

Keith Nicholson



# Geothermal Fluids

Chemistry and Exploration Techniques

With 30 Figures

Springer-Verlag  
Berlin Heidelberg New York  
London Paris Tokyo  
Hong Kong Barcelona  
Budapest

---

# Contents

---

Preface .....	v
Acknowledgements .....	vii

## Part I Geothermal Fluid Chemistry

### 1 GEOTHERMAL SYSTEMS

1.1 SYSTEM TYPES AND CHARACTERISTICS .....	1
Classification .....	3
1.2 GENESIS OF GEOTHERMAL FLUIDS .....	6
Origin of water and solutes .....	6
Evolution of geothermal fluids .....	7
Evolution of steam: boiling point-depth relations .....	8
Age of geothermal fluids and geothermal systems .....	12
1.3 THERMAL, HYDROLOGICAL AND CHEMICAL STRUCTURE .....	12
Liquid-dominated systems .....	14
Vapour-dominated systems .....	16

### 2 WATER CHEMISTRY

2.1 WATER TYPES .....	19
Chloride .....	19
Sulphate .....	20
Bicarbonate .....	22
Sulphate-chloride .....	22
Dilute chloride-(bicarbonate).....	23
A diagnostic plot of water chemistry .....	27

2.2 PROCESSES AFFECTING WATER COMPOSITION .....	28
Mineral-fluid equilibria .....	28
Boiling (adiabatic) cooling .....	34
Conductive cooling .....	34
Mixing (dilution) with other waters .....	35
2.3 INTERPRETATION OF WATER CHEMISTRY .....	35
pH .....	36
Common solutes .....	39
Chemical behaviour of common species .....	39
Chemical indicators of physico-chemical processes .....	49
Statistical analysis of water chemistry .....	50
2.4 MIXING MODELS .....	52
Enthalpy - chloride diagrams .....	52
Enthalpy - silica diagrams .....	62
Carbonate - silica/chloride .....	65
2.5 SOLUTE GEOTHERMOMETERS .....	67
Silica .....	69
Na/K geothermometer .....	72
Na-K-Ca geothermometer .....	73
Na/Li geothermometer .....	76
K/Mg and Li/Mg geothermometers .....	77
Na-K-Mg geothermometer .....	78
Ca/Mg & SO <sub>4</sub> /F geothermometers for carbonate reservoirs .....	80
2.6 CALCULATING RESERVOIR FLUID CHEMISTRY .....	80
Heat and mass balance equation .....	80
Steam fraction calculation .....	81
Weirbox composition .....	82
Reservoir fluid composition .....	82
Total discharge (TD) composition .....	83
Reservoir fluid pH .....	83
<b>3 GAS CHEMISTRY</b>	
3.1 INTRODUCTION .....	87
3.2 DISCHARGE FEATURES .....	88

3.3 PROCESSES AFFECTING STEAM COMPOSITION .....	89
Geothermal system .....	90
Solubility .....	90
Steam formation .....	96
Condensation .....	102
Oxidation .....	102
Rock-steam reactions .....	102
Mineral equilibria and buffering .....	102
Seismicity .....	103
Contamination .....	103
3.4 INTERPRETATION OF GAS CHEMISTRY .....	103
Behaviour of common geothermal gases .....	104
Indicators of physico-chemical processes .....	108
3.5 GAS GEOTHERMOMETERS .....	112
CO <sub>2</sub> -H <sub>2</sub> S-H <sub>2</sub> -CH <sub>4</sub> geothermometer (D'Amore & Panichi) .....	112
CO-based geothermometer .....	113
CO <sub>2</sub> -geothermometer .....	114
H <sub>2</sub> -Ar geothermometer .....	114
gas/Σwater - based geothermometers .....	114
<b>4 ISOTOPE CHEMISTRY</b>	
4.1 INTRODUCTION .....	117
Notation .....	118
Standards .....	120
4.2 GEOTHERMAL APPLICATIONS OF ISOTOPES .....	120
Stable isotope .....	120
Radioactive isotopes .....	125
4.3 ISOTOPE GEOTHERMOMETERS .....	126
Isotope geothermometry equations .....	127
Oxygen isotope geothermometers .....	128
Hydrogen isotope geothermometers .....	134
Carbon isotope geothermometers .....	135
Sulphur isotope geothermometer .....	137

Part II  
Exploration Techniques & Surveys

## 5 EXPLORATION TECHNIQUES

5.1 INTRODUCTION .....	141
5.2 EXPLORATION SURVEYS .....	142
Active systems .....	142
Fossil/epithermal systems .....	145
<b>6 WATER SURVEYS</b>	
6.1 PRE-FIELD LABORATORY PREPARATION .....	151
Collection bottles.....	151
Bottle cleaning .....	152
Sampling equipment .....	154
6.2 FIELD SURVEY .....	154
Mapping springs .....	155
Field notes .....	155
Field measurements .....	155
Selection and prioritizing springs for sampling .....	157
6.3 SAMPLING METHODS .....	158
Springs and pools .....	158
Wells.....	160
Specialised sampling requirements .....	162
Sample storage .....	163
6.4 ANALYTICAL METHODS .....	163
Introduction .....	163
Aluminium .....	164
Ammonia .....	165
Arsenic .....	167
Bicarbonate, Carbonate .....	168
Boron .....	169
Caesium .....	172

Calcium .....	172
Chloride .....	173
Fluoride .....	174
Hydrogen sulphide .....	175
Iodide, Bromide .....	176
Iron .....	177
Lithium .....	178
Magnesium .....	179
Mercury .....	179
pH .....	180
Potassium .....	181
Rubidium .....	182
Silica .....	182
Sodium .....	184
Sulphate .....	184
Total Dissolved Solids .....	186
6.5 DATA QUALITY AND PRESENTATION .....	186
Quality control checks .....	186
Ionic balance .....	187
Mass balance .....	188
Units .....	188
Tabulation of results .....	192

## 7 GAS SURVEYS

7.1 PRE-FIELD LABORATORY PREPARATION .....	195
Sample flasks .....	195
Flask cleaning and preparation .....	195
Sampling equipment .....	196
7.2 FIELD SURVEY .....	197
Selection and prioritizing fumaroles for sampling .....	197
7.3 SAMPLING METHODS .....	197
Fumaroles .....	197
Gas discharges from pools .....	198
Wells.....	198
General notes on sampling gases .....	199
Sample storage .....	199

7.4 ANALYTICAL METHODS .....	200
Gas chromatographic determinations .....	201
Wet chemical determinations.....	203
Calculation of gas in the total discharge (TD <sub>gas</sub> ) .....	205
7.5 GAS CONCENTRATION UNITS .....	205

## 8 SOIL AND SOIL-GAS SURVEYS

8.1 INTRODUCTION .....	209
8.2 SURVEY ORGANISATION .....	210
Orientation survey .....	210
Sampling grid .....	211
8.3 SOIL SURVEYS .....	211
Soil sampling .....	212
Sample preparation .....	213
Ammonia .....	214
Antimony .....	214
Arsenic .....	214
Boron .....	214
Mercury .....	215
8.4 SOIL-GAS SURVEYS .....	216
Soil-gas sampling .....	216
Carbon dioxide .....	217
Helium .....	217
Mercury vapour .....	218
Radon .....	219
8.5 DATA QUALITY, PRESENTATION AND INTERPRETATION.....	220
Presentation methods .....	220
Anomaly identification and interpretation .....	220

## APPENDICES

1. Steam tables .....	225
2. Atomic weights .....	233

REFERENCES .....	235
------------------	-----

SUBJECT INDEX .....	255
---------------------	-----