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ECONOMIC GEOLOGY
Volume 1

FLUID-MINERAL EQUILIBRIA IN HYDROTHERMAL SYSTEMS

with a contribution by J.A. Whitney

CONTENTS

Introduction to Chemical Calculations
Chemical Structure of Geothermal Systems
Chemical Geothermometers for Geothermal Exploration
Gaseous Components in Geothermal Processes
More Mileage from your Gas Analyses: The Gas Geothermometers
Hydrolysis Reactions in Hydrothermal Fluids
pH Calculations for Hydrothermal Fluids
Redox Reactions in Hydrothermal Fluids
Metals in Hydrothermal Fluids
Stable Isotopes in Hydrothermal Systems
Aquifer Boiling and Excess Enthalpy Wells
Volatiles in Magmatic Systems
High Temperature Calculations in Geothermal Development
High Temperature Calculations Applied to Ore Deposits

Editors
R.W. Henley, A.H. Truesdell, and P.B. Barton, Jr.

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Fluid-Mineral Equilibria in Hydrothermal Systems

R.W. Henley, A.H. Truesdell, and P.B. Barton, Jr., Editors
with a contribution by J.A. Whitney
J.M. Robertson, Series Editor
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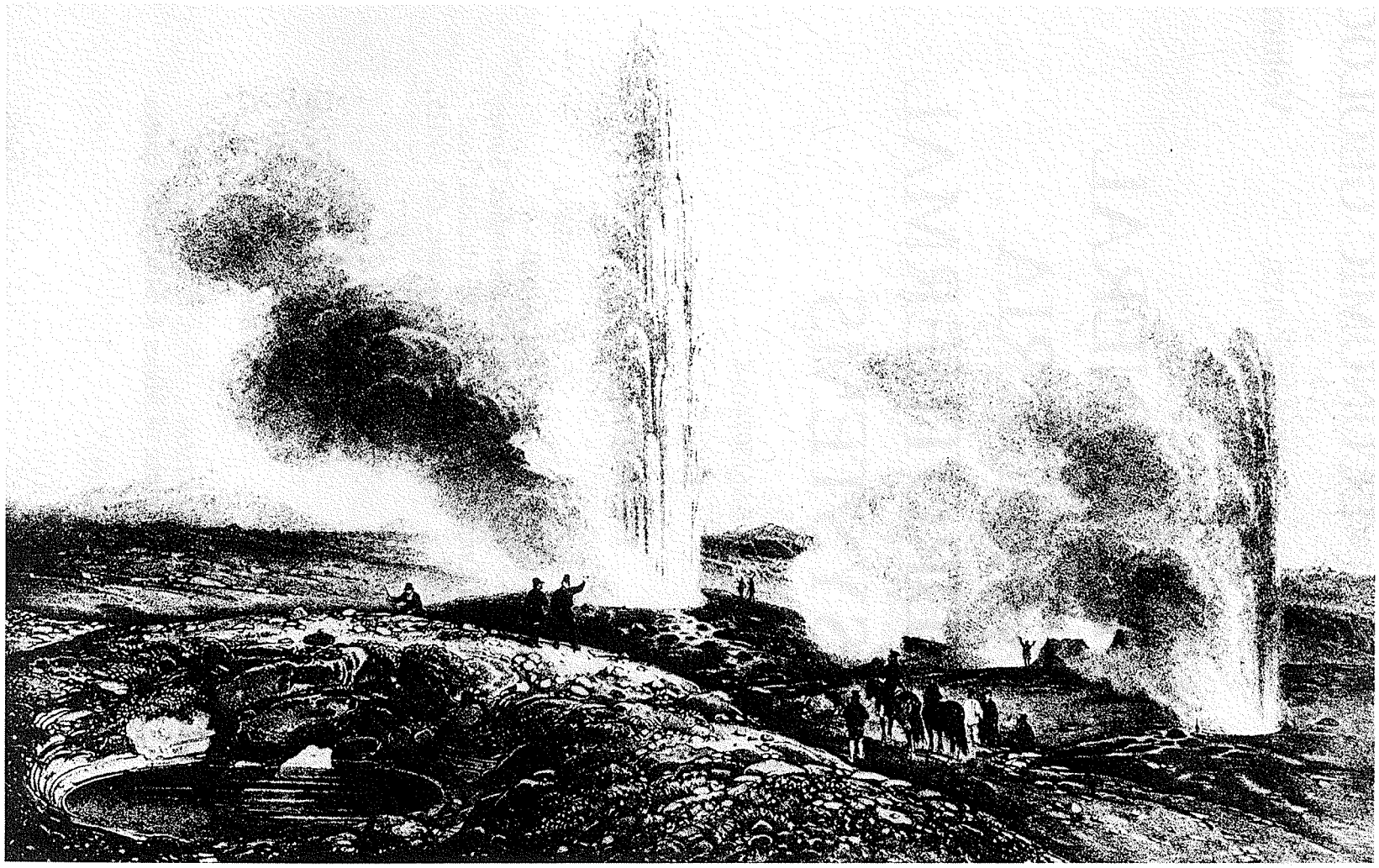

Frontispiece The Great Geyser and Strokkur erupting simultaneously

FLUID–MINERAL EQUILIBRIA IN HYDROTHERMAL SYSTEMS

Table of Contents

Page

FOREWORD ix

PREFACE x

Objectives
Format
Acknowledgments

BIOGRAPHIES xii

Chapter 1

INTRODUCTION TO CHEMICAL CALCULATIONS
(AHT)

CONCENTRATION UNITS 1

MASS ACTION CONSTANTS 2

ACTIVITY-CONCENTRATION RELATIONS 3

MASS AND HEAT BALANCES 4

CHARGE BALANCE 6

THERMODYNAMICS OF WATER 7

SUMMARY OF CHEMICAL COMPUTATIONS 7

RECOMMENDED READING 7

REFERENCES 8

Chapter 2

CHEMICAL STRUCTURE OF GEOTHERMAL SYSTEMS
(RWH)

STRUCTURE OF ACTIVE GEOTHERMAL SYSTEMS 9

BOILING POINT - DEPTH RELATIONS 11

RECALCULATION OF GEOTHERMAL WELL DATA TO AQUIFER CONDITIONS 15

The Steam Fraction
Concentration Changes During Phase Separation

COMPARATIVE CHEMISTRY OF GEOTHERMAL WELL DISCHARGES 17

Sampling and Analysis of Geothermal Fluids
Total Discharge Compositions

MIXING OF GEOTHERMAL FLUIDS 22

GASES IN GEOTHERMAL FLUIDS 22

SUMMARY PROBLEMS 25

REFERENCES 27

Chapter 3

CHEMICAL GEOTHERMOMETERS FOR GEOTHERMAL EXPLORATION
(AHT)

SILICA GEOTHERMOMETERS 31

ALKALI GEOTHERMOMETERS 33

ISOTOPE METHODS 36

CHEMISTRY AND GEOTHERMOMETRY OF SHOSHONE HOT SPRINGS 37

REFERENCES 43

Chapter 4

GASEOUS COMPONENTS IN GEOTHERMAL PROCESSES
(RWH)

DISTRIBUTION OF GASES BETWEEN LIQUID AND VAPOR 45

Single Step Steam Separation
Multistep Steam Separation
Continuous Steam Separation
A Chemical Method For Measuring Discharge Enthalpy

GEOTHERMAL GASES - CONCENTRATION UNITS 49

GAS PRESSURES 51

Gas Solubility Expressions
Aquifer Gas Pressure

REFERENCES 55

Chapter 5

MORE MILEAGE FROM YOUR GAS ANALYSES: THE GAS GEOTHERMOMETERS
(AHT)

SIMPLE GAS GEOTHERMOMETERS 57

Methane Breakdown Geothermometer
Ammonia Geothermometer
Hydrogen-Carbon Dioxide Geothermometer

AN EMPIRICAL GAS GEOTHERMOMETER 61

COMPARISON OF PUBLISHED GEOTHERMOMETRY EQUATIONS 62

REFERENCES 63

Chapter 6

HYDROLYSIS REACTIONS IN HYDROTHERMAL FLUIDS
(RWH)

SIMPLE METHODS FOR THE ESTIMATION OF RESERVOIR FLUID pH 65

Individual Ion Activity Coefficients

ACTIVITY DIAGRAMS 69

Silicate-Water Reactions

The Na_2O-K_2O-Al_2O_3-SiO_2-H_2O System

Drawing an Activity Diagram From Thermodynamic Data
Adding Other Components to the Diagram - The Use of Field Data
Calcite
Effect of Silica Activity
Using Activity Diagrams
Boiling
Fluid-rock ratios

REFERENCES 81

Chapter 7

pH CALCULATIONS FOR HYDROTHERMAL FLUIDS
(RWH)

SALINITY - pH RELATIONSHIPS 83

ION CONCENTRATIONS AND pH AT HIGH TEMPERATURES 88

Calculation of Ion Concentrations
Calculation of pH at Elevated Temperatures
Alternative Calculation Procedures
Problems with Aquifer Boiling and Excess Steam
Coupling Mineral Stability and Fluid Composition

REFERENCES 97

Chapter 8

REDOX REACTIONS IN HYDROTHERMAL FLUIDS
(PBB)

OXIDATION STATE OF GEOTHERMAL SYSTEMS 99

f_{O2}-pH AND OTHER ACTIVITY - ACTIVITY DIAGRAMS 101

NITROGEN AS AN OXIDANT? 106

BUFFER SYSTEMS 107

EFFECT OF BOILING ON REDOX STATE 110

CONVENTIONS: HALF CELLS AND GAS FUGACITIES 110

REFERENCES 112

Chapter 9

METALS IN HYDROTHERMAL FLUIDS
(RWH)

METALS IN ACTIVE GEOTHERMAL SYSTEMS 115

METAL COMPLEXING IN HYDROTHERMAL SOLUTIONS 116

Case History I: Lead
Activity coefficients
Solubility of metal sulfides
Deposition of galena
Case History II: Gold

SUMMARY PROBLEMS 125

REFERENCES 126

Chapter 10

STABLE ISOTOPES IN HYDROTHERMAL SYSTEMS
(AHT)

COLLECTION AND ANALYSIS 129

Oxygen - 18 Analysis
Deuterium Analysis
Tritium Analysis

NOTATION AND FRACTIONATION 130

APPLICATIONS OF WATER ISOTOPES 131

Water Origins
Reservoir Processes
Conductive heat loss
Mixing with cold water
Boiling and steam loss
Steam-heated waters
Graphing reservoir processes

ISOTOPIC GEOTHERMOMETERS 139

Mineral Isotope Geothermometers

REFERENCES 141

Chapter 11

AQUIFER BOILING AND EXCESS ENTHALPY WELLS
(RWH)

NORMAL AND EXCESS ENTHALPY WELLS 143

ORIGIN OF EXCESS ENTHALPY DISCHARGES 144

INTERPRETING EXCESS ENTHALPY DISCHARGES 146

Multiple Feed Zone Wells
Gas Ratios and Geothermometry
Vapor Saturation in Steam Wells in Vapor-dominated Fields

REFERENCES 153

Chapter 12

VOLATILES IN MAGMATIC SYSTEMS
(JAW)

CALCULATION OF OXYGEN AND SULFUR FUGACITIES 155

THE $Fe-O-S-SiO_2$ SYSTEM 156

COMPOSITION OF A GAS IN EQUILIBRIUM WITH A MAGMA 160

SEPARATION OF A VOLATILE PHASE FROM A CRYSTALLIZING MAGMA 167

ADDITIONAL RESEARCH REQUIRED 172

REFERENCES 173

Chapter 13

HIGH TEMPERATURE CALCULATIONS IN GEOTHERMAL DEVELOPMENT
(RWH)

pH CALCULATIONS AND STEAM SEPARATION 177

SILICA DEPOSITION 178

Rates of Silica Scaling

CALCITE DEPOSITION 182

STEAM CONDENSATES 186

REFERENCES 188

Chapter 14

HIGH TEMPERATURE CALCULATIONS APPLIED TO ORE DEPOSITS
(PBB)

THE MINERAL WORLD: WHY THE RECORD IS SO HARD TO INTERPRET 191

Metastability
Inadequately Characterized Phases
Surface Energy
Overlooked Chemical Species
Inaccurate or Incomplete Data

APPLICATIONS TO MINERAL DEPOSITS 195

THE PUZZLE OF THE MISSISSIPPI VALLEY-TYPE ORES 199

REFERENCES 200

APPENDIX I: SAMPLE PROGRAMS FOR HP41 CALCULATORS 203

APPENDIX II: ANSWERS TO SELECTED QUESTIONS AND PROBLEMS 233

APPENDIX III: STEAM TABLES — THERMODYNAMIC DATA FOR WATER AT SATURATED VAPOR PRESSURES AND TEMPERATURES 245

GLOSSARY OF SYMBOLS 253

USEFUL CONSTANTS AND CONVERSION FACTORS 256

FIGURE, TABLE, AND PLATE CREDITS 257

INDEX 258

ATOMIC WEIGHTS TABLE . . . . . Inside Back Cover

FOREWORD

In June 1982, the Society of Economic Geologists (SEG) Council appointed an Ad Hoc Committee on SEG Short Courses to develop a set of recommendations for initiating and operating a new short-course series. That committee's report, representing a major and sustained effort on the part of a number of individuals, but especially Bill Kelly and Phil Bethke, was formally presented in February 1983 in Atlanta. Included in the report was the suggestion that a printed set of "short-course notes" be produced as part of each course offering.

In November 1983, the Society of Economic Geologists sponsored its first official short course — Fluid-Mineral Equilibria in Hydrothermal Systems — held prior to the annual meetings of the Geological Society of America and Associated Societies in Indianapolis, Indiana. Primary course organizers and lecturers were R. W. Henley, A. H. Truesdell, P. B. Barton, Jr., and J. A. Whitney. These individuals produced a text for the course that has become the first volume of Reviews in Economic Geology, the newest publishing venture of the SEG.

Reviews in Economic Geology is designed to accompany the Society's short-course series. Present plans call for a volume to be produced annually in conjunction with each new short course. A volume will first serve as a textbook for the short course, and subsequently will be available to SEG members and others at a modest cost.

Normally, a volume will appear in its final, published form in time for its related course. This first time, however, the Indianapolis short course was supplemented by a "pre-production" model of Volume 1. What follows here is a substantially revised and, we hope, improved version of that book; it incorporates course participants' suggestions, and a modicum of organizational changes and standardization on the part of the Series Editor.

In addition to the authors, significant contributors to the production of this volume include: Dan Hayba of the U.S. Geological Survey (Reston), who convinced his word processor to speak clearly to mine, a feat of no small proportions; Jim Cheek of the University of New Mexico Printing Plant, whose artistic sense and layout experience were instrumental in creating the cover design; Lynne McNeil of the New Mexico Bureau of Mines and Mineral Resources, whose professionalism with a word processor, patience with the Series Editor, and continued good humor made the final editing and formating much less of a chore than it might have been. Lastly, I gratefully acknowledge the support and encouragement of Frank Kottlowski, Director of the New Mexico Bureau of Mines and Mineral Resources, whose perception of his staffs' professional obligations and personal opportunities gives each of us just enough rope.

James M. Robertson
Series Editor
Socorro, NM
July, 1984

This volume was reprinted in the summer of 1985 with many corrections and limited additions to the text, tables, and references. RWH and AHT, who continue to demonstrate a strong parental interest in the useability, accuracy, and scientific timeliness of the volume, identified a number of minor sins of omission and commission. Special thanks go to Carol Hjellming of the New Mexico Bureau of Mines and Mineral Resources editing staff, who read for content, balanced equations, and still found time to reconcile numerous references with seemingly unrelated (or only distantly related) text and figure citations.

JMR
May, 1985

PREFACE

The approach to hydrothermal ore deposits through geothermal chemistry benefits from the detailed physical, chemical and isotopic data now available from the exploration and exploitation of a large number of active geothermal systems. These provide an understanding of the processes common to both geothermal and hydrothermal ore deposits.

The present text has arisen from a number of seminars on geothermal chemistry presented in recent years. These include the Geothermal Institute (University of Auckland, New Zealand), Geothermal Resources Council (San Francisco, 1982), the Society of Economic Geologists Short Course (Indianapolis, 1983) and shorter courses in Mexico and Switzerland. These courses focused on applications in the geothermal industry but encompassed applications to epithermal ore deposits. A chapter contributed by Jim Whitney deals with the chemistry of magmatic gases in order to extend the quantitative approach of this text to a wider range of hydrothermal environments.

The present text is very much a combined effort, but for the convenience of the reader we have indicated by initials, in the table of contents, the principal author of each chapter.

Objectives

The text is designed as a practical but informal guide to the more frequently encountered hydrothermal calculations in common use today and not as a thermodynamic text. We hope that it may help to dispel some of the mystery surrounding such calculation procedures and make them available to a larger number of practicing geothermal scientists, economic geologists and geochemists. We also hope that it may help to bridge a growing information gap between applied geothermal science and research into the origin of hydrothermal ore deposits.

Format

The text is designed primarily for the practising geothermal scientist or economic geologist as a self-help guide but the format is such that it may in total or in part form the basis of university undergraduate or graduate courses. Only an elementary knowledge of thermodynamics and physical chemistry is assumed with references to the standard literature given for background reading. The text also provides a literature resource and compilation of commonly used data and equations. Of necessity much of the descriptive matter is highly condensed and is not intended as a substitute for reading the available literature on geothermal systems and hydrothermal ore deposits.

Since many readers will be unfamiliar with geothermal phenomena, we have included a few illustrative plates, in many cases with a historical perspective provided in the caption.

Each chapter has been designed as a separate entity cross-referenced to others to maintain continuity. If used in graduate or undergraduate courses, a basic geochemistry and thermodynamics course will be a prerequisite. Each chapter of this text will require some 3-4 hours teaching laboratory time and time for assignments based on the text. The material in Chapter 2 is unfamiliar to most earth scientists and may require an introductory lecture; particular hurdles are often encountered in the use of Steam Tables and the concept of the steam or water fraction.

The calculations contained in this book are not difficult but can be arduous without calculator assistance. In particular iterative calculations are frequently used and many of the calculations are required routinely. For these applications a programmable calculator is highly desireable and in order to present programs for the more involved calculations we have standardized on the Hewlett Packard 41C series. Other programmable calculators and of course (at higher cost) computers would serve as well.

Some illustrative programs for the HP41C are given in Appendix I. Readers will develop individual programing styles and applications during the course of study and are encouraged to develop their own versions of these programs. One of the most useful programs which may be applied to sets of field or experimental data is the curve-fitting program provided in the HP41C Standard Applications Manual or Applications Modules. It is reproduced in Appendix I by courtesy of Hewlett-Packard.

Students should be encouraged to write their own calculator programs but class use of the illustrative programs provided in Appendix I allows rapid progression to the essential conclusions without diversion by programming problems. These programs may be rapidly provided to a class using an HP41C light wand and bar codes.

Team problem solving is a useful method of rapidly achieving good class results.

Boxes like this are scattered throughout this book. They are used to set off useful digressions and special problems. Other problems are given in continuity in the text.

Answers to some of the more intricate problems and/or comments on their solution are provided in Appendix II. Such problems are identified in the text by the symbol $ in the adjacent left margin.

Text format has required raising some subscripts, and for clarity, omission of some valence symbols; e.g., HCO_3^- may sometimes be written HCO_3 or HCO3 and H_2 as H2.

Figure and plate credits are given in the back of the book.

Acknowledgements

In completing this guide to hydrothermal chemistry a number of acknowledgements are due. The authors' approaches to the chemistry of geothermal systems have been greatly influenced by Jim Ellis, Don White, and Bob Garrels, and this work bears some of their imprint. More recent influences have been our colleagues at Chemistry Division, DSIR (New Zealand) and at the U.S. Geological Survey, as well as the many students participating in earlier courses. The perceptive reader may recognize these workers in the Frontispiece.

One of us (RWH) wishes to thank DSIR for overseas study leave and the Fulbright Foundation for a 1983 Travel Award, both of which provided the opportunity to complete this text. Also a special word of thanks to Meg and the boys for their patience during the mammoth task of preparing this publication.

Review comments from Sue Kieffer and Rosemary Vidale were greatly appreciated and have contributed substantially to the text. Thanks are also due to Phil Bethke for his enthusiasm for the whole project, and to Pan Eimon for providing her sketch of the Creede district. Our thanks go to all those who worked so hard to prepare the manuscript, especially to Corrine Weaver, Irene Harrell, Pat Dick, and Sharon Thorne; to Dan Hayba for drafting most of the diagrams; to Paul Delaney for programming the steam table; and to the drafting and photographic personnel at the U.S. Geological Survey. Jeff Hedenquist and Harald Heinz kindly located many of the typographical errors in the first printing.

Dick Henley, Al Truesdell, Paul Barton

BIOGRAPHIES

RICHARD W. HENLEY received a BSc. in Geology in 1968 from the University of London and a PhD. in geochemistry from the University of Manchester in 1971 following experimental studies of gold transport in hydrothermal solutions and the genesis of some Preeambrian gold deposits. He was Lecturer in Economic Geology at the University of Otago, New Zealand from 1971 to 1975, and at Memorial University, Newfoundland until 1977. Research interests have focussed on the mode of origin of a number of different types of ore deposits including post-metamorphic gold-tungsten veins, porphyry copper, massive sulphide, and placer gold deposits. He is currently Head of the Geothermal Chemistry Section of the Department of Scientific and Industrial Research at Wairakei, New Zealand, and a visiting lecturer at the Auckland Geothermal Institute. His present research includes a number of isotope and chemical studies relating to the exploration and development of geothermal systems and geothermal implications for the origin of ore deposits.

ALFRED H. TRUESDELL received a B.A. in chemistry and geology from Oberlin College in 1956 and, after a few years working on uranium mineralogy at the U. S. Geological Survey, received a M.A. and Ph.D. in Geochemistry, Petrology, Mineralogy and Physical Chemistry from Harvard in 1962. Since then he has done experimental and modeling studies on low and high temperature mineral-solution equilibria, specializing, since 1967, in geothermal systems. He has worked on exploration for geothermal systems in the U. S., Mexico, Indonesia, Taiwan, China, India, and the Azores. At present his main interest is in the effects of development on reservoir processes and chemistry. His main field areas are the exploited fields of Cerro Prieto (Mexico), Larderello (Italy) and The Geysers. He is a member of several societies and a past editor of Geochimica et Cosmochimica Acta.

PAUL B. BARTON, JR. received a B.S. in Geology and Mineralogy from Pennsylvania State University in 1952 and a PhD in Geology (specialization in Economic Geology) from Columbia University in 1955. Since then he has been a research geologist with the U. S. Geological Survey in the Washington area, although he did spend three years as Deputy Chief for Scientific Program in the Survey's Office of Mineral Resources. His research has dealt with the thermodynamic properties of minerals (particularly those in the system Fe-S Zn, Cu, As, Sb, Bi), and he has been active in the application of such results to mineral deposits, particularly to epithermal base and precious metal ores, to massive sulfide ores, and to Mississippi Valley ores. He is a member of several professional societies (including being Past President of The Society of Economic Geologists) and the National Academy of Sciences. He has served on several National Research Council committees, including chairing a panel on non-fuel minerals.

JIM WHITNEY received B.S. and M.S. degrees in Geology and Geophysics, and Earth and Planetary Sciences from Massachusetts Institute of Technology in 1969, and the PhD in Geology from Stanford University in 1972. Since that time, he has taught and conducted research at the University of Georgia where he is currently Professor and Head of the Geology Department. His research has included experimental and field studies of granitic systems, solubility of metals in chloride solutions at high temperatures, activities of gaseous species in silicic magmas, and the possible contribution of magmatic fluids to ore deposits.