical"	10
COMPOSITION AND PHASE STATE OF COMMON CRUSTAL FLUIDS	
ACKNOWLEDGMENTS	12
REFERENCES	12

# 2

1

### **Experimental Studies in Model Fluid Systems**

#### Axel Liebscher

INTRODUCTION	15
DATA COMPILATION AND PRESENTATION	16
EXPERIMENTAL TECHNIQUES APPLIED TO FLUID-FLUID STUDIES	17
P-V-T-x RELATIONS IN BINARY MODEL FLUID SYSTEMS	19
H <sub>2</sub> O-non polar gas systems	19
H <sub>2</sub> O-salt systems	21
Other binary system	29
P-V-T-x RELATIONS IN TERNARY MODEL FLUID SYSTEMS	29
H <sub>2</sub> O-NaCl-CO <sub>2</sub> system	29
$H_2O-CaCl_2-CO_2$ system	
H <sub>2</sub> O-NaCl-CH <sub>4</sub>	32

Limits of immiscibility in ternary H <sub>2</sub> O-salt-non polar gas systems	
Other ternary systems	
TRACE ELEMENT AND STABLE ISOTOPE FRACTIONATION	
Trace element fractionation	
Stable isotope fractionation	
FLUID-MINERAL AND FLUID-ROCK INTERACTIONS UNDER	
TWO-FLUID PHASE CONDITIONS	
CONCLUDING REMARKS	
ACKNOWLEDGMENTS	
REFERENCES	43

## **Equations of State for Complex Fluids**

### Matthias Gottschalk

INTRODUCTION	49
PRINCIPLES	49
TYPES OF EOS	53
Ideal gas	53
Virial equation	53
Cubic EOS	54
Hard-sphere extension of the EOS	
Integrated EOS	57
MIXING AND COMBINING RULES	59
SPECIFIC EOS FOR MIXTURES APPLICABLE TO GEOLOGIC SETTINGS	61
Holloway (1976), Holloway (1981)	62
Bowers and Helgeson (1983)	62
Kerrick and Jacobs (1981), Jacobs and Kerrick (1981a,b)	63
Rimbach and Chatterjee (1987)	63
Grevel and Chatterjee (1992)	64
Grevel (1993)	64
Spycher and Reed (1988)	64
Saxena and Fei (1987, 1988)	65
Shi and Saxena (1992)	66
Belonoshko and Saxena (1992c), Belonoshko et al. (1992)	66
Duan et al. (1992c, 1996)	67
Duan et al. (1992a,b)	68
Duan and Zhang (2006)	69
Anderko and Pitzer (1993a,b), Duan et al. (1995)	69
Duan et al. (2003)	72
Jiang and Pitzer (1996), Duan et al. (2006)	72
Churakov and Gottschalk (2003a,b)	72
CALCULATION OF PHASE EQUILIBRIA	73
CONCLUSIONS	73
ACKNOWLEDGMENTS	75
REFERENCES	75

APPENDIX A	78
Derivations	78
P and T as state variables	79
V and T as state variables	
v and T as state variables	
$\rho$ and T as state variables	
U, H, and S as a function of the state variables V, P and T	88
APPENDIX B	91
Fugacity coefficients	91
Excess Helmholtz free energy <i>a</i> <sup>excess</sup>	91
Compressibility factor z	94
Derivatives of $a^{excess}$ with respect to $x_{j}$	95
Fugacity coefficients	97
Other versions and misprints of constants in parameter functions	97
• •	

## Liquid Immiscibility in Silicate Melts and Related Systems

4

Alan B. Thompson, Maarten Aerts, Alistair C. Hack

INTRODUCTION TO NATURAL IMMISCIBLE SYSTEMS
Immiscible anhydrous silicate melts and magmas 101
LIQUID IMMISCIBILITY IN SILICATE MELTS
Silicate-oxide anhydrous molten binary systems and the role of
network-forming and network-modifying cations
Factors controlling immiscibility or supercriticality in anhydrous
silicate-oxide binary molten systems
Effect of higher pressure on liquid immiscibility in anhydrous
molten silicate binaries
Simplified representations of immiscibility, miscibility and supercriticality
TERNARY AND HIGHER ANHYDROUS MOLTEN SILICATE SYSTEMS 107
The double role of Al <sub>2</sub> O <sub>3</sub> in silicate melts
Immiscibility in mineral ternary alkali-aluminosilicate melts
Summary for anhydrous silicate melt systems114
MOLTEN SILICATE-CARBONATE SYSTEMS114
ANHYDROUS MOLTEN SILICATE SYSTEMS WITH PHOSPHOROUS,
FLUORINE, CHLORINE, BORON, SULFUR118
SUPERCRITICAL OR SUPERSOLVUS MELTS IN ANHYDROUS SILICATE ROCK
SYSTEMS AT HIGHER PRESSURE?119
Simplified peridotite mantle
Simplified basaltic crust
Simplified felsic crust
CONCLUDING REMARKS122
ACKNOWLEDGMENTS122
REFERENCES

## Phase Relations Involving Hydrous Silicate Melts, Aqueous Fluids, and Minerals

Alistair C. Hack, Alan B. Thompson, Maarten Aerts

IMMISCIBILITY IN NATURAL SYSTEMS INVOLVING HYDROUS	
SILICATE MELTS	129
Supercritical H <sub>2</sub> O	130
Critical behavior systematics for H <sub>2</sub> O with added components	130
Phase separation in subsolidus and supersolidus systems	131
The general role of H <sub>2</sub> O and other volatiles in silicate melt immiscibility	131
Brief history of supercritical fluid research	132
INTRODUCTION TO FLUID PHASE RELATIONS:	
LIMITATIONS OF SOLID-WATER SYSTEMS AS IDEAL BINARIES	132
Two basic phase relation topologies of A-H <sub>2</sub> O binary systems	133
Further types of L-V phase relations	137
MINERAL-H <sub>2</sub> O SYSTEMS	139
SiO <sub>2</sub> (quartz)-H <sub>2</sub> O	140
NaAlSi <sub>3</sub> O <sub>8</sub> (albite)-H <sub>2</sub> O	143
Effect of added volatiles on critical behavior in SiO <sub>2</sub> -H <sub>2</sub> O and NaAlSi <sub>3</sub> O <sub>8</sub> -H <sub>2</sub> O	) 146
Effects of non-volatile components on critical behavior in	
NaAlSi <sub>3</sub> O <sub>8</sub> -H <sub>2</sub> O and Si $O_2$ -H <sub>2</sub> O	148
ROCK-H <sub>2</sub> O SYSTEMS	149
General A-B-H <sub>2</sub> O ternary phase relations involving L-V supercriticality	149
NaAlSiO <sub>4</sub> -SiO <sub>2</sub> -H <sub>2</sub> O (nepheline-quartz-H <sub>2</sub> O)	151
Haplogranite-water (quartz+albite+K-feldspar+H2O±anorthite)	155
Pegmatites	157
Peridotite-water: MgO-SiO <sub>2</sub> -H <sub>2</sub> O (forsterite+enstatite+quartz+H <sub>2</sub> O)	158
Eclogite-water (garnet+omphacite+coesite+kyanite+rutile+H <sub>2</sub> O)	163
FLUID PHYSICAL PROPERTIES, COMPOSITION AND P-T PATHS	166
Clapeyron slope of critical curves and fluid density	166
Cooling or decompression paths crossing critical curves	168
Viscosity of silicate-bearing aqueous fluids	168
Precipitation and dissolution on flow paths, L-V immiscibility, single-phase	
fluids and metasomatism	170
FLUID EVOLUTION IN LARGE SCALE TECTONIC PROCESSES	172
Oceanic lithosphere subduction environments	173
Supercritical fluids in the earth's mantle?	174
NATURAL SYSTEMS: WHERE ARE IMMISCIBILITY, SUPERCRITICALITY	
LIKELY TO OCCUR?	175
Natural systems	175
Extent of immiscibility and supercriticality in natural processes	176
What to do next?	176
ACKNOWLEDGMENTS	177
REFERENCES	177

## Numerical Simulation of Multiphase Fluid Flow in Hydrothermal Systems

#### Thomas Driesner, Sebastian Geiger

INTRODUCTION	187
METHODS	188
Model discretization	188
Mass conservation equations	189
Momentum conservation	189
Energy conservation equation	190
Computation of pressure changes	191
Solving the equations	191
PERMEABILITY AND THERMAL EVOLUTION OF HYDROTHERMAL	
SYSTEMS	192
Permeability, discharge, recharge and efficiency of heat transfer	193
Thermal evolution patterns above a cooling pluton	195
COMPARING FLUID INCLUSION DATA AND SIMULATION PREDICTIONS	
FLOW OF SALINE FLUIDS IN MAGMATIC-HYDROTHERMAL SYSTEMS	203
Porphyry case study	204
OUTLOOK	207
ACKNOWLEDGMENTS	210
REFERENCES	210

# 7

# Fluid Phase Separation Processes in Submarine Hydrothermal Systems

#### Dionysis I. Foustoukos, William E. Seyfried, Jr.

INTRODUCTION	213
PHASE RELATIONS IN THE NaCI-H2O SYSTEM	215
FIELD OBSERVATIONS OF PHASE SEPARATION IN SUBMARINE	
HYDROTHERMAL SYSTEMS	218
EXPERIMENTAL STUDIES OF PHASE SEPARATION IN THE	
NaCl-H <sub>2</sub> O SYSTEM	221
Empirical expressions and theoretical modeling	221
Elemental partitioning between vapor-liquid and vapor-halite	222
Stable isotope fractionation in the two-phase region of the NaCl-H <sub>2</sub> O system	225
Phase separation and mineral-fluid equilibria	228
FINAL REMARKS - NUMERICAL SIMULATIONS	232
ACKNOWLEDGMENTS	233
REFERENCES	233

## Fluids in Hydrocarbon Basins

#### Karen S. Pedersen, Peter L. Christensen

INTRODUCTION	241
PHASE DIAGRAMS	242
Pure components: methane (CH <sub>4</sub> ) and ethane ( $C_2H_6$ )	242
Multicomponent hydrocarbon fluids	243
PHYSICAL AND TRANSPORT PROPERTIES OF HYDROCARBON FLUIDS	245
PROPERTIES OF HYDROCARBON SYSTEMS EXPRESSED IN	
BLACK OIL TERMS	248
COMPOSITIONAL VARIATIONS WITH DEPTH	248
HYDROCARBON-WATER PHASE FOUL IBRIA	252
CO. SEOUESTRATION	253
REFERENCES	



## Fluid-Fluid Interactions in Geothermal Systems

## Stefán Arnórsson, Andri Stefánsson, Jón Örn Bjarnason

INTRODUCTION	
BASIC FEATURES OF GEOTHERMAL SYSTEMS	
Types of geothermal systems	
Geological structure of volcanic geothermal systems	
Temperature and pressure	
TRANSFER OF HEAT	
GEOTHERMAL FLUIDS	
Primary and secondary geothermal fluids	
Chemical composition of primary fluids	
Secondary fluids	
BOILING AND PHASE SEGREGATION	
The boiling point curve	
Effect of dissolved gases	271
Liquid-vapor separation under natural conditions	272
Vapor-dominated systems	272
Boiling and fluid phase segregation in wells and producing aquifers	273
INITIAL AND EQUILIBRIUM VAPOR FRACTIONS	278
GAS CHEMISTRY	
BOILING AND CHANGES IN MINERAL SATURATION	
Changes in fluid composition during boiling and degassing	
Mineral deposition with special reference to calcite	
MODELING OF AQUIFER FLUID COMPOSITIONS	
Boiling hot springs	
Wet-steam well discharges	
FUTURE DIRECTIONS	

LIST OF SYMBOLS	298
REFERENCES	300
APPENDIX 1 – DERIVATION OF EQUATIONS TO CALCULATE AQUIFER STEA	Μ
FRACTIONS AND FLUID COMPOSITIONS FOR WET-STEAM WELLS	306
Model 1: Isolated system	307
Model 2: Closed system; conductive heat flow to fluid	308
Model 3: Open system; liquid retained in formation	309
Model 4: Open system; liquid retained in formation; steam inflow	310
Model 5: Open system; liquid retained in formation; conductive heat	
flow to fluid	311

## Fluid Immiscibility in Volcanic Environments

#### James D. Webster, Charles W. Mandeville

INTRODUCTION	
BACKGROUND	
OBSERVATIONAL, ANALYTICAL, AND THEORETICAL EVIDENCE	
FOR MULTIPLE FLUIDS IN VOLCANIC ENVIRONMENTS	
Fluid immiscibility in model systems	
Intensive properties of fluids in volcanic environments	
Volcanic crater lakes	
Submarine volcanic environments	
Magma conduits and shallow plutonic magmas that underlie volcanoes	
Alkaline and carbonate-rich magmas	
Experimental petrology: evidence of multiple fluids coexisting with	
aluminosilicate melts	
Constraints from stable isotope geochemistry	
SYNTHESIS AND APPLICATION TO VOLCANIC PROCESSES	
Review of two fluids in volcanic environments	
Fractionation of volatile components between fluids	344
Consequences of two fluids in volcanic environments	
ACKNOWLEDGMENTS	
REFERENCES	349

# 11

## Fluid-Fluid Interactions in Magmatic-Hydrothermal Ore Formation

#### Christoph A. Heinrich

INTRODUCTION	
CHEMICAL CONSEQUENCES OF FLUID PHASE SEPARATION	
Principles of hydrothermal ore formation	

Mineral precipitation by low-pressure boiling	366
Ore-metal fractionation between vapor and hypersaline liquids	366
OROGENIC GOLD DEPOSITS: CRUSTAL-SCALE ORE SYSTEMS	370
FLUID MIXING AND ORE DEPOSITION: GRANITE-RELATED Sn-W VEINS	371
LIQUID - VAPOR EVOLUTION IN PORPHYRY - EPITHERMAL SYSTEMS	375
Geological observations	375
Fluid evolution paths in Cu-Au mineralizing systems	376
SUMMARY AND CONCLUSIONS	381
ACKNOWLEDGMENTS	382
REFERENCES	382

# **12** Fluid Immiscibility in Metamorphic Rocks

#### Wilhelm Heinrich

INTRODUCTION	389
FLUID PHASE RELATIONS	390
Binary fluid systems	390
Phase relations in the system H <sub>2</sub> O-CO <sub>2</sub> -NaCl	391
H <sub>2</sub> O-CO <sub>2</sub> -CaCl <sub>2</sub>	393
H <sub>2</sub> O-CH <sub>4</sub> -NaCl	394
PHASE RELATIONS AND FLUID EVOLUTION IN THE CaO-MgO-	
SiO2-H2O-CO2-NaCl MODEL SYSTEM	394
PHYSICAL BEHAVIOR OF IMMISCIBLE FLUIDS	403
The record of fluid inclusions in metamorphic rocks: problems with selective	
entrapment and post-entrapment modifications.	403
Fluid phase separation and two fluid flow in metamorphic rocks	406
Geophysical consequences of fluid unmixing	407
FIELD STUDIES	407
The seminal studies: marbles from Campolungo, Lepontine Alps	408
Contact metamorphism.	409
Regional and subduction-related metamorphism	419
CONCLUDING REMARKS	423
ACKNOWLEDGMENTS	424
REFERENCES	424