

Geofluids

Developments in Microthermometry, Spectroscopy, Thermodynamics, and Stable Isotopes

Combines direct methods (fluid inclusion microthermometry and spectroscopy) and indirect methods (thermodynamics, stable isotopes) within geofluid research

- Features working examples in each chapter with step-by-step explanations and calculations
- Broad range of case studies aid analytical and experimental data
- Includes appendices with equations of state, stable isotope fractionation equations, and Raman identification tables that aid in identification of fluid inclusion daughter minerals and dissolved compounds
- Authored by a team of expert scientists who have more than 60 years of related experience in the field and classroom combined

Geofluids: Developments in Microthermometry, Spectroscopy, Thermodynamics, and Stable

Isotopes is the definitive source of information on paleofluids in the Earth's crust and mantle—ideal for graduate and post-graduate students and researchers in mineral, oil, and gas exploration.

There has been rapid development in new non-destructive analytical methods and interdisciplinary research that makes it difficult to find a single source of content on the subject of geofluids. Geoscience researchers commonly use multiple tools to interpret geologic problems, particularly if the problems involve fluid-rock interaction. This book perfectly combines the techniques of fluid inclusion microthermometry, stable isotope analyses, and various types of spectroscopy, including Raman analysis, to thoroughly contribute to research. Through a practical and intuitive step-by-step approach, the authors explain sample preparation, measurements, analysis, and interpretation of data related to mineral-fluid-melt equilibria.

Vratislav Hurai, PhD has been a researcher and instructor in the geosciences with a focus on the study of fluids in all geologic environments for more than 30 years. He was a founder of the Geofluids Research Lab at Comenius University, co-sponsored by the Alexander von Humboldt Foundation. Currently he is a senior researcher of the Geological Institute at the Slovak Academy of Science in Bratislava, Slovakia.

Monika Huraiová, PhD is associate professor and current head of the Geofluids Research Lab at Comenius University in Bratislava, Slovakia. She teaches courses on magmatic petrology, optical mineralogy, and applied thermodynamics.

Marek Slobodník, PhD is associate professor at the Institute of Geological Sciences, Masaryk University, Brno, Czech Republic, where he maintains microthermometric lab and teaches courses on mineral deposits, industrial materials, and mineral-forming processes.

Rainer Thomas, DrSc has more than 45 years of experience in geoscience and material research with a focus on melt inclusions in minerals in the last 30 years spent in the Central Institute of Physics of the Earth and the GeoforschungsZentrum in Potsdam, Germany. He has more than 70 journal articles and books to his credit, and is also recognized for developing a Raman spectroscopic method for measuring trace to major amounts of water in glasses and silicate melt inclusions.



store.elsevier.com

Geochemistry

ISBN 978-0-12-803241-1



9 780128 032411

Contents

Preface	xi
List of Abbreviations	xiii
CHAPTER 1 General Characteristics of Geofluids	1
1.1 Brief History of Geofluid Observation and Research	2
1.2 Entrapment of Fluids in Minerals	5
1.3 Basic State Properties of Geofluids	10
1.3.1 Temperature	12
1.3.2 Pressure	13
1.3.3 Quantity and Concentration	13
1.3.4 Volume and Density	15
1.3.5 Viscosity	16
1.4 Changes in Fluid Inclusions	16
1.4.1 Phase Changes	16
1.4.2 Volume Changes	18
1.4.3 Compositional Changes	20
CHAPTER 2 Phase Diagrams	23
2.1 Unary Systems	23
2.2 Properties of Water	25
2.3 Aqueous Systems with Salts	31
2.3.1 H ₂ O–NaCl System	31
2.3.2 Multicomponent H ₂ O–Salt Systems	34
2.4 Aqueous Systems with Gases	35
2.4.1 H ₂ O–CO ₂ and H ₂ O–CH ₄ Systems	35
2.4.2 H ₂ O–CO ₂ –NaCl and H ₂ O–CH ₄ –NaCl Systems	42
2.5 Gas Mixtures	44
2.6 Hydrocarbons	48
2.7 Silicate Melt	51
CHAPTER 3 Equations of State	53
3.1 Behavior of Ideal Gas	53
3.2 Equations of State for Geofluids	54
PROBLEM 3.1 Calculating Pressure of a Mixed-Volatile Fluid	57
CHAPTER 4 Fluid and Melt Inclusion Microthermometry	59
4.1 Observation and Imaging	60
4.2 Sample Handling and Storage	65

4.3	Calculating Volumetric Phase Ratios.....	65
PROBLEM 4.1	Calculating Vapor Volume in Aqueous Inclusion.....	68
PROBLEM 4.2	Calculating Phase Volumes in Brine Inclusion.....	68
PROBLEM 4.3	Calculating Phase Volumes in Carbonic-aqueous Inclusion.....	68
4.4	Calculating Fluid Inclusion Volumes.....	69
4.5	Evaluating Trapping Modes of Fluid Inclusions	70
4.6	Measuring Temperatures of Phase Transitions.....	73
4.6.1	Freezing-Heating Stages	73
4.6.2	Phase Changes	74
4.6.3	Phase Transitions in a Unary System	76
4.6.4	Phase Transitions in Aqueous Inclusions.....	79
PROBLEM 4.4	Calculating Vapor-saturated Halite Liquidus	89
PROBLEM 4.5	Calculating Molar Volume of an H_2O - NaCl - CaCl_2 Inclusion	90
4.6.5	Phase Transitions in Gaseous Inclusions	91
PROBLEM 4.6	Calculating Molar Volume of a Gaseous Inclusion	100
4.6.6	Phase Transitions in H_2O - CO_2 and H_2O - CO_2 - NaCl Inclusions.....	100
4.6.7	Phase Transitions in H_2O - CH_4 and H_2O - CH_4 - NaCl Inclusions.....	106
4.6.8	Phase Transitions in Petroleum Inclusions	108
4.6.9	Phase Transitions in Melt Inclusions	110
CHAPTER 5	Interpretation of Microthermometric Data.....	117
5.1	Calculating Densities and Isochores	117
5.1.1	Aqueous Inclusions.....	118
5.1.2	Hydrocarbon Inclusions.....	121
5.1.3	Gaseous Inclusions	125
5.2	Calculating Fluid and Melt Viscosities.....	126
PROBLEM 5.1	Calculating Viscosity of Silicate Melt I	128
PROBLEM 5.2	Calculating Viscosity of Silicate Melt II.....	129
5.3	P - T Estimates	130
5.3.1	Homogeneous Fluids	130
5.3.2	Heterogeneous Aqueous Fluids.....	132
5.3.3	Heterogeneous Gas-Aqueous Fluids	137
PROBLEM 5.3	Calculating Pressure Correction for a CO_2 - H_2O Inclusion	144
5.3.4	Heterogeneous Hydrocarbons and Water-Petroleum Mixtures	146
5.3.5	P - T Constraints from Melt Inclusions	148
PROBLEM 5.4	Calculating Behavior of a Melt Inclusion on Heating	153
5.3.6	Pressure Estimates from Re-Equilibrated Fluid Inclusions	153
5.4	Calculating Depths and Geothermal Gradients.....	155
PROBLEM 5.5	Calculating Depth of Burial	160
5.5	Trend Analysis.....	163
5.5.1	T_h -Salinity Plots from Aqueous Inclusions	163
5.5.2	T_h - F_v Plots of Petroleum Inclusions.....	168

CHAPTER 6	Fluid Thermodynamics	171
6.1	Thermodynamic Laws	172
6.2	Free Energy of Reaction	175
6.3	Gas Fugacity	177
6.4	Calculating the Fluid Composition from Thermodynamic Data	180
6.4.1	C–O System	180
PROBLEM 6.1	Calculating Equilibrium Constant of a Reaction	182
PROBLEM 6.2	Calculating Oxygen Fugacity from Fluid Composition	183
6.4.2	Graphite–C–O–H System	183
PROBLEM 6.3	Calculating Water and Methane Contents in Mixed-Volatile Fluid	185
6.4.3	C–O–H–S System	186
PROBLEM 6.4	Calculating Temperature of Graphite Precipitation	186
6.4.4	Oxygen Buffers	189
PROBLEM 6.5	Calculating Oxygen Fugacity from a Mineral Buffer	192
PROBLEM 6.6	Calculating Oxidation State Of Inclusion Fluid	194
6.4.5	Sulfur Buffers	194
6.5	Calculating Phase Diagrams and Mineral-Fluid Equilibria	196
6.5.1	Computational Methods	196
6.5.2	Using the PERPLE_X	198
6.5.3	Estimating f_{O_2} and f_{S_2} from Hydrothermal Minerals	204
6.5.4	Calculating Magmatic Oxythermometer	207
6.5.5	Calculating Metamorphic Mineral–Fluid Equilibria	212
6.5.6	Thermobarometry in Pseudosections	217
PROBLEM 6.7	Calculating Isopleths Of End-Members In Solid Solutions	229
CHAPTER 7	Raman and Infrared Spectroscopic Analysis	231
7.1	Fundamentals	232
7.2	Gases and Their Mixtures	236
PROBLEM 7.1	Calculating Positions of Vibration Modes of Simple Gas Molecule	240
PROBLEM 7.2	Calculating Fluid Composition	244
PROBLEM 7.3	Calculating Fluid Density	246
7.3	Aqueous Fluids	246
7.4	Graphite and Carbonaceous Substances	250
PROBLEM 7.4	Graphite Thermometry	254
7.5	Petroleum and Bitumen	255
7.6	Silicate Melts	260
7.7	Magmatic Volatiles and Fluxing Species	260
PROBLEM 7.5	Calculating Water Content in Single Melt Inclusion	270
PROBLEM 7.6	Calculating Water Content in a Group of Melt Inclusions	272
7.8	Raman Mapping and Modeling	276

CHAPTER 8	Miscellaneous Spectrometric and Chromatographic Methods.....	281
8.1	Crush-Leach Analysis of Aqueous Inclusions	281
8.2	Bulk Gas Analysis	282
8.3	Laser Ablation Analysis	283
8.4	Selected Applications	286
8.4.1	Cation-Exchange Thermometry	286
8.4.2	Origin of Fluids Constrained by Solute Chemistry	288
PROBLEM 8.1	Element Balance During Seawater Evaporation	292
CHAPTER 9	Stable Isotope Geochemistry of Geofluids	293
9.1	Terminology and Principles	294
9.2	Stable Isotope Composition of Geofluid Reservoirs	296
9.3	Stable Isotopes in Fluid Inclusions	300
9.4	Stable Isotope Thermometry	300
PROBLEM 9.1	Calculating Temperature from Stable Isotope Data	307
PROBLEM 9.2	Stable Isotope Thermometry from Quadratic Equation	308
9.5	Isotope Fractionation in Open and Closed Systems	309
9.5.1	Rayleigh Fractionation	309
9.5.2	Batch Fractionation.....	311
9.6	Magmatic Devolatilization–Crystallization	313
9.6.1	Carbonatite–CO ₂ System.....	313
PROBLEM 9.3	Calculating Temperature and Devolatilization Degree of Carbonatite	315
9.6.2	Carbonatite–CO ₂ –H ₂ O System	316
9.7	Hydrothermal Devolatilization–Precipitation	318
9.7.1	Rayleigh Precipitation of Carbonate from H ₂ O–CO ₂ Fluid.....	318
9.7.2	Precipitation–Devolatilization Model for Carbonates	319
9.8	Fluid–Rock Interaction	322
9.9	Hydrothermal Alteration.....	324
9.10	Fluid Mixing and Infiltration.....	326
9.11	Isotope Fractionation Trends in Natural Hydrothermal Carbonates	327
9.12	Interpretation of Stable Isotopes and Fluid Inclusions in Siderite and Magnesite Deposits of Western Carpathians	336
Appendix I. Eutectic and Peritectic Points of Aqueous Systems with Salts		345
Appendix II. Selected Equations of State		349
Appendix III. Optical Properties of Fluid Inclusion Phases.....		357
Appendix IV. Stable Isotope Fractionation Factors		359

Appendix V. Raman Bands Sorted by Vibrations	369
Appendix VI. Raman Bands Sorted by Name	419
Appendix VII. Data Sources, Computer Programs, Websites	439
References	441
Index	485