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**Fluid circulation in a submarine paleohydrothermal system,
Troodos ophiolite, Cyprus: Fluid inclusion evidence for
deep-seated circulation of brines in the oceanic crust**

by

Deborah Sue Kelley



Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

at

Dalhousie University
Halifax, Nova Scotia
October, 1990

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DEDICATION

In memory of Wesley C. Kelley.

TABLE OF CONTENTS

Table of Contents	page
List of Figures	v
List of Tables	vii
Abstract	x
Acknowledgments	xi
CHAPTER I INTRODUCTION	1
1.0 General Statement	1
1.1 Previous Hydrothermal Studies	8
1.1.2 Downflow Zone	8
1.1.3 Upflow Zone	9
1.1.4 Feeder Zone	10
CHAPTER II GEOLOGY	12
2.0 Introduction	12
2.1 The Troodos Ophiolite	12
2.1.1 Extrusive Sequence	14
2.1.2 Sheeted Dike Complex	16
2.1.3 Plutonic Complex	18
2.1.4 Upper Level Plutonic Rocks	19
2.1.4.1 Upper level Gabbros	19
2.1.4.2 Diorites and Plagiogranites	29
CHAPTER III FLUID INCLUSIONS	43
3.0 Introduction	43
3.1 Fluid Inclusions in Rocks From Troodos	43
3.2 Methods	54
3.3 Fluid Inclusion Types and Results	56
TYPE 1: Liquid-Dominated, Low-Salinity Inclusions	56
TYPE 2: Vapor-Dominated, Low-Salinity Inclusions	56
TYPE 3: Liquid-Dominated, High-Salinity Inclusions	64
3.4 Laser Raman Microprobe Spectroscopy Results (LRM)	74
3.5 Inclusion-Specific Mass Spectrometric Analyses and Results	76
CHAPTER IV DISCUSSION	85
4.0 Introduction	85
4.1 Generation of High-Salinity Fluids in the Oceanic Crust	85

4.1.1	Hydration Reactions	page 89
4.1.2	Retrograde Solubility	92
4.1.3	Two-Phase Separation	93
4.2.0	The System NaCl-H ₂ O	95
4.2.1	Pressure-Depth Relationships	100
4.3	Models of Brine Generation and Fluid Circulation in the Upper Plutonic Sequence of Troodos	104
4.3.1	Fluid Sources	104
4.3.1.1	Seawater Source Model	106
4.3.1.2	Magmatic Source Model	111
4.3.2	Fluid Flow Models for Seawater-Derived Fluids	116
4.4	Generation of Low-Temperature, Low-Salinity Fluids	125
4.5	A Comprehensive Model of a Brine-Dominated Hydrothermal System in Troodos	126
4.6	Comparison with Other Hydrothermal Systems	131
4.6.1	Application of Flow Models to Troodos	137
CHAPTER V CONCLUSIONS		141
APPENDICES		143
A. Fluid Inclusion Analyses		143
B. Cracking Front Model		147
REFERENCES		154

	<u>LIST OF FIGURES</u>	page
1.0	Flow Zones in a Submarine Hydrothermal System	4
1.1	Location of Tethyeen Ophiolites	6
1.2	General Geology Map of Cyprus	7
2.0	Geology Map of the Troodos Ophiolite	13
2.1	Extrusive Sequence	15
2.2	Epidotized Dikes	17
2.3	Plagioclase-Hosted Fluid Inclusions	20
2.4	Sample Locations	21
2.5	Plagiogranite Intruding Gabbro	23
2.6	Dikes Cutting Plagiogranite	23
2.7	Alteration Halo Rimming Plagiogranite	24
2.8	Varitextured Gabbro	25
2.9	Microphotograph of Uralitized Gabbro	26
2.10	Uralitized Gabbro	26
2.11	Microphotograph of Magnetite Gabbro	28
2.12	Late Stage Gabbro Pegmatite	30
2.13	Plagiogranite Screens in Dike Complex	31
2.14	Gabbro-Diorite Cupola	31
2.15	Diabase Xenoliths in Plagiogranite	32
2.16	Localized Mixing Zone Between Mafic and Felsic Melts	33
2.17	Microphotograph of Plagiogranite	33
2.18	Granophyric Texture Plagiogranite	34
2.19	Granophyric Felsic Vein in Plagiogranite	36
2.20	Epidotized Shear Zone in Plagiogranite	37
2.21	Epidotized Plagiogranite	38
2.22	Podiform Epidosite	39
2.23	Microphotograph of Epidote in Shear Zone	40
2.24	Microphotograph of Podiform Epidote in Plagiogranite	42
3.1	Microphotographs of Secondary Fluid Inclusions in Quartz	45
3.2	Microphotographs of Fluid Inclusions in Clinopyroxene and Amphibole	47
3.3	Microphotographs of Fluid Inclusions in Plagioclase and Epidote	49
3.4	Microphotographs of Fluid Inclusions in Epidote, Quartz and Apatite	51
3.5	Quartz-Hosted Fluid Inclusions in Epidosite	53
3.6A	Microphotograph of Secondary Inclusions in Quartz	55
3.6B	Microphotograph of Primary Fluid Inclusions in Plagioclase	55
3.7	Change of Volume Percent Vapor and Liquid Composition for a Vapor-Dominated Inclusion	57
3.8	Fluid Inclusion Types I-III	60

3.9	Temperatures of Vapor Bubble Disappearance and Corresponding Fluid Salinities of Individual Inclusions	page 61
3.10A	Histogram of Homogenization Temperatures	62
3.10B	Histogram of Equivalent Fluid Salinities	62
3.11A	Simplified Geologic Map Near Mt. Olympus, Cyprus	63
3.11B	Sample Locations	63
3.12A	Linear Array of Brine- and Vapor-rich Fluid Inclusions	65
3.12B	Array of Vapor-Dominated, Low-Salinity Inclusions	65
3.13A	Corresponding Temperatures of Vapor Bubble Disappearance and Equivalent Fluid Salinities	66
3.13B	Corresponding Temperatures of Halite Dissolution and Vapor Bubble disappearance for Halite-Bearing Inclusions	66
3.14	Corresponding Vapor Bubble Disappearance Temperatures and Equivalent Fluid Salinities for Sample CY88-9.	68
3.15	P-T Projection of the High-Salinity Portion of the NaCl-H ₂ O System	69
3.16	Temperature-Compositional Results for Halite- and Sylvite-Bearing Inclusion	71
3.17	Vapor-Saturated Solubility Surface in the NaCl-KCl-H ₂ O Ternary System	72
3.18	Sample Spectrum for ALV1011-1	78
3.19	Spectrum for Sample CY1181.75	79
3.20	Ternary Diagram for AMU'S 17, 18, and 44 (CY1181.75)	80
3.21A	Spectrum for Sample ALV1011-1	82
3.21B	Spectrum for Sample ALV1011-1	82
3.22	Ternary Diagram for AMU'S 17, 18, and 44 (ALV1011-1)	83
3.23	Ternary Diagram for AMU's 16, 17, and 44 (ALV1011-1)	84
4.0	Corresponding Temperatures of Vapor Bubble Disappearance and Equivalent Fluid Salinities for Low-Temperature Inclusions	86
4.1	Chlorine and Sodium Concentrations of Fluids in Submarine Hydrothermal Systems	87
4.2	Generalized P-T Relationships for the NaCl-H ₂ O System	96
4.3	Pressure-Temperature-Compositional Relationships for the NaCl-H ₂ O System	98
4.4	Isoplethal P-T-depth Projection in the System NaCl-H ₂ O	99
4.5	Relationship Between Pore Fluid Pressure and Depth As A Function of the Deformational Regime Within the Crust	101
4.6	Isothermal (P-X) Projection of NaCl-H ₂ O System and Effects of Multiple Phase Separation Events	105
4.7	Hydrothermal Seawater Model for Brine Generation	107
4.8	Effects of Two Phases on Fluid Flow	109
4.9	Plagiogranite with Abundant Diabase Xenoliths	112
4.10	Magmatic Model for Brine Generation	114

	page
4.11 Single-Pass Flow Model	117
4.12 Cracking Front Model	118
4.13 Cracking Temperatures vs Water Temperature	120
4.14A Fluid Temperature in Cracks vs Permeability	121
4.14B Fluid Temperature in Cracks vs Thermal Flux	121
4.15 Properties of H ₂ O as a Function of Temperature	123
4.16 Zone of Optimum Transport Efficiency	124
4.17 Temperatures of Homogenization and Equivalent Fluid Salinities for Inclusions in Xenolith and Host Rock	127
4.18 Homogenization Temperatures and Fluid Salinities for Epidosite and Shear Zone-Hosted Inclusions	128
4.19 Conceptual Model for Fluid Circulation in Troodos	130
4.20 Temperature-Composition-Depth Relationships for Fluid Inclusions in Troodos	132
4.21 Vapor-Dominated Circulation Model for Porphyry Copper Systems	133
4.22A Homogenization Temperatures and Salinities of Fluid Inclusions in the Santa Rita Porphyry Copper Deposit	136
4.22B Homogenization Temperatures and Salinities of Fluid Inclusions from Troodos and the Kane Fracture Zone	136
4.23 Circulation Model for Fluid Evolution in a Marine Environment	138
4.24 Double Diffusive Convection Model for Mid-Ocean Ridge Spreading Centers	139

LIST OF TABLES

	page
Table I Petrography of Troodos Samples	22
Table II Fluid Inclusion Nomenclature	58
Table III Troodos Ophiolite Fluid Inclusion Results	59
Table IV Sylvite- and Halite-bearing Fluid Inclusion Results	73
Table V Raman Analyses of Fluid Inclusions	75
Table VI Chlorine & Sodium Concentration in Submarine Hydrothermal Fluids	88
Table VII Fluid Inclusion Studies on Submarine Samples	90
Table VIII Hydrothermal Circulation Models	135
Table IX Cracking Front Model Results	148

ABSTRACT

Detailed temporal, thermal, and compositional data on aqueous fluid inclusions from a suite of plutonic rocks from the Troodos ophiolite, Cyprus provide the first documentation that generation of high-temperature brines may be common at depth in the oceanic crust. Anastomosing arrays of fluid inclusions in rocks of the upper intrusive sequence are believed to record episodic fracturing events. The earliest event at temperatures $>400\text{--}500^{\circ}\text{C}$ resulted in pervasive entrapment of brine-rich aqueous fluids with salinities greater than 15 times that of seawater. The high-temperature brines are most reasonably interpreted in terms of two-phase separation of either pore or magmatic fluids at, or near, solidus temperatures. Migration and segregation of brine and vapor phases along fractures near the margins of the crystallizing plagiogranite and gabbroic bodies resulted in preferential entrapment of the brines in the deep-seated, high-temperature portions of the hydrothermal system. In localized areas, the high-temperature brines ($\text{NaCl}+\text{KCl}+\text{CaCl}_2$) caused extreme alteration of the plagiogranite bodies and formation of podiform epidiosites. Lack of brine-enrichment in fluid inclusions hosted in rocks of the sheeted dike complex suggests development of multi-tiered circulation cells in the upper plutonic sequence and sheeted dikes.

Arrays of low-temperature, low-salinity fluid inclusions, which crosscut fractures dominated by brine inclusions, indicate penetration of seawater during subsequent fracturing events at temperatures $>200\text{--}400^{\circ}\text{C}$. Hydration reactions under greenschist facies conditions, or limited mixing with phase-separated fluids, resulted in salinity variations in these fluids from 70% below to 200% above seawater concentrations. Temperatures and compositions of the inclusions are similar to those found in stockwork systems beneath Troodos ore deposits and to those of fluids exiting active submarine hydrothermal vents at mid-ocean ridge spreading centers. The low-temperature fracture networks may represent an extensive deep-seated feeder system which coalesced to form zones of concentrated hydrothermal upflow.

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CHAPTER I

INTRODUCTION

1.0 GENERAL STATEMENT

Hydrothermal circulation at mid-ocean ridge spreading centers plays a major role in dissipating the thermal energy stored in the earth's crust (Sleep et al., 1983; Converse et al., 1984). Chemical and thermal interaction between the convecting fluids and oceanic crust moderates seawater chemistry (Edmond et al., 1979; Thompson, 1983; Bowers and Taylor, 1985), governs the development of massive sulfide deposits associated with hydrothermal vents (Macdonald et al., 1980; Rona et al., 1986; Tivey and Delaney, 1986) and supports chemosynthetically-based biological communities on the seafloor (Jannasch, 1983; Grassle, 1985). The common recovery of hydrothermally altered rocks from the ocean ridges, in conjunction with the discovery of 350-400°C hydrothermal vents along slow-, medium-, and fast-spreading centers indicates that fluid circulation plays an important role in crustal evolution throughout the ridge crest environment.

The shallow portions of submarine hydrothermal systems have been generally well characterized by recent studies of hydrothermal vent deposits and vent effluent (Tivey and Delaney, 1986; Rona et al., 1986; Campbell et al., 1988; Von Damm, 1988; Butterfield et al., 1990), of stockwork systems and massive sulfide deposits in ophiolites (Spooner, 1980; Oudin et al., 1981; Constantinou, 1987; Nehlig and Juteau, 1988; Richards and Cann, 1989), and metabasalt- and diabase-hosted veins in rocks recovered from ocean basins and ophiolites (Humphris and Thompson, 1978; Alt et al., 1986a; Alt et al., 1986b; Gillis, 1986; Delaney et al., 1987; Nehlig and Juteau, 1988). Few studies, however, have examined the geometry, conditions, and extent of fluid flow in the deep-seated, high-temperature portions of these systems hosted in the plutonic rocks. Only recently has evidence for circulation of high-temperature (>700°C) fluids been documented in the oceanic crust (Kelley and Delaney, 1987; Vanko, 1988). Although

it is clear that fluid flow is driven by thermal perturbations as a result of magma emplacement, little is known about fracture-fluid evolution and fracture distribution near the brittle-ductile transition zone that must exist near magma chamber margins. Understanding this dynamic zone is crucial for development of comprehensive thermal-chemical models for mid-ocean ridge systems. The extent to which fluids circulate near magma chamber margins has a large effect on the hydrothermal heat flux for the system (Lister, 1983; Sleep, 1983) and circulation of fluids in this zone probably affects the depth and geometry of crustal magma chambers on mid-ocean ridges (Cann et al., 1988). One of the most important, but least well constrained parameters governing the temperatures of migrating fluids in this zone is the initial thermal condition under which rocks fail brittlely. Obtaining the P-T-X conditions of fluid flow in these high-temperature systems provides rate-limiting controls on the longevity of mid-ocean ridge magma chambers and temperature-composition constraints on fluids exiting hydrothermal vents.

Sampling of active vents, coupled with studies of seawater-basalt interaction, indicate that vent solutions are dominated by seawater-derived fluids (Bowers et al., 1988; Von Damm, 1988). As seawater migrates to depth and interacts with hot basaltic host rocks it becomes enriched in Fe, Si, and H^+ , and depleted in Mg and SO_4^{2-} (Seyfried and Bischoff, 1981; Mottl, 1983; Seyfried, 1987). Chemical equilibria studies suggest that this evolution is controlled by fluid-rock reactions under near supercritical pressures and temperatures that produce secondary mineral assemblages at depth (Seyfried, 1987; Bowers et al., 1988; Berndt et al., 1989). However, subsurface mixing of deeply circulating seawater with brines and vapor-rich fluids generated by phase separation may also be an important effect.

It has been suggested that enrichment or depletion of Na and Cl with respect to seawater in vent fluids may indicate phase separation (Von Damm, 1988; Butterfield et al., 1990). However, fluids directly undergoing two-phase separation have yet to be

sampled on the seafloor. Only a few studies of submarine plutonic samples (Kelley and Delaney, 1987; Delaney et al., 1987; Cowan and Cann, 1988; Vanko, 1988) document deep circulation of brines and vapors (now preserved as fluid inclusions). Although the conditions and extent of brine generation have been well documented in the high-temperature plutonic environment associated with porphyry copper deposits (White et al., 1971; Henley and McNabb, 1978; Bodnar and Beane, 1980; Reynolds and Beane, 1985), the extent to which brine- and vapor-dominated hydrothermal systems are developed in the oceanic crust remains unknown. Recent theoretical models for the evolution of submarine hydrothermal systems postulate that significant amounts of brine are likely to be generated during high temperature circulation of seawater at depth (Fournier, 1987; Bischoff and Rosenbauer, 1989).

This thesis was undertaken to test this hypothesis and to develop a model for fracture-fluid evolution in the plutonic-hosted, high-temperature portion of a submarine hydrothermal system (Fig. 1.0). Formulation of comprehensive thermal-chemical models for the structure of mid-ocean ridge magma-hydrothermal systems require quantitative information regarding conditions of circulation along the entire path of fluid flow. Predicting conditions of fluid-rock interaction at depth by using vent fluid chemistry and chemical modeling is difficult and must depend on inferences concerning equilibrium of mineral and fluid assemblages at depth, the significance of fluid mixing, and conductive heat loss. Thermodynamic data on fluid-rock reactions must be extrapolated to high pressure and temperature conditions, which under supercritical conditions are not well constrained. Although alteration studies can provide information on the thermal conditions of fluid-rock interaction at depth, secondary mineral assemblages commonly record the integrated chemical effects of multiple hydrothermal pulses. Fluid inclusions provide a powerful tool with which to study fracture-fluid evolution in these systems because they yield a relatively instantaneous record of the P-T-X conditions of hydrothermal flow at depth.

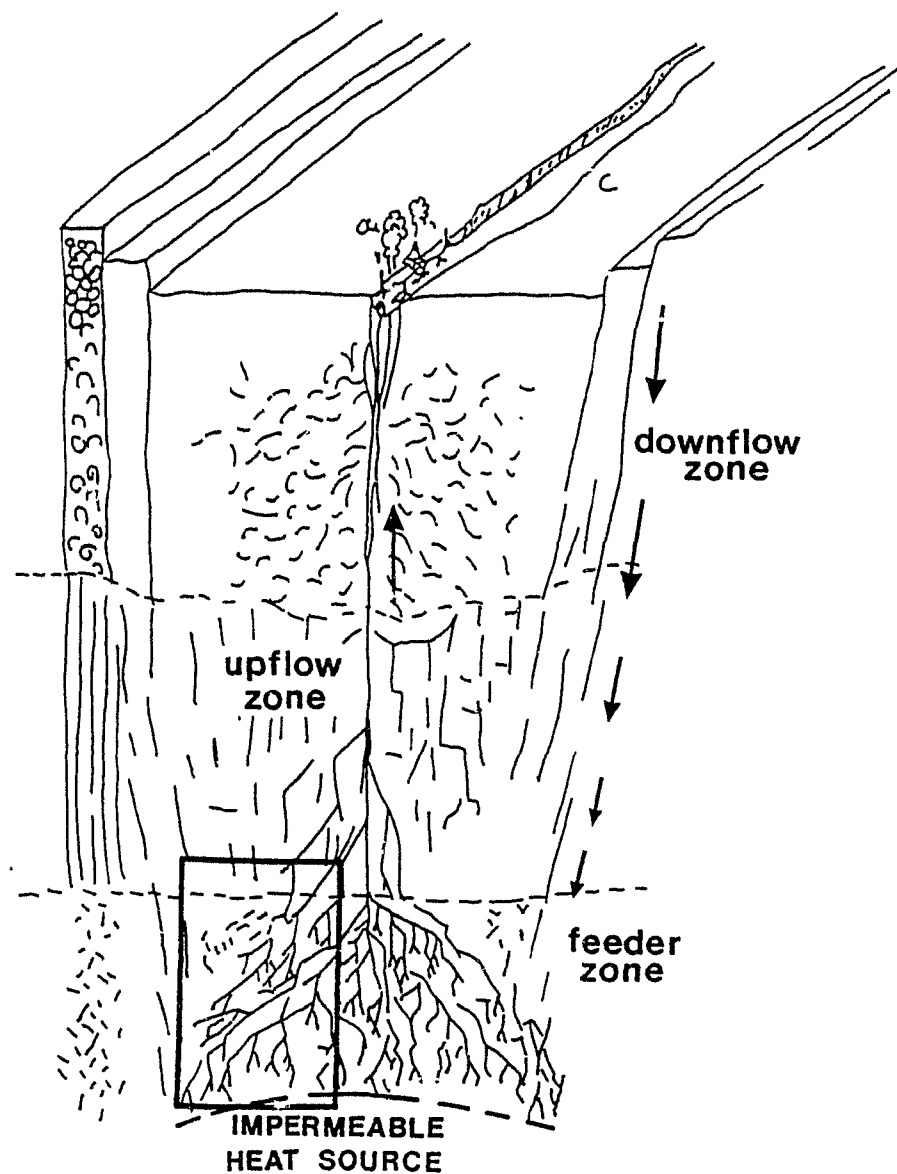


Figure 1.0 Schematic diagram illustrating probable flow zones in a submarine hydrothermal system (after Goldfarb and Delaney, 1988). Area of study is outlined by open rectangle.

The Troodos ophiolite, located in south-central Cyprus (Fig. 1.1 and 1.2), is one of the best exposed and most studied ophiolites in the world and provides an optimal area to study the conditions of deep-seated fluid flow in a submarine hydrothermal system. Detailed mapping and petrologic studies of the massif provide abundant information on conditions of subseafloor hydrothermal alteration and on circulation of fluids deep within an exposed section of oceanic crust (Heaton and Sheppard, 1977; Gillis and Robinson, 1985; Gillis, 1986; Richardson et al., 1987; Schiffman and Smith, 1988; Robinson et al., 1990). These studies, in conjunction with those of massive polymetallic sulfide deposits in Cyprus (Constantinou and Govett, 1973; Spooner, 1980; Oudin et al., 1981; Richards and Cann, 1989), have been used to formulate models describing physicochemical processes in hydrothermal vent systems at modern oceanic spreading centers (Cann et al., 1986).

In this study, detailed temporal, thermal, and compositional data on fluid inclusions from a suite of plutonic rocks from the Troodos ophiolite provide temperature and compositional information on some of the earliest- and deepest-circulating fluids in a submarine paleohydrothermal environment. Application of microanalytical techniques including standard microthermometry, laser raman microprobe spectroscopy, and inclusion-specific mass spectrometric analyses allowed accurate determination of fluid chemistry. Microthermometric and petrographic analyses of inclusion populations entrapped along healed microfractures provided thermal and chemical information on fluid evolution. Results of fluid inclusion analyses from this study closely overlap with those from other submarine systems. The similarities indicate that the conditions of deep-seated fluid flow in submarine systems are not unique to a specific spreading environment; therefore, study of fracture-fluid evolution in the Troodos plutonic section offers an important window through which to study circulation of fluids in an area which is largely inaccessible in modern hydrothermal systems.

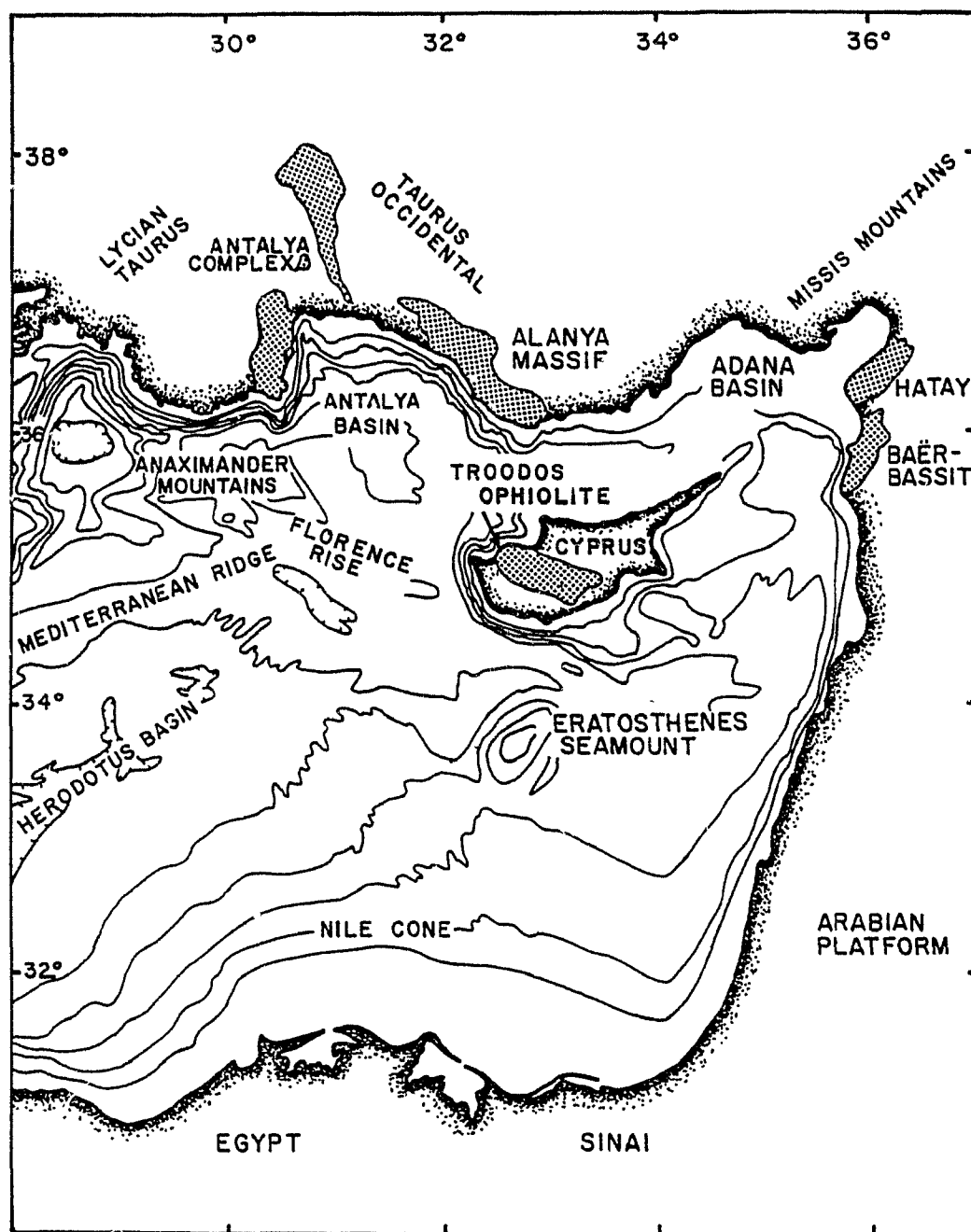


Figure 1.1 Map of the eastern Mediterranean showing the location of the Troodos ophiolite and other Tethyan ophiolites and complexes (after Robertson and Woodcock, 1980).

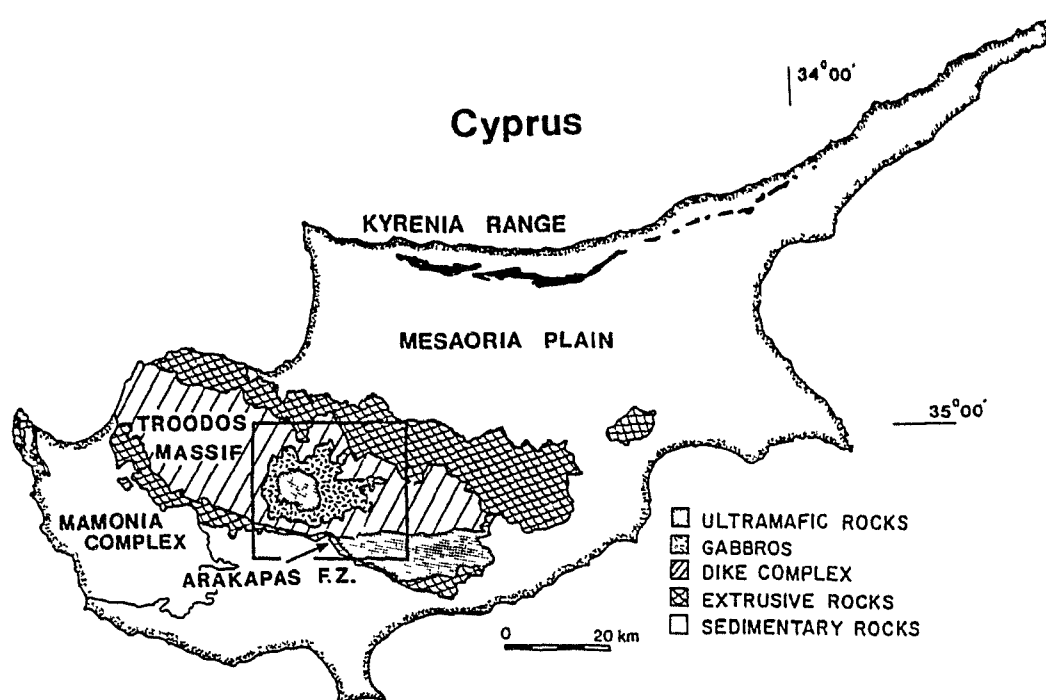


Figure 1.2 Generalized geology map illustrating the location of the four main terrains which dominate the geology of Cyprus: the Kyrenia Range, the Mesaoria Plain, the Troodos ophiolite, and the Mamonia complex. The study area is outlined by open square.

1.1 Previous Hydrothermal Studies

Hydrothermal studies of the Troodos massif (Fig. 1.1 and Fig. 1.2) have concentrated on the spatial distribution of alteration mineral assemblages to define conditions of hydrothermal flow. Early workers suggested that hydrothermal alteration of the massif resulted in the development of regional subhorizontal metamorphic zones which increased regularly in grade with increasing depth (Gass and Smewing, 1973; Gass, 1980). Subsequent work has shown that regional metamorphic zones do not adequately describe the effects of hydrothermal alteration on the oceanic crust. In Troodos, alteration intensity is highly variable and strongly dependent on factors such as permeability, temperature, fracture configuration and rate of sedimentation on the seafloor (Gillis and Robinson, 1985; Gillis, 1986; Gillis and Robinson, 1988; Mehegan, 1988). Five alteration zones at shallow crustal levels have been identified in Troodos and in in situ oceanic crust, which develop during successive and overlapping stages of alteration (Gillis and Robinson 1985, Gillis, 1986; Gillis and Robinson, 1988). They include: (1) a seafloor weathering zone, (2) a low-temperature zone, (3) a transition zone, (4) an upper dike zone, and (5) a mineralized zone. These alteration zones reflect conditions of fluid flow in zones of hydrothermal circulation which broadly include the downflow zone, the basal feeder zone, and the upflow zone, shown in Figure 1.0.

1.1.2 Downflow Zone

In the downwelling limbs of convection cells, diffuse flow of cold seawater is thought to occur over broad areas, with more localized zones of downflow occurring along listric normal faults. At shallow crustal levels near the sediment-lava interface temperatures of circulating fluids are low ($<50^{\circ}\text{C}$), water-rock ratios are high (>50), and alteration is limited to zeolite facies metamorphism (Gillis, 1986). Depending on the permeability conditions and sedimentation rate this seafloor weathering zone may migrate downward during crustal aging, and overprint previous hydrothermal events. In Troodos, shallow circulation of cold fluids in the seafloor weathering zone is thought

to have been active for 10-30 m.y., after which the system became sealed by sediments and mineral precipitation (Gillis and Robinson, 1985; Gillis, 1986; Gillis and Robinson, 1988).

The seafloor weathering zone is underlain by a low-temperature zone and a transition zone which grades abruptly into a high-temperature zone hosted in the sheeted dikes. In the high-temperature zone permeabilities decrease and fluid temperatures rise steeply as downgoing fluids traverse the pillow lava-sheeted dike transition (Alt et al., 1986a; Mottl, 1983; Gillis and Robinson, 1988). Secondary mineral phases in basalts and diabases indicate alteration under greenschist facies conditions at low water-rock ratios (<5-10). Depending on fracture distribution, flow morphologies, and dike distribution, alteration in this zone may be extremely heterogeneous. Depth of the high-temperature zone in Troodos varies from <150 m to >1400 m (Gillis and Robinson, 1988). The sheeted dike-gabbro interface has been inferred to represent the base of the hydrothermal systems (Richardson et al., 1987). However, major shifts in $\delta^{18}\text{O}$ values in drill core from Cyprus Crustal Study Project Hole CY4 have been attributed to large influxes of seawater-derived fluids into the plutonic sequence (Vibetti et al., 1989).

1.1.3 Upflow Zone

Field studies of Troodos indicate that vein diameter and continuity increase upsection, forming near vertical conduits at shallow crustal levels (Constantinou, 1987; Richardson et al., 1987), however, the exact nature of the funnelling system is not well understood. Mineralized alteration pipes extend to depths of 700 m below the massive sulfide deposits and consist of quartz- and pyrite-filled veins in dikes and pillow lavas (Constantinou, 1987; Robinson et al., 1990). Alteration haloes associated with the stockwork system extend out into the country rock and consist predominantly of variable assemblages of chlorite, quartz, pyrite, and smectite. The stockwork system may extend to feed overlying exhalative bodies analogous to modern vent deposits

(Oudin and Constantinou, 1984; ICRDG, 1984), or terminate in the overlying pillow lavas (Constantinou, 1987). Limited fluid inclusion data indicate temperatures are high (300-350°C, Spooner and Bray, 1977) in the upflow zones and flow may be in the range of cm/sec (Cann et al., 1986; Richards and Cann, 1989). Isotopic studies in conjunction with fluid inclusion analyses, indicate that the circulating fluid was dominantly seawater (Spooner et al., 1977; Heaton and Sheppard, 1977).

Beneath the stockwork zones, near the base of the sheeted dike complex are localized zones of pervasive alteration in which the dikes have been completely transformed into assemblages of quartz + epidote $\pm$ chlorite (epidosites) (Richardson et al., 1987; Schiffman and Smith, 1988). These zones, characterized by extreme metal depletion, are believed to reflect intense high-temperature (300-400°C) alteration at high water/rock ratios (Richardson et al., 1987; Schiffman and Smith, 1988) and have been interpreted as feeders for major conduits of hydrothermal upflow which fed the higher-level stockworks and vent systems.

1.1.4 Feeder Zone

Isotopic studies and thermal modelling of igneous complexes and of the Semail ophiolite in Oman suggest that decoupling of hydrothermal circulation cells occurs near the sheeted dike-gabbro interface. A lower-temperature, less vigorously convecting cell develops in the overlying extrusive rocks, underlain by a high-temperature cell in the plutonic rocks (Gregory and Taylor, 1981; Taylor, 1983; Norton et al., 1984). Formation of the two cells results in a lower heat flux and, therefore, longer lived magma chambers, because cold fluids no longer have direct access to the crystallizing rocks. In contrast, on the basis of D/H and $^{18}\text{O}/^{16}\text{O}$ analyses of rocks from the Troodos complex, Heaton and Sheppard (1977) suggested that large-scale hydrothermal circulation cells penetrate the crust to 3-5 km and that upflow of fluids occurs along discrete, narrow channelways.

The geometry, conditions, and extent of fluid flow in the plutonic rocks of Troodos have not been well constrained as few studies document fossil hydrothermal flow channels in these rocks. Although it has been recognized that rocks of the intrusive sequence have been affected by greenschist to amphibolite facies metamorphism (Heaton and Sheppard, 1977; Aldiss, 1978; Malpas et al., 1987; Robinson et al., 1990) little attention has been paid to the style or conditions of fluid flow in these deep-seated rocks. The intimate relationship between magmatic and hydrothermal processes at mid-ocean ridges clearly makes understanding fluid flow in this zone critical for understanding spreading ridge systems. Determination of cell geometry and the extent to which circulating fluids in different crustal levels mix has important implications for episodicity of magma chambers and chemistry of hydrothermal vents.

CHAPTER II

GEOLOGY

2.0 INTRODUCTION

The Troodos massif dominates the geology of Cyprus, constituting approximately one third of the island. It is the western-most ophiolite in the circum-Arabian ophiolite belt, which forms an arcuate band along the northern coast of the Mediterranean sea (Fig. 1.1). The Troodos ophiolite is bordered to the northeast by the Mesaoria Plain and Kyrenia Range, and to the south and southwest by the Mamonia Complex (Fig. 1.2). The reader is referred to other studies for additional information on the geology of the adjacent terrains (Cleintauer et al., 1977; Robertson and Woodcock, 1980; Xenophontos et al., 1987; and Robinson et al., 1990).

2.1 The Troodos Ophiolite

The Troodos complex has been taken as a type example for ophiolites and studies of this complex and related ophiolites have affected many of the ideas concerning crustal evolution and the geometry of magma chambers at mid-ocean ridge spreading centers (Casey and Karson, 1981; Pallister and Hopson, 1981). It forms an uplifted elongate dome in which the stratigraphically deepest plutonic rocks occur at the center (Fig. 2.0). In the core of the complex, tectonized harzburgite and serpentinite are overlain by highly deformed layered and transitional ultramafic rocks. These cumulates, in turn, are intruded by a later undeformed plutonic suite of pyroxenite, two-pyroxene gabbro, and hornblende gabbro (Malpas et al., 1987; Robinson et al., 1990). Mg-rich gabbro, diorites, and plagiogranites form discontinuous pods and screens in the upper level plutonic sequence. The upper-level plutonic rocks are overlain by an extensive sheeted dike complex which passes upward into the extrusive section, forming the flanks of the massif.

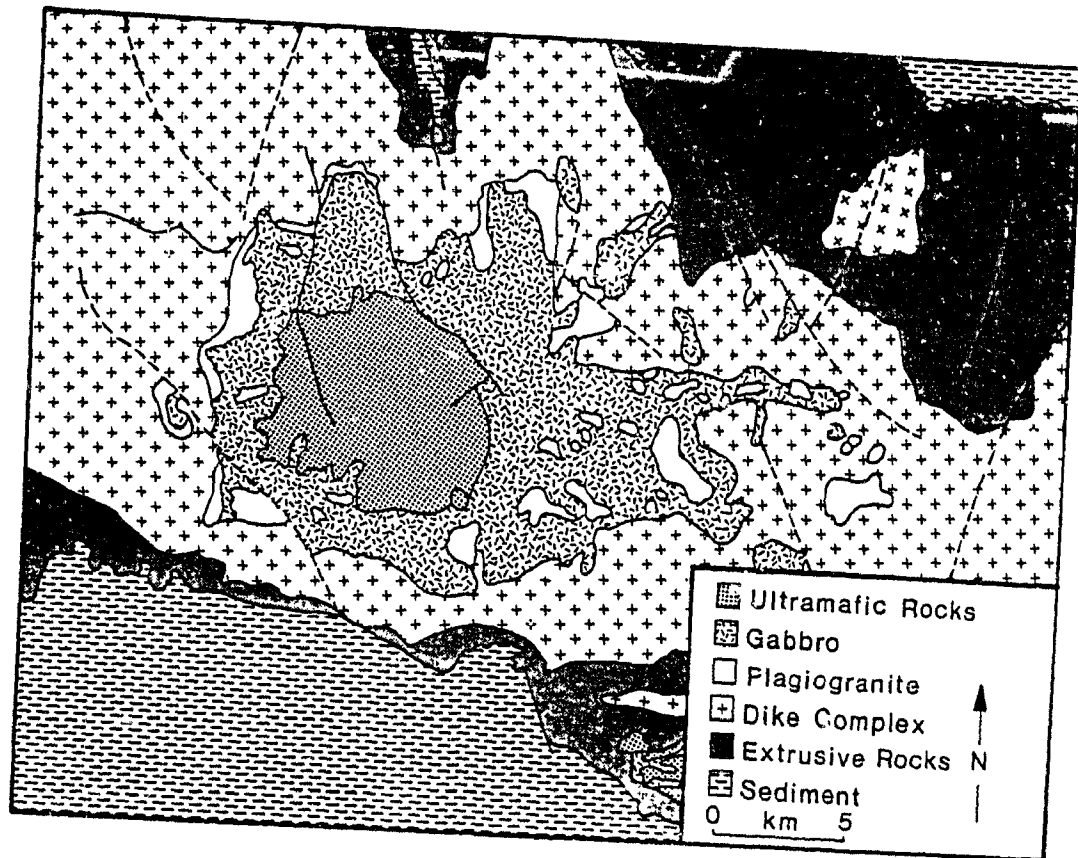


Figure 2.0 Generalized geologic map of part of the Troodos ophiolite, including area of study.

The Troodos massif was originally thought to represent "normal" mid ocean crust (Moore and Vine, 1971), however, subsequent workers have suggested formation of the ophiolite in a mature island arc setting (Ewart and Bryan, 1972; Miyashiro, 1973), a marginal or backarc basin (Pearce, 1975; Smewing, 1975; Saunders et al., 1980), and an incipient arc or fore-arc environment (Robinson et al., 1983; Moore et al., 1984; Rautenschlein, 1985; Thy et al., 1985). Uranium-lead isotopic ages of plagiogranite-hosted zircon indicate crystallization ages of 90.3 ± 0.7 and 92.4 ± 0.7 Ma. (Mukasa and Ludden, 1987). These ages are in good agreement with radiolarian ages (89-91 Ma.); Bloom and Irwin, 1985), but are older than K-Ar, and Rb-Sr dates of whole rocks and mineral separates (75-86 Ma., Delaloye and Desmet, 1979; Staudigel et al., 1986). Moore et al. (1984) suggest that the ophiolite was emplaced and rotated during collision of the Tethyan spreading centers with Africa.

2.1.1 Extrusive Sequence

The extrusive section, composed of pillow lavas, sheet and massive flows, flow breccias, and hyaloclastites, forms a 200-2000 m thick sequence which flanks the massif. On the basis of secondary mineral assemblages, color, and the location of ore deposits, the sequence was initially divided into two units; the Upper Pillow Lavas (UPL) and Lower Pillow Lavas (LPL) (Fig. 2.1, after Gillis, 1986). These divisions were subsequently redefined on the basis of alteration mineralogy into an axis sequence including the Lower Pillow Lavas and sheeted dike complex, and the off-axis sequence, comprising the Upper Pillow Lavas (Gass and Smewing, 1973).

Recent geochemical analyses of fresh volcanic glasses, in conjunction with detailed mapping, indicate the presence of at least three geochemical suites within the extrusive sequence, which overlap with previously defined stratigraphic boundaries (Fig. 2.1; Robinson et al., 1983; Schminke et al., 1983; Gillis and Robinson 1985; Gillis, 1986; Mehegan, 1988). The basal unit consists of an andesite - dacite - rhyodacite assemblage with arc tholeiite affinity, which is composed of numerous lithologic units

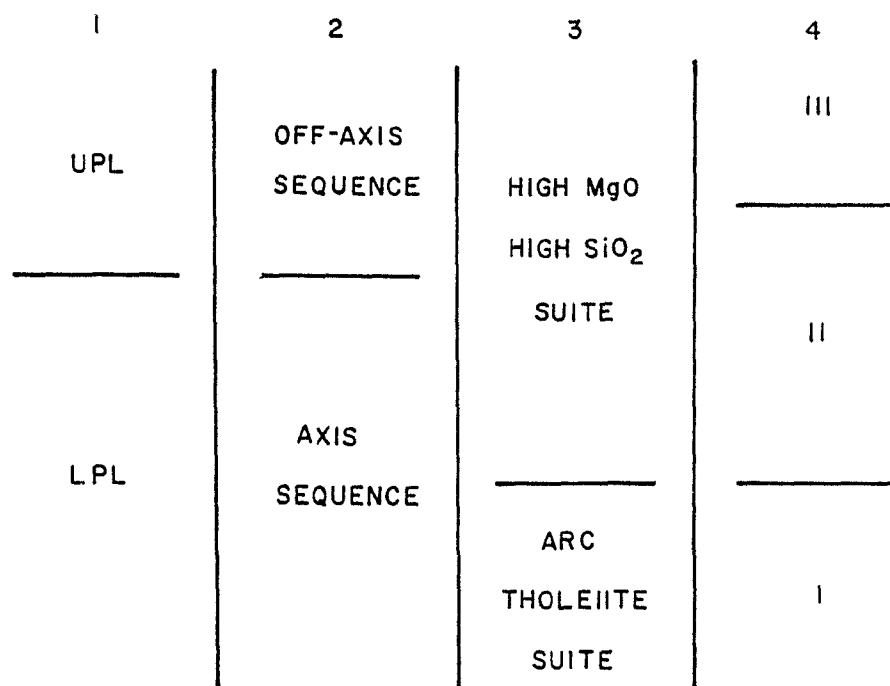


Figure 2.1 Schematic stratigraphic column illustrating divisions of the extrusive sequence (after Gillis, 1986). 1. Bear (1960), Gass (1960) 2. Gass and Smewing (1973) 3. Robinson et al., (1983) 4. Gillis (1986)

including clinopyroxene- and plagioclase-phyric lavas. Dikes which cut this lower sequence increase in abundance with depth. A picrite - basalt- andesite assemblage with depleted arc tholeiite affinity constitutes the upper suite of lavas. These are olivine- and clinopyroxene-phyric units with basalt- to basaltic-andesite compositions. The predominance of picritic lavas in the upper part of the extrusive section suggests they were derived from the lower parts of a fractionated magma chamber (Robinson et al., 1990).

2.1.2 Sheeted Dike Complex

The sheeted dike complex, separating the extrusive rocks from the plutonic sequence, is 1-1.5 km thick (Fig. 2.0). The transition zone between pillow lavas and dikes occurs rapidly over a distance of 10's of meters (Baragar et al., 1989), whereas the transition between the sheeted dikes and gabbros is more complex and variable. Near the base of the transition zone gabbros and plagiogranites are cut by, and cut, dikes. Dikes range from a few cm to 10 m wide, but most are 1-2 meters (Baragar et al., 1989; Robinson et al., 1990). They are dominantly aphyric but may contain sparse phenocrysts of plagioclase and clinopyroxene ($\pm$ pseudomorphs after olivine). The intensity of dike alteration is highly variable, but most commonly the rocks are altered to greenschist and lower amphibolite facies assemblages. Epidosite zones within the sheeted dikes (Fig. 2.2) are thought to represent focused zones of hydrothermal upflow which fed surficial hydrothermal vents (Richardson et al., 1987; Schiffman and Smith, 1988). The dike compositions closely match those of the volcanic glasses, suggesting the dikes were derived from similar magmas (Baragar et al., 1987; Baragar et al., 1989). Domains with dikes of similar orientation within the sheeted complex, which are bounded by listric and normal faults, are believed to represent relict axial grabens similar to those formed at modern slow-spreading ridges (Varga and Moores; 1985; Moores et al., 1987).



Figure 2.2 Epidosite zones in sheeted dike complex. Cores of dikes are altered to epidote and rimmed by a chlorite-rich zone (outcrop on road to Kykko Monastery).

2.1.3 Plutonic Complex

The plutonic rocks of the Troodos ophiolite form the core of the complex. On the basis of crosscutting relationships and relative ages of deformation two major plutonic suites have been recognized (Malpas et al., 1987; Malpas et al., 1989). The early suite consists of highly deformed tectonized harzburgite, dunite, olivine pyroxenite and gabbro. Deformation has resulted in the development of penetrative L-S fabrics, isoclinal folds, and transposition of layering parallel to the tectonite fabric (Malpas et al., 1987; Robinson et al., 1990). Intrusions of undeformed peridotite, two-pyroxene gabbro, hornblende gabbro, diorite and plagiogranite, which post-date the older suite, indicate that the high temperature deformation probably occurred near the ridge axis as a result of upward and lateral migration associated with spreading (Malpas et al., 1987; Malpas and Robinson, 1987). Mutually intrusive relationships between and within the intrusive suites provide strong evidence for the presence of multiple magma chambers beneath the Troodos paleospreading axis (Malpas et al., 1989). On the basis of pyroxene compositions and the relationship of dike contacts to the upper intrusive sequence, Malpas and Robinson (1987) suggest the early plutonic suite is correlative with the arc-tholeiite suite of the lower extrusive sequence, whereas the later suite tentatively correlates with the high-Mg, high-SiO₂ lavas of the upper extrusive sequence.

The early plutonic suite is dominated by pervasively serpentinized tectonized harzburgite. The harzburgite is a massive, coarse-grained rock with 70-85% olivine, 15-30% orthopyroxene forming elongate aggregates throughout the harzburgite, and traces of spinel and clinopyroxene (George, 1978). Small pods and lenses of dunite enclosed in the harzburgite contain 95-100% olivine, a trace to 5% chromite, and trace amounts of clinopyroxene. Chromite is concentrated near the harzburgite-dunite contact where it occurs as disseminated grains, massive chromite, and deformed lenses (George, 1978; Malpas and Robinson, 1988). Interaction between meteoric water and the harzburgite and dunite bodies resulted in pervasive partial serpentinization (40-100%).

Units of wehrlite, dunite, lherzolite and harzburgite mark the transition zone between the tectonized harzburgite and gabbro cumulates. A sequence of melagabbros, olivine-rich to olivine-poor gabbros, and pyroxene gabbros overlies the ultramafic rocks (Robinson et al., 1990). A notable feature of the two-pyroxene gabbros is that they commonly contain plagioclase-hosted primary fluid inclusions associated with zones of glass inclusions. These inclusions are concentrated in the cores of grains and mimic grain boundaries (Fig. 2.3). Distribution of the gabbros varies throughout the plutonic section; however amphibole-rich and varitextured gabbros are more common near the upper parts of the section. Field sampling for this study concentrated on the later, undeformed varitextured gabbros, hornblende gabbros, magnetite-hornblende gabbros, diorites and plagiogranites (Fig. 2.4, Table I).

2.1.4 Upper Level Plutonic Rocks

Intrusive relationships within the plutonic sequence are complicated and variable. Gabbro intrudes gabbro and plagiogranite, plagiogranite intrude gabbro and dikes (Fig. 2.5), and dikes cut gabbros and plagiogranites (Fig. 2.6). Intrusive bodies may have chilled margins and or alteration haloes, but such features are not always present (Fig. 2.7). Pegmatitic veins and patches in the varitextured gabbros are common as are quartz-rich pods and veins. These felsic zones are thought to be due to the segregation of silica-rich residual fluids from a crystal mush (Aldiss, 1978). Alteration minerals in all the gabbros commonly exhibit disequilibrium textures

2.1.4.1 Upper Level Gabbros

The upper level gabbros are massive, coarse-grained rocks (Fig. 2.8) which commonly contain large pegmatitic patches composed dominantly of uralitized clinopyroxene and plagioclase, with lesser amounts of quartz and magnetite (Fig. 2.9, Fig 2.10). The plagioclase grains commonly exhibit complex oscillatory zoning, although unzoned crystals are present as well. Plagioclase grain boundaries in the finer-grained gabbros exhibit resorption textures and may be rimmed by fine-grained anhedral quartz.



Figure 2.3 Primary fluid inclusions associated with glass inclusions in two-pyroxene gabbro (Sample CY1017.65). Inclusions are concentrated in the cores of plagioclase grains and inclusion-rich bands mimic grain boundaries. Scale bar is equal to 50 microns.

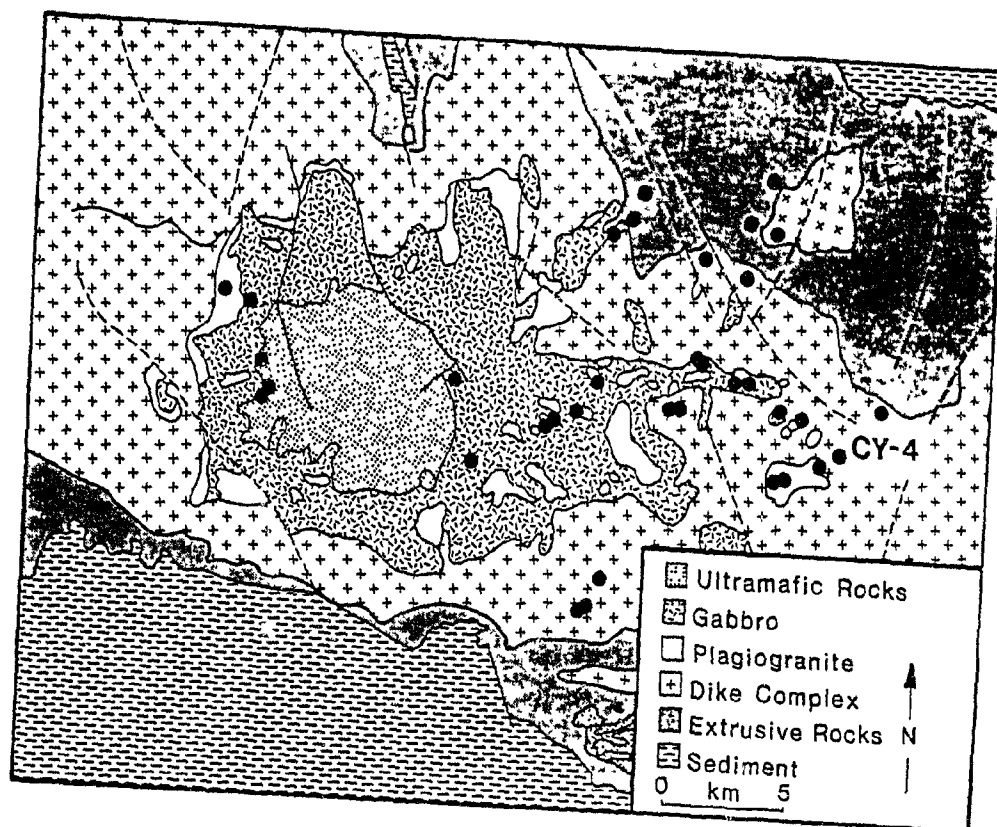


Figure 2.4 Location of samples used in this study.

TABLE I
PETROGRAPHY OF TROODOS SAMPLES

SAMPLE	DESCRIPTION	MINERALOGY	MODE%	SAMPLE	DESCRIPTION	MINERALOGY	MODE%
CY87-1	Plagiogranite Feldspars are highly altered and commonly replaced by Qtz. Cpx occurs minor interstitial phase. Rare diabase xenoliths are highly resorbed.	Feldspar Quartz Cpx Epidote Opaques	53.2 32.2 2.1 11.7 Trace	CY88-58	Amphibole Gabbro Fibrous pale-green to light-brown amphibole forms coarse-grained patches which completely enclose fine-medium grained feldspar. Feldspars are very fresh and exhibit a weak preferred orientation.	Amphibole Feldspar	56.0 44.0
CY88-5	Plagiogranite Highly altered feldspars form poorly developed granophyric intergrowths with Qtz. Secondary Qtz replacing feldspars is common. Chlorite and opaques replace cpx. Sample is cut by epidote veinlet.	Feldspar Quartz Epidote Chlorite Opaques	41.8 34.4 7.8 9.4 6.6	CY88-78	Quartz Vena in Gabbro Cockscomb undeformed quartz forms radiating coarse-grained patches surrounded by finer-grained quartz. Epidote-rich pods are rare. Vein cutting upper level gabbro is 27 cm in width.	Quartz Epidote Opaques	96.5 2.2 1.3
CY88-9	Podiform Epidosite Relict feldspars are pervasively altered. Qtz completely encloses laths forming Qtz-rich patches. Locally only Qtz + epidote are present. Epidote forms pods up to 3 cm in diameter.	Feldspar Quartz Epidote Opaques	15.9 50.1 33.9 Trace	CY1017.62	Two-pyroxene Gabbro Fine-grained opx contains exsolution lamellae of cpx and occurs as fine-grained inclusions in feldspar. Fine-grained cpx forms rare interstitial phase. Feldspars exhibit a weak preferred orientation and contain abundant glass and fluid inclusions.	Feldspars Orthopyroxene Clinopyroxene Opaques	77.0 17.2 5.8 Trace
CY88-17	Uratitized Gabbro Coarse-grained gabbro containing moderately altered feldspars. Fibrous amphibole after cpx is common, forming coarse patches. Relict cpx is rare. Quartz and epidote occur as isolated pods.	Feldspar Amphibole Quartz Epidote Cpx	55.0 32.2 7.3 3.4 2.1	CY1181.75	Gabbro-hosted pegmatite vein Coarse-grained hydrothermal clinopyroxenes contain abundant vapor inclusions. Brown and pale green amphibole is intergrown with cpx and occurs inclusions in cpx. Feldspars are zoned and associated with quartz-rich patches.	Amphibole Clinopyroxene Quartz Feldspar Opaques	39.1 26.9 22.0 10.0 2.0
CY88-36	Plagiogranite Med.- coarse-grained feldspars are highly zoned and exhibit little alteration. Anhedral Qtz grains exhibit undulatory extinction. Fine-grained opaques are commonly associated with dark green amphiboles. Highly resorbed diabase xenoliths containing amphibole and epidote are common.	Feldspar Quartz Amphibole Opaques Epidote	46.8 35.6 10.2 5.2 2.2	CY88-77	Plagiogranite Altered plagioclase from mod-well developed granophyric intergrowths with Qtz. Fine- to med.-grained amphibole is commonly associated with opaques. Fine veinlets of epidote cut sample	Feldspar Quartz Amphibole Epidote Opaques	41.9 36.5 17.5 1.4 2.7
CY88-39	Plagiogranite Zoned, moderately altered feldspars form well-developed granophyric intergrowths with quartz. Replacement of feldspars by Qtz + epidote is common. Blue-green amphibole associated with opaques form fibrous patches. Sample is cut by epidote veinlet.	Feldspar Quartz Epidote Amphibole Chlorite Opaques	46.9 42.5 2.4 4.5 2.0 Trace	CY10N.16	DIABASE Plagioclase is highly-altered. Fibrous amphibole- and chlorite-rich pods are associated with opaques. Fine epidote veinlets cut sample.	Feldspar Quartz Amphibole Chlorite Opaques	49.6 10.6 13.9 12.0 12.9



Figure 2.5 Plagiogranite intruding moderately deformed gabbro (road outcrop east of Khandria village).

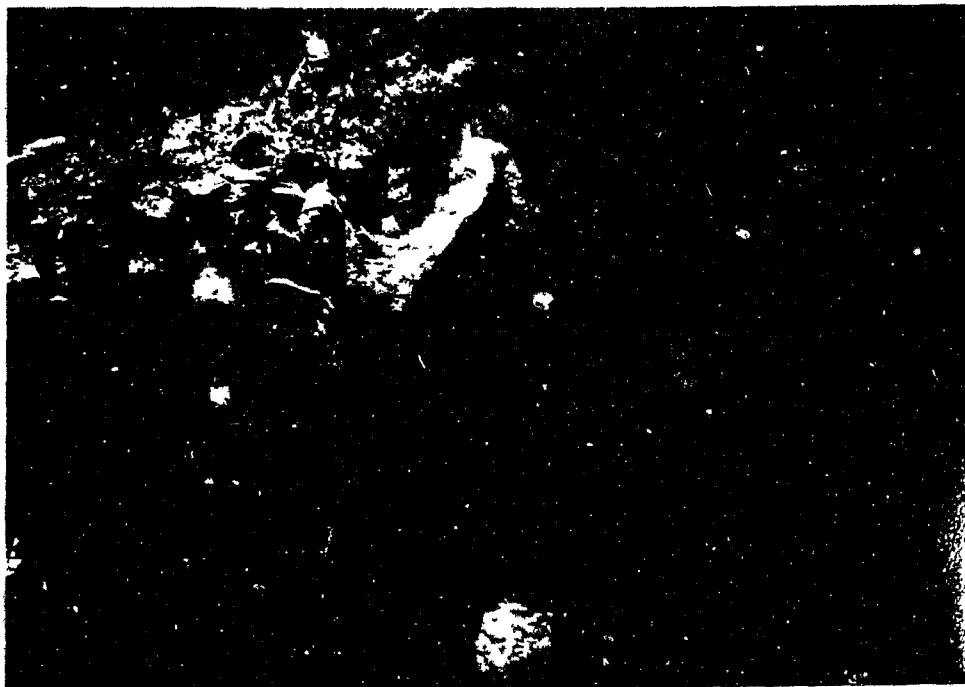


Figure 2.6 Large block of plagiogranite cut by dikes (outcrop on road N.E. of Zoopiyi village). Dike on right is .6 m in width.



Figure 2.7 Alteration halo rimming plagiogranite veinlet shooting off from main intrusive body. Plagiogranite is intruding an older layered and moderately deformed gabbro. Plagiogranite contains highly resorbed fine xenoliths of more mafic material. Brine-dominated, hematite-bearing fluid inclusions are abundant in the plagiogranite. Sample location for CY87-1 (outcrop on road east of Khandria village).

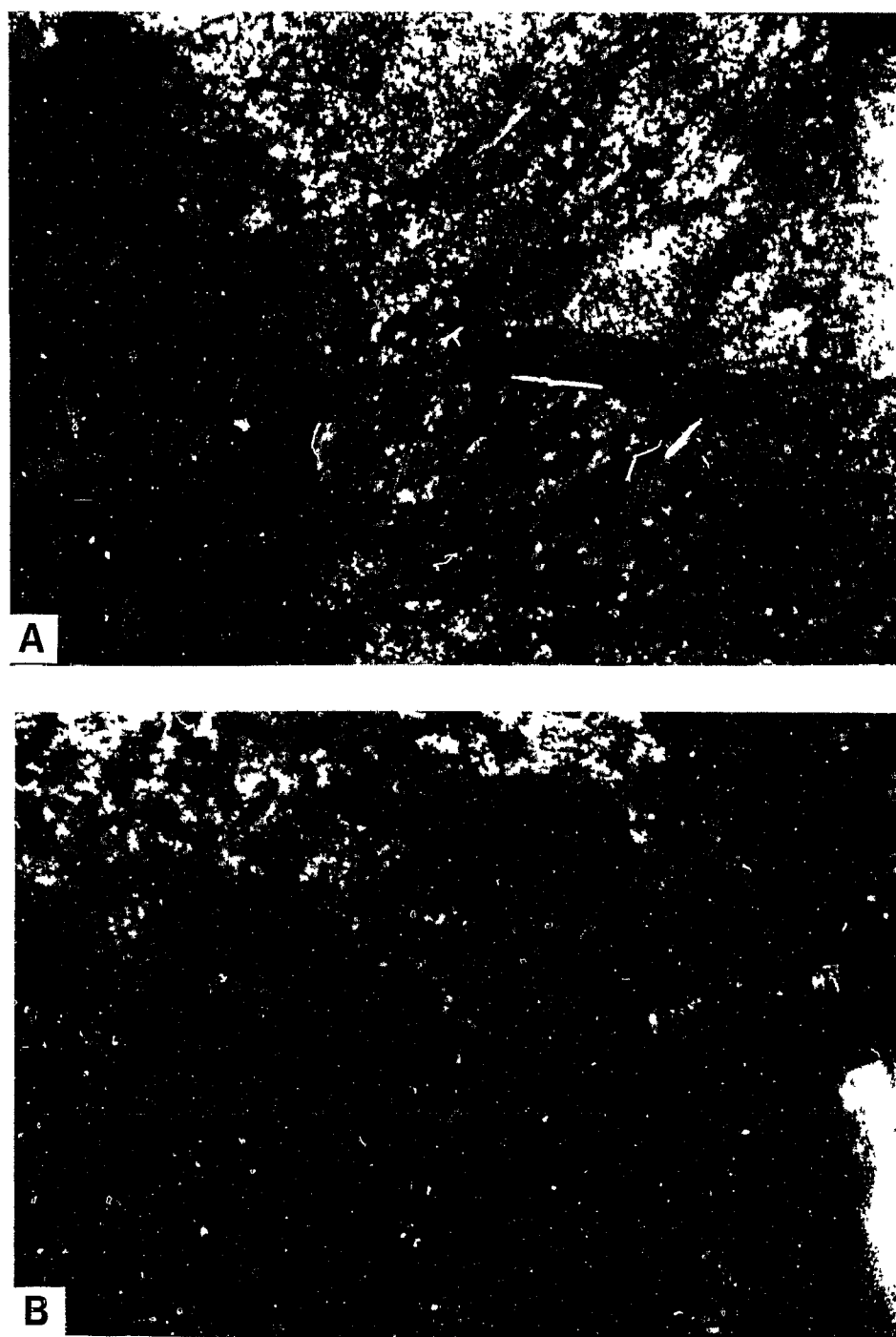


Figure 2.8 (A) Varitextured pegmatitic gabbro composed of coarse-grained uralitized clinopyroxene and plagioclase, with lesser amounts of quartz and magnetite (outcrop is on small ridge overlooking Pano Amiandos asbestos mine). (B) Close up of varitextured gabbro adjacent to plagiogranite body (outcrop is on Kykko Monastery road).



Figure 2.9 Massive gabbro containing mats of fine-grained amphibole and plagioclase. Field of view is 8 mm across. Sample CY88-58.

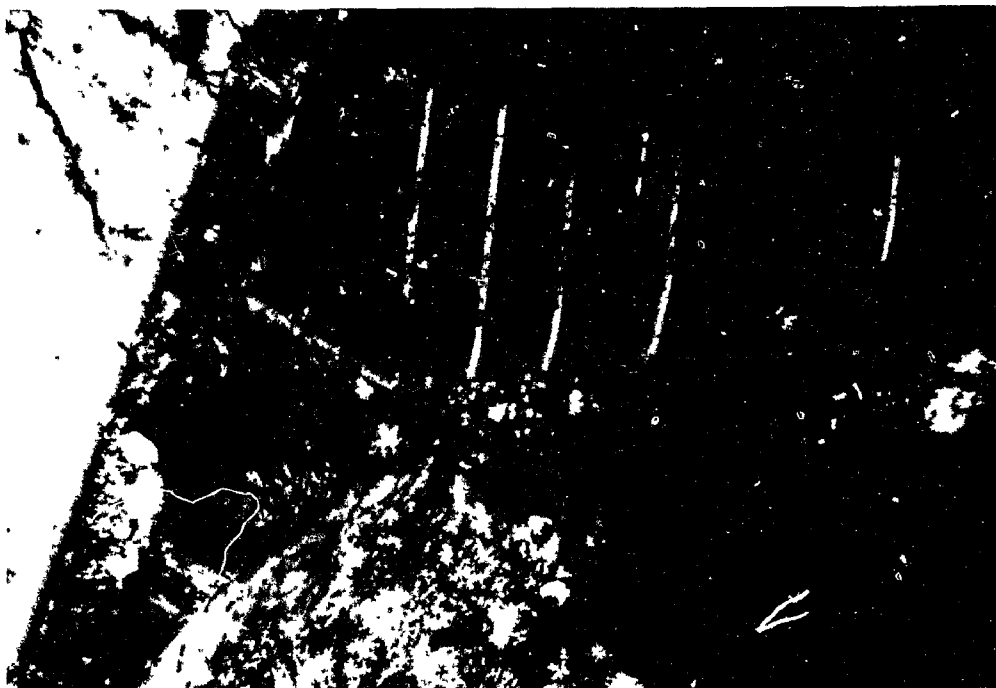


Figure 2.10 Clinopyroxene altered to fibrous amphibole bordering coarse-grained zoned plagioclase. Fine-grained secondary quartz is disseminated along grain boundaries. Field of view is 4 mm across.

Clinopyroxenes are extensively altered to fine-grained, pale-green to colorless fibrous amphibole and coarse-grained actinolite, and less commonly rimmed by brown amphibole. Some clinopyroxenes, which contain complex intergrowths of olive-green to brown-green amphibole, are rimmed by high calcium, hydrothermal clinopyroxene. These pyroxenes are distinctive in that they always contain abundant primary vapor-rich fluid inclusions. Exsolution lamellae of opaque minerals are ubiquitous in the clinopyroxenes. Fine-grained, interstitial quartz is disseminated throughout the gabbros. The quartz grains commonly contain secondary(?) brine-rich fluid inclusions and secondary liquid-dominated inclusions. Localized pods and veinlets of clinozoisite and epidote after plagioclase are abundant in the pegmatitic and finer grained gabbroic rocks. Rare interstitial patches of chlorite after clinopyroxene and amphibole occur between plagioclase and clinopyroxene. Anastomosing veinlets of smectite(?) form the latest vein networks.

The magnetite gabbros are massive medium-grained rocks which contain abundant clinopyroxene, plagioclase, magnetite, and variable amounts of quartz (Fig. 2.11). The clinopyroxenes are commonly replaced by concentrated mats of fine-grained amphibole, and coarser-grained actinolite along grain boundaries. Clinopyroxenes have a mottled appearance due to exsolution of oxides. Plagioclase grains exhibit oscillatory zoning and undulatory extinction, and are partially enclosed by pyroxene. Discontinuous veinlets of fibrous amphibole, and less commonly chlorite, cut some plagioclase grains. Complex microfractures in plagioclase, lined with liquid-dominated fluid inclusions, are pervasive in some samples. Interstitial granophyric intergrowths of quartz and plagioclase are locally abundant, as is secondary quartz rimming plagioclase grains. Magnetite forms subhedral to anhedral, coarse- to medium-grained crystals, which comprise 5-10 modal percent of the gabbros.

Pegmatitic gabbro veins containing hydrothermal clinopyroxene, quartz, amphibole, plagioclase, and magnetite commonly cut both undeformed and deformed

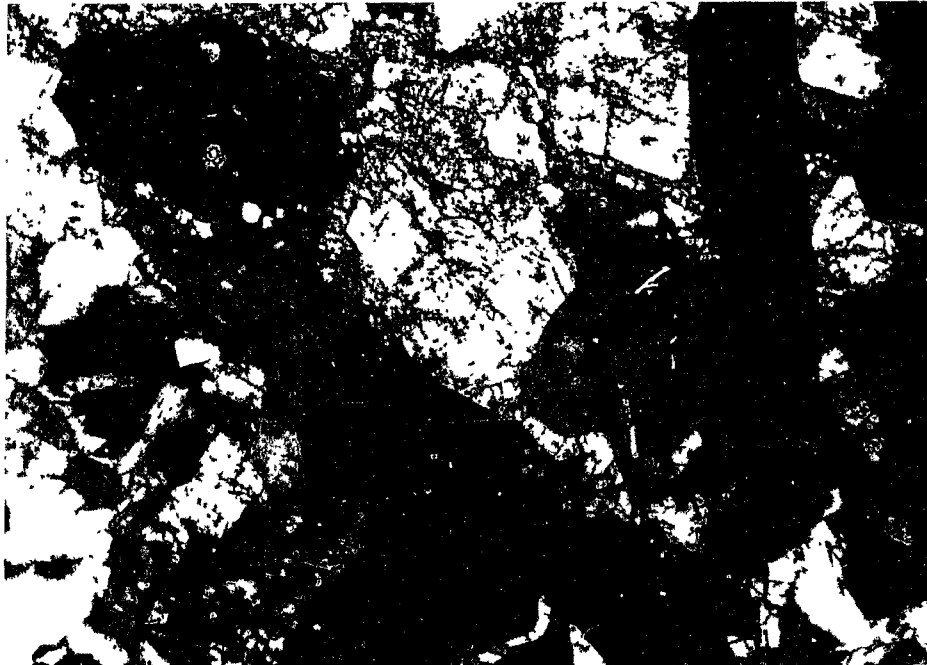


Figure 2.11 Magnetite gabbro containing coarse-grained plagioclase, fibrous amphibole, and magnetite. Microfractures are lined with liquid-dominated fluid inclusions. Field of view is 8 mm. Sample CY88-1.

gabbro (Fig. 2.12). Widths of pegmatite veins are variable, but zones 10 cm wide and extending for several meters are common. The pegmatites may exhibit gradational contacts with their finer-grained gabbroic host. In some areas, fine-grained gabbroic layers grade into coarser-grained gabbro, ending in pegmatitic zones. The pegmatite, in turn, is abutted by an abrupt transition to finer-grained gabbro. This cycle is repeated 2-3 times and may represent volatile fluxing where the pegmatitic zones form during build up of residual fluid. Brine-rich fluid inclusions are abundant in quartz, and less common in hydrothermal clinopyroxene in these veins. Vapor-dominated inclusions are ubiquitous in the clinopyroxenes.

2.1.4.2 Diorites and Plagiogranites

In the upper level plutonic sequence plagiogranites and diorites occur as a series of discontinuous veins, screens (Fig. 2.13), and cupolas (Fig. 2.14) which form part of the roof assemblage. Spatial-compositional relationships of the plagiogranites in Cyprus are thought to indicate formation by low-pressure fractional crystallization of the more mafic melts (Malpas et al., 1989). Extensive compositional and mineralogical modification of the plagiogranites has occurred in some areas, resulting from assimilation of stopped, hydrothermally altered diabase (Malpas et al., 1987). Xenoliths commonly show high degrees of resorption (Fig. 2.15) and locally approach a dioritic composition (Malpas et al., 1989). Zones of mixing between mafic and felsic melts occur locally (Fig. 2.16).

Plagiogranites sampled include fresh and highly altered tonalites, trondhjemites, and quartz diorites. The plagiogranites consist predominantly of fine- to medium-grained plagioclase, quartz, and epidote, with lesser amounts of clinopyroxene, amphibole, sphene, chlorite, and opaque minerals (Fig. 2.17). Plagioclase typically exhibits moderately- to well-developed granophyric intergrowths with quartz and is commonly turbid and saussuritized (Fig. 2.18). The development of granophyric intergrowths in these rocks is thought to result from the simultaneous crystallization of

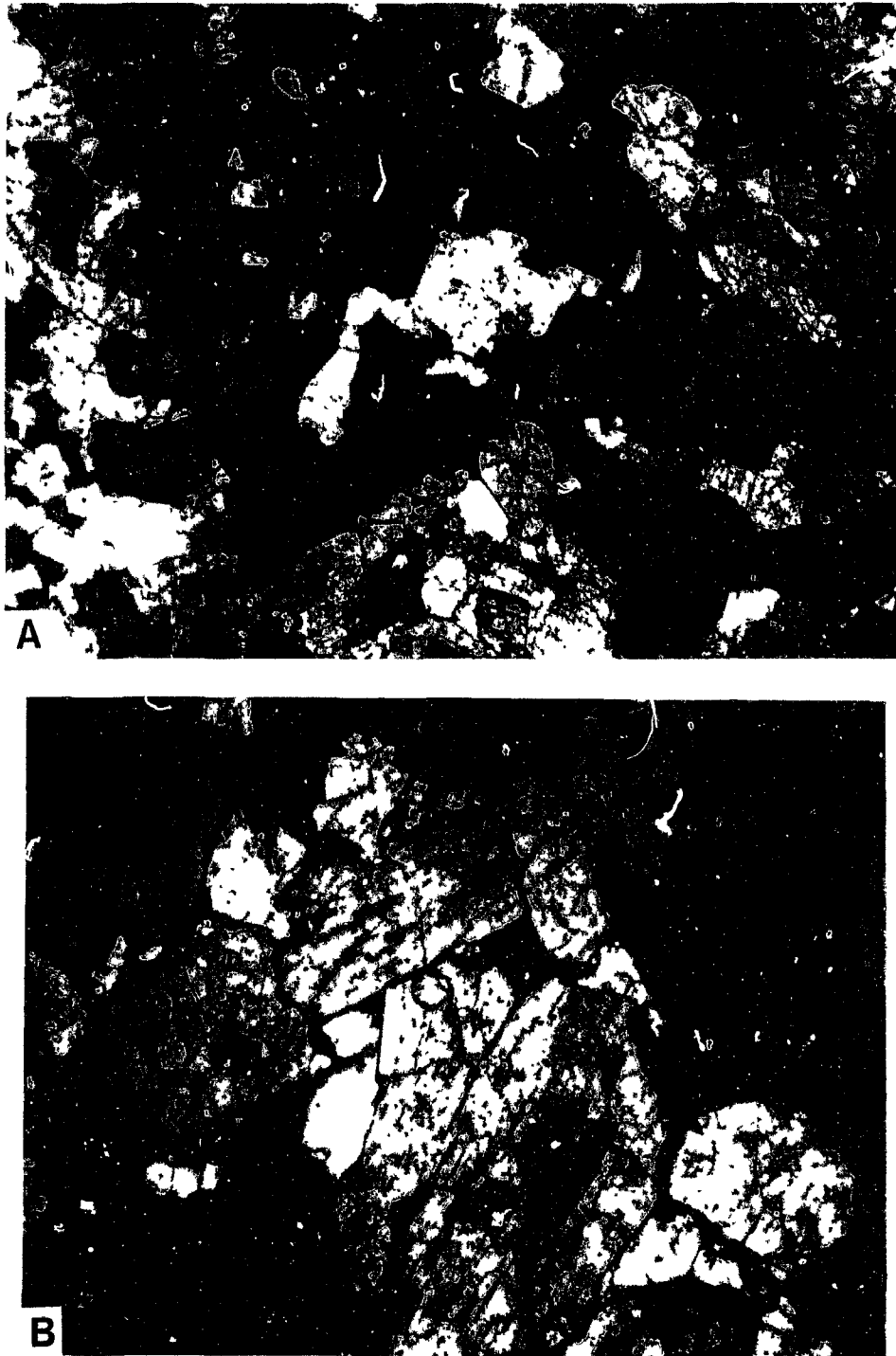


Figure 2.12 (A) Microphotograph of late stage gabbro pegmatite vein cutting undeformed gabbro. Vein is composed dominantly of amphibole, hydrothermal clinopyroxene and undeformed quartz, and lesser amounts magnetite and plagioclase. Field of view is 8 mm across (Sample CY1181.75). (B) Hydrothermal clinopyroxene in sample CY1181.75 containing abundant vapor-dominated fluid inclusions (dark blebs).

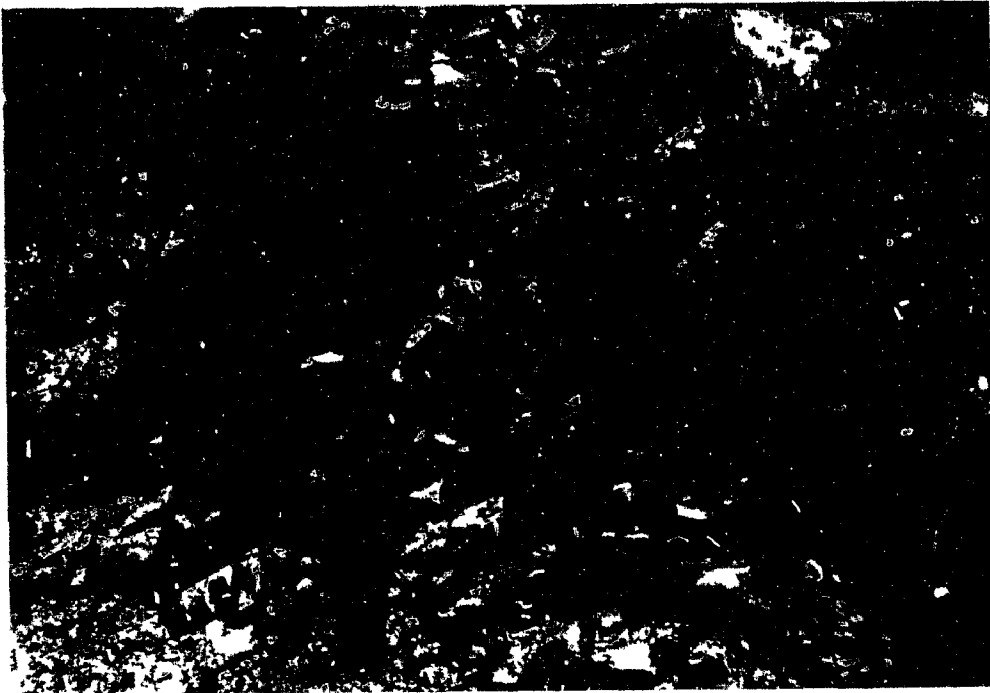


Figure 2.13 Plagiogranite cut by dikes. Average dike width is about 1 m across (road cut N.E. of Zoopiyi village).

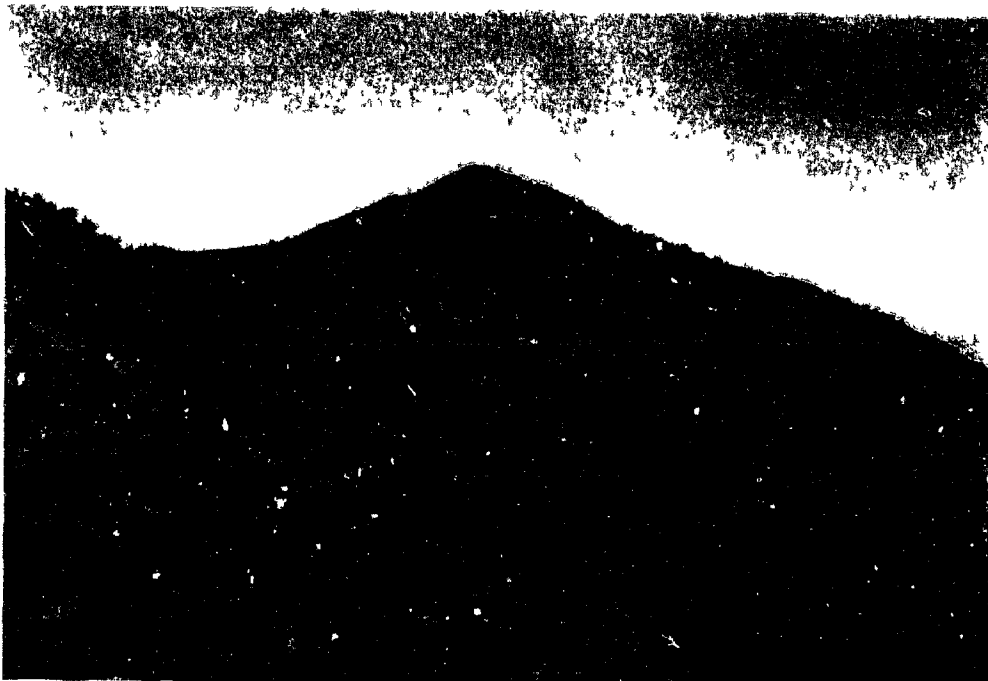


Figure 2.14 Dioritic cupola intruding overlying sheeted dike complex. The quartz-rich rocks commonly contain abundant secondary (?) brine-rich fluid inclusions. Cupola is about 500 meters across (located east of Phterykoudhi village).

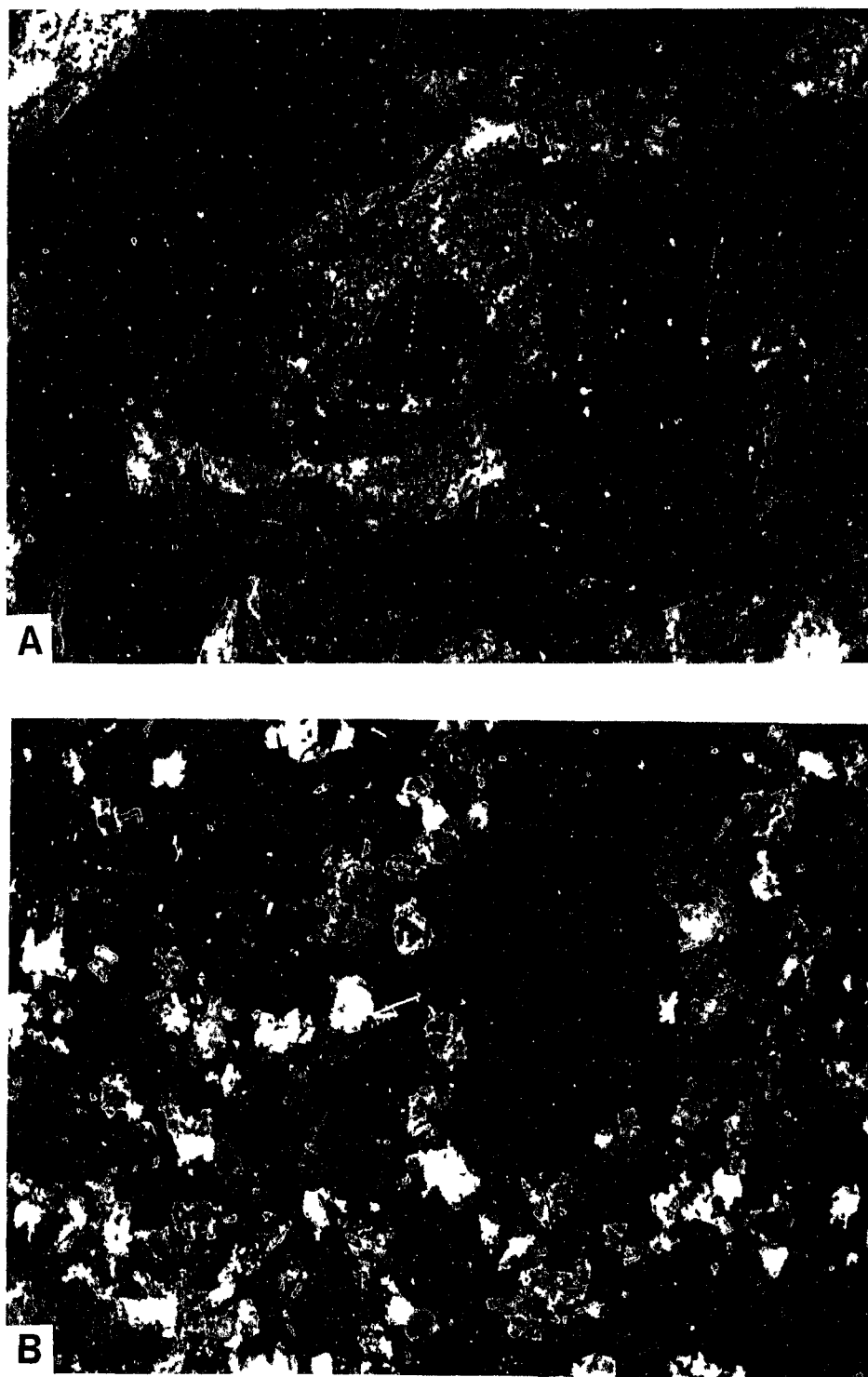


Figure 2.15 (A) Diabase xenoliths in plagiogranite (roadcut N.W. of Zoopiya village). Sample location for CY88-36 and CY88-39. (B) Microphotograph of mafic xenolith in plagiogranite (Sample C87-1). Field of view is 8 mm.



Figure 2.16 Localized zone of mixing between mafic and felsic melts (road cut N.W. of Zoopiya village).

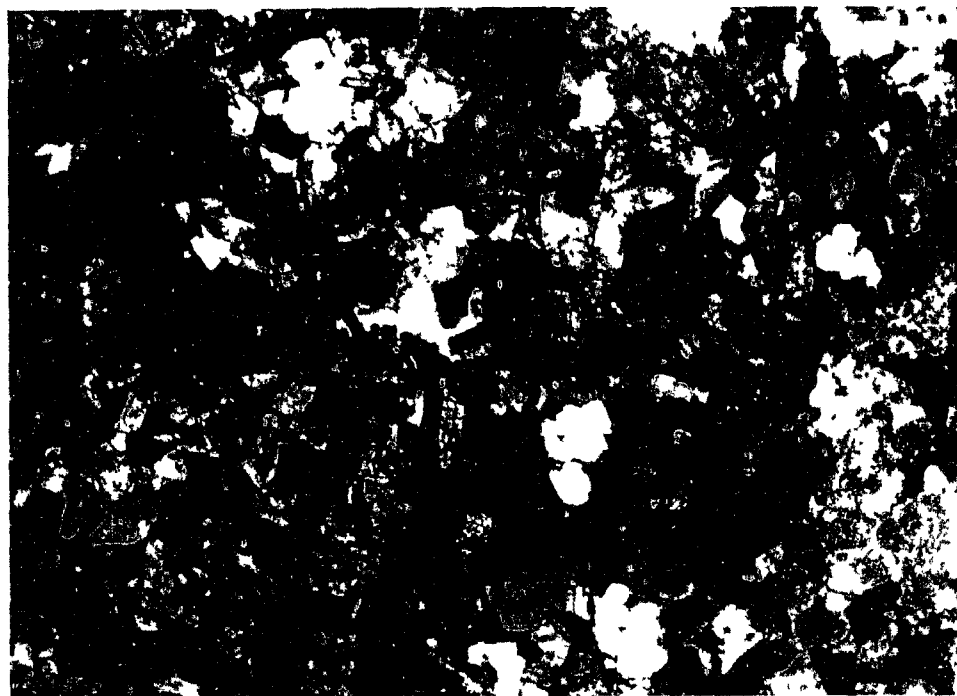


Figure 2.17 Microphotograph of plagiogranite containing turbid feldspars intergrown with quartz. Field of view is 8 mm. Sample CY88-35.

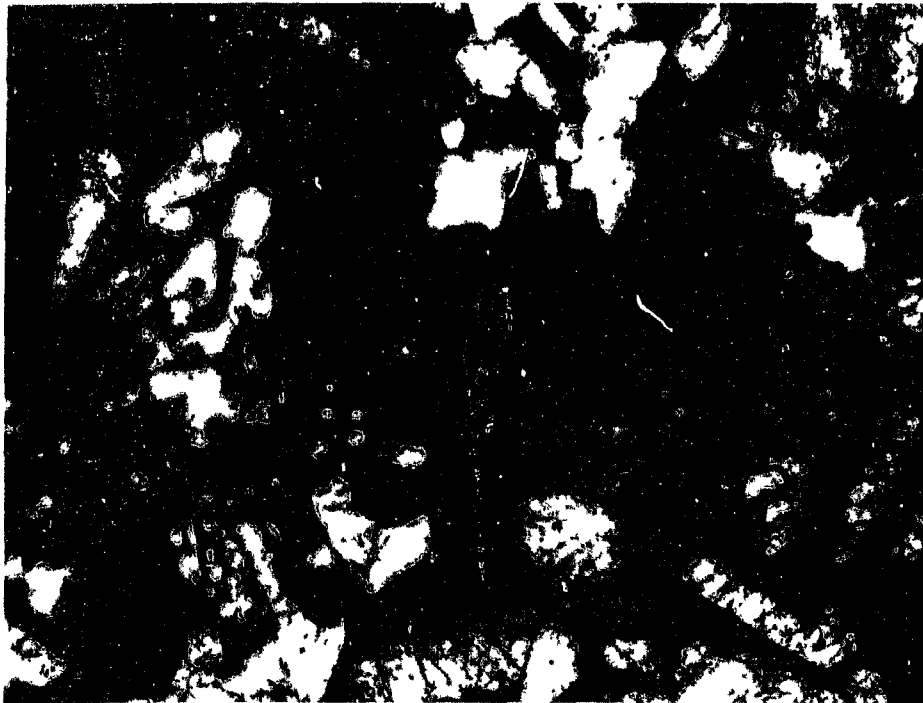


Figure 2.18 Complex intergrowths of quartz and altered feldspar exhibiting well developed granophyric texture in plagiogranite (Sample CY88-17). Field of view is 12 mm across.

quartz and feldspar from late stage, silica-enriched melts (Aldiss, 1978). Relict zoning is still preserved in some samples and many grains exhibit sieve textures in their cores, resulting from abundant inclusions of secondary epidote. Plumose and skeletal quartz is also common, as is granular secondary quartz which replaces feldspar. Rare interstitial grains of clinopyroxene are commonly altered to pale-green, fibrous amphibole. Amphibole also forms coarse-grained, blue-green to olive-green fibrous patches in the plagiogranites, and lines vein margins. Pods of chlorite, associated with fine-grained opaque minerals, form pseudomorphs after clinopyroxene and amphibole. Quartz-feldspar veins with well developed granophyric intergrowths of quartz and plagioclase and fine veinlets of epidote cut some samples (Fig. 2.19).

Diabase xenoliths within the plagiogranites are pervasively altered to fine-grained, olive-green to blue-green amphibole, and granular epidote. Feldspars in the xenoliths are turbid. Amphiboles are coarsest-grained in disseminated pods of diabase bordering less assimilated xenoliths, and near xenolith margins. Patches of interstitial anhedral quartz contain abundant liquid-dominated, and vapor-rich fluid inclusions. Fine-grained opaque minerals are abundant.

Alteration of the plagiogranites is extremely variable and heterogeneous. In the most highly altered samples, coarse-grained quartz and epidote almost completely replace primary minerals, resulting in epidiosites. The epidiosites are concentrated in shear zones (Fig. 2.20, 2.21) and also occur as localized pods (Fig. 2.22). Epidiosites in the shear zones are composed almost entirely of fine-grained masses of epidote which host very fine (< 5 micron) liquid-dominated and vapor-rich inclusions, rare euhedral quartz crystals, and contain open pore spaces (Fig. 2.23). Bordering plagiogranites are extremely altered, leached, and have a chalky white appearance. These zones are probably analogous to the epidiosites hosted in the sheeted dikes (Richardson et al., 1987; Schiffman and Smith, 1988) which are thought to represent fossilized upflow zones (Fig. 2.2). In contrast, the epidotized plagiogranite

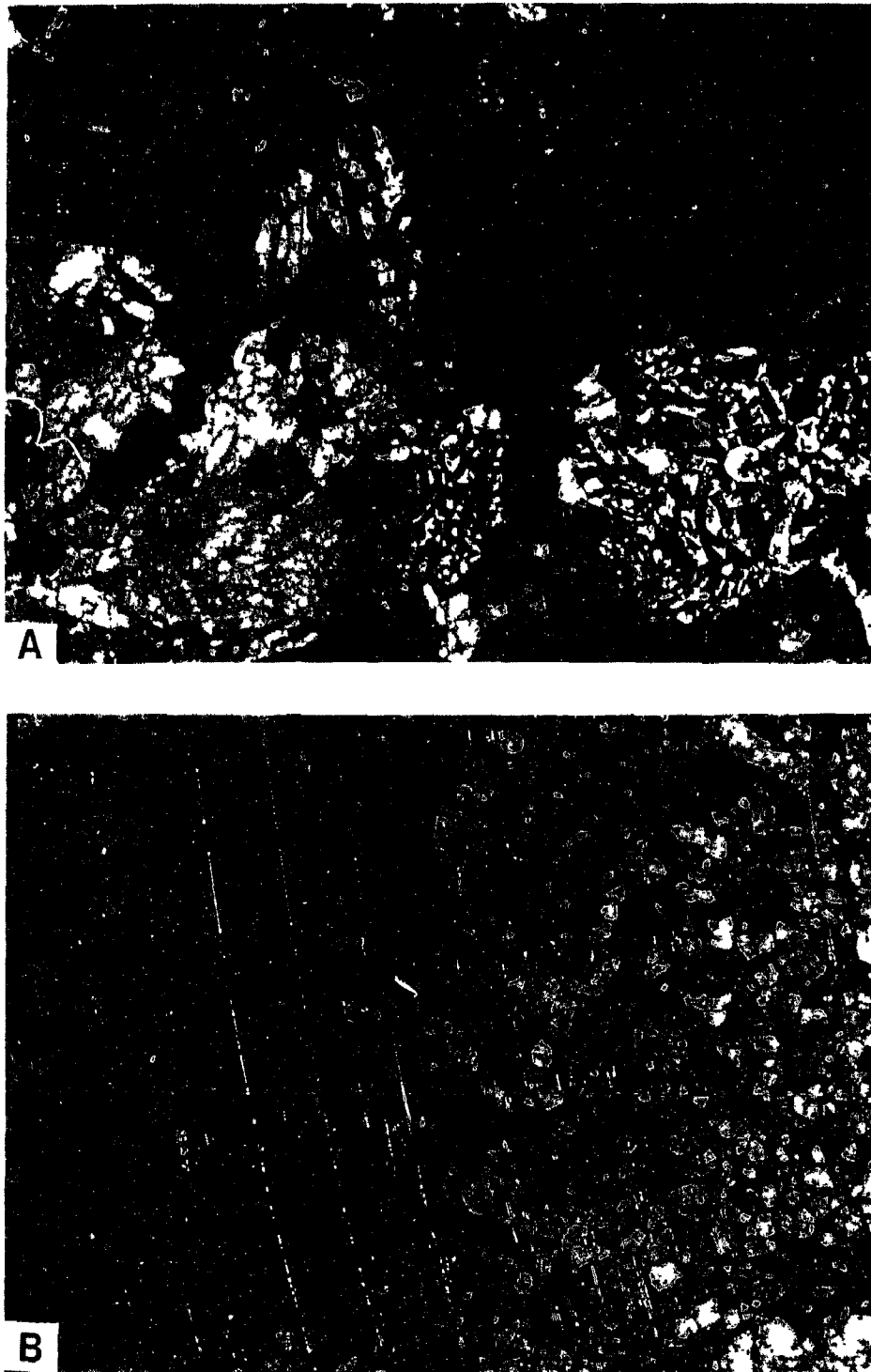


Figure 2.19 (A) Granophyric quartz-plagioclase vein in plagiogranite (Sample CY88-39). Quartz contains extremely abundant low-salinity, liquid-dominated inclusions. (B) Core of vein in plain light containing turbid feldspars and quartz. Field of view is 15 mm across.



Figure 2.20 Epidotized shear zone in plagiogranite. Plagiogranite has been completely transformed into very fine-grained epidote with minor quartz (located on Alona-Polystipos road). Sample CY88-5 is from bordering plagiogranite, which contains abundant quartz-hosted, brine-Fe-rich fluid inclusions.



Figure 2.21 Close up of epidote-rich pod in shear zone shown in Figure 2.20.

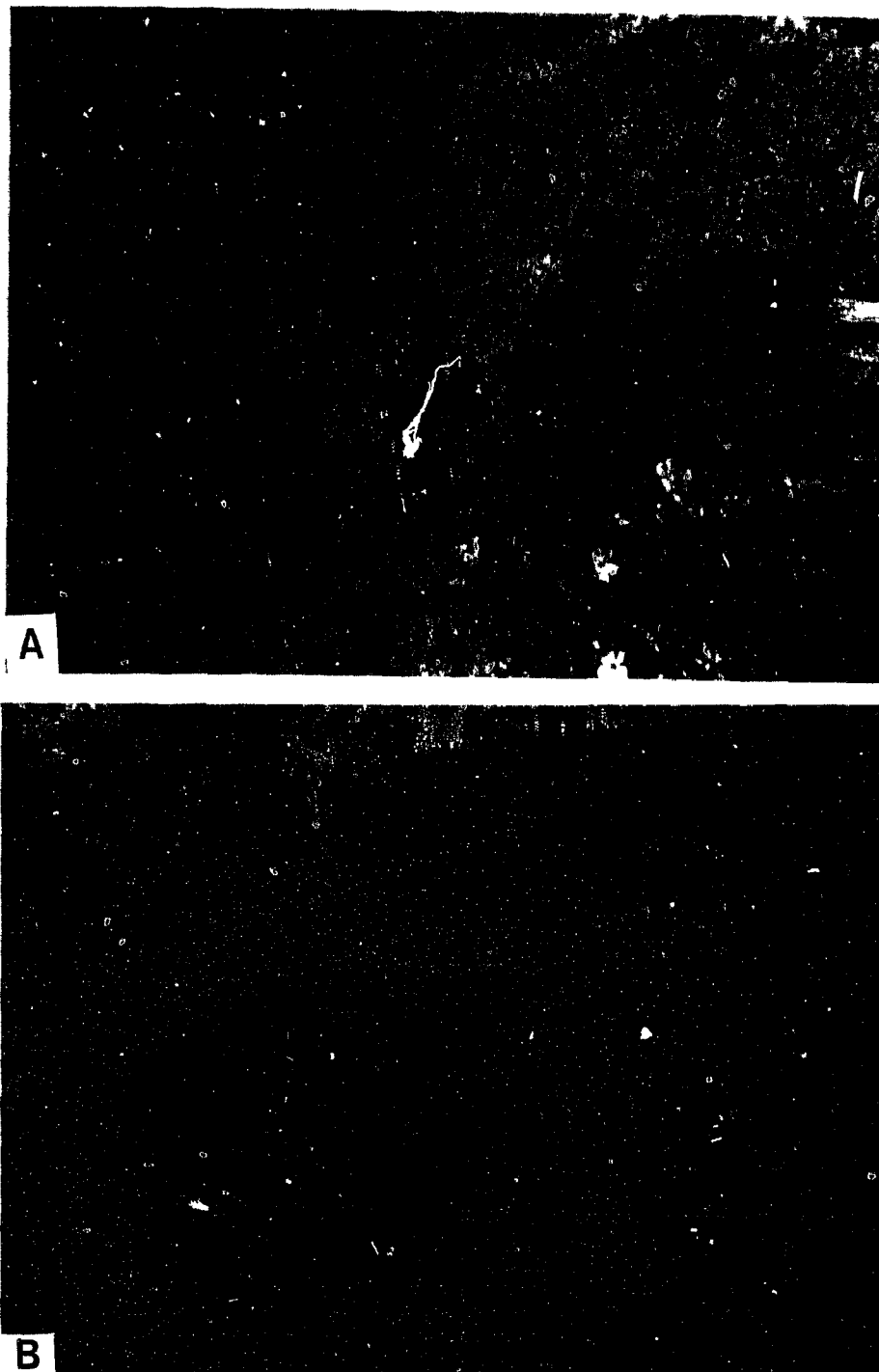


Figure 2.22 (A) Epidotized plagiogranite which contains abundant small epidote pods. The epidosite body is localized within the plagiogranite and contains areas of less altered plagiogranite in which plagioclase is still visible. Localized alteration appears to be deuteric in origin. Sample location for CY88-9, which contains 2 generations of fluid inclusions; a brine-rich ($\text{NaCl-KCl} \pm \text{CaCl}_2$), high-temperature population, and a low-temperature, low-salinity population. Epidosite body is located near Platanistasa village. (B) Close up of outcrop shown in (A).

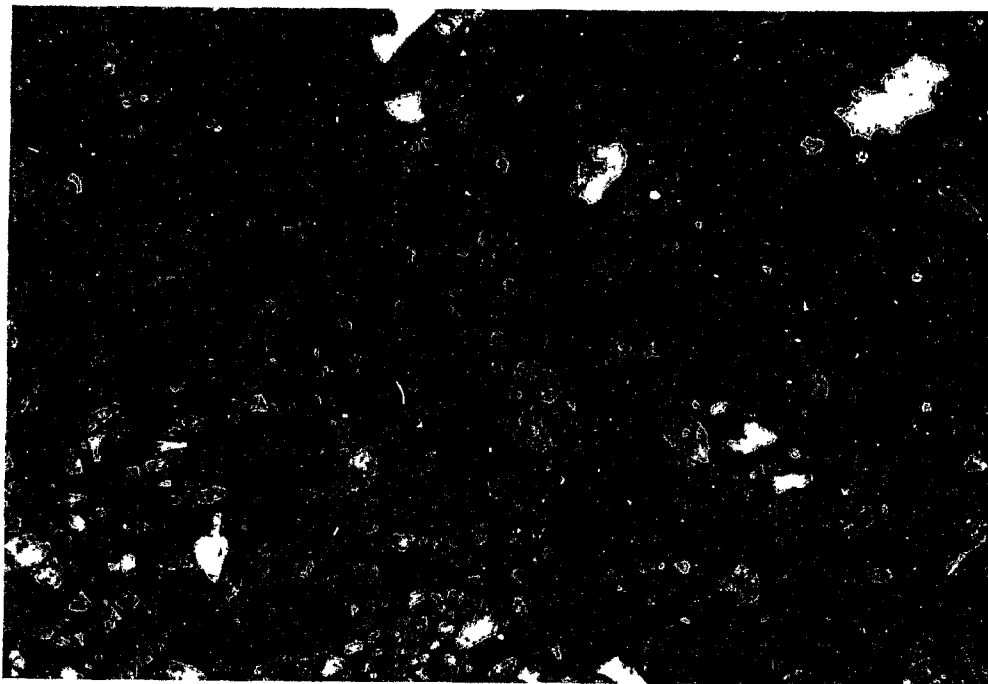


Figure 2.23 Microphotograph of epidotized shear zone sample (CY88-6). Sample contains 95% fine-grained epidote, 1-3% quartz, and 1-2% fine-grained hematite. Epidote hosts abundant vapor-rich fluid inclusions (< 5 microns in size). Field of view is 4 mm across.

bodies which occur as localized pods are less leached in appearance and are not laterally or vertically extensive. Epidote in these samples forms abundant pods up to 3 cm in diameter (Fig. 2.24). The epidote is intergrown with anhedral, fluid inclusion-rich quartz grains. Relict patches of saussuritized and turbid plagioclase are preserved locally. These areally restricted epidosite pods may result from deuterite alteration of volatile-rich plagiogranites. Subsequent incorporation of released fluids into the hydrothermal system is thought to account for observed low values of potassium and rubidium in the plagiogranites (Malpas et al., 1987; Malpas et al., 1989).

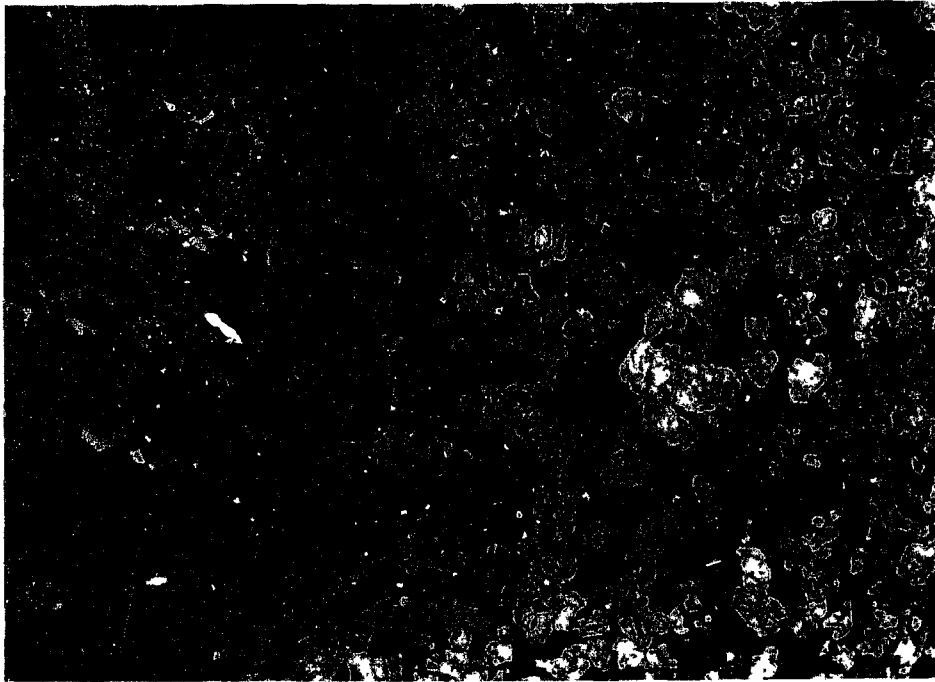


Figure 2.24 Microphotograph of podiform epidosite after diorite (Sample CY88-9). Coarse-grained epidote and quartz almost completely replace primary mineralogy. Field of view is 8 mm across.

CHAPTER III FLUID INCLUSIONS

3.0 INTRODUCTION

Chemical evolution of fluids at depth in the oceanic crust, as well as temperature and pressure conditions of fluid circulation, have been inferred from studies of hydrothermal vent solutions (Bowers et al., 1988; Von Damm, 1988), rock chemistry and alteration products (Mottl, 1983; Ito et al., 1983; Alt et al., 1986a&b; Mevel, 1987), and experimental studies of seawater-rock interaction (Berndt and Seyfried, 1990; Bischoff and Pitzer, 1988). Although these studies have made significant contributions to the understanding of submarine hydrothermal systems at shallow crustal depths, the extent to which the results may be accurately extrapolated to deeper levels of the crust is not clear.

Fluid inclusions provide a powerful tool by which to study paleohydrothermal systems at depth, because they represent small capsules of actual fluids which once circulated deep in the crust. They have been used for many years by industry to characterize heat and mass transfer in hydrothermal systems associated with porphyry ore deposits, but only recently have they been applied to the study of submarine hydrothermal systems (Kelley and Delaney, 1987; Vanko, 1988; Nehlig and Juteau, 1988). Secondary inclusions entrapped during episodic fracturing events are particularly useful in the study of fracture-fluid evolution in submarine systems, in that they provide a record of chemical and thermal variation of the fluid through time (Kelley and Delaney, 1987).

3.1 Fluid Inclusions In Rocks From Troodos

In the upper-level gabbros and plagiogranites of Troodos, aqueous fluid inclusions are ubiquitous in quartz, epidote, and hydrothermal clinopyroxene, and less common in amphibole and plagioclase (Fig. 3.1-3.5). The inclusions commonly form anastomosing arrays along healed microfractures and, therefore, are interpreted to be

Figure 3.1. Microphotographs of secondary fluid inclusions in quartz. Scale bar in all photographs is equal to 25 microns. **A)** Multiple planes of liquid-dominated, low-salinity inclusions and halite-bearing inclusions (Sample CY88-9). **B)** Liquid-dominated inclusions containing a small vapor bubble (V) surrounded by a low-salinity liquid (L) (Sample CY88-9). **C)** High-salinity fluid inclusions containing a halite daughter mineral (H), liquid (L), and a small vapor bubble (V) (Sample CY88-5). **D)** Brine-rich inclusions containing halite (H) and sylvite (S) daughter minerals (Sample CY88-54).

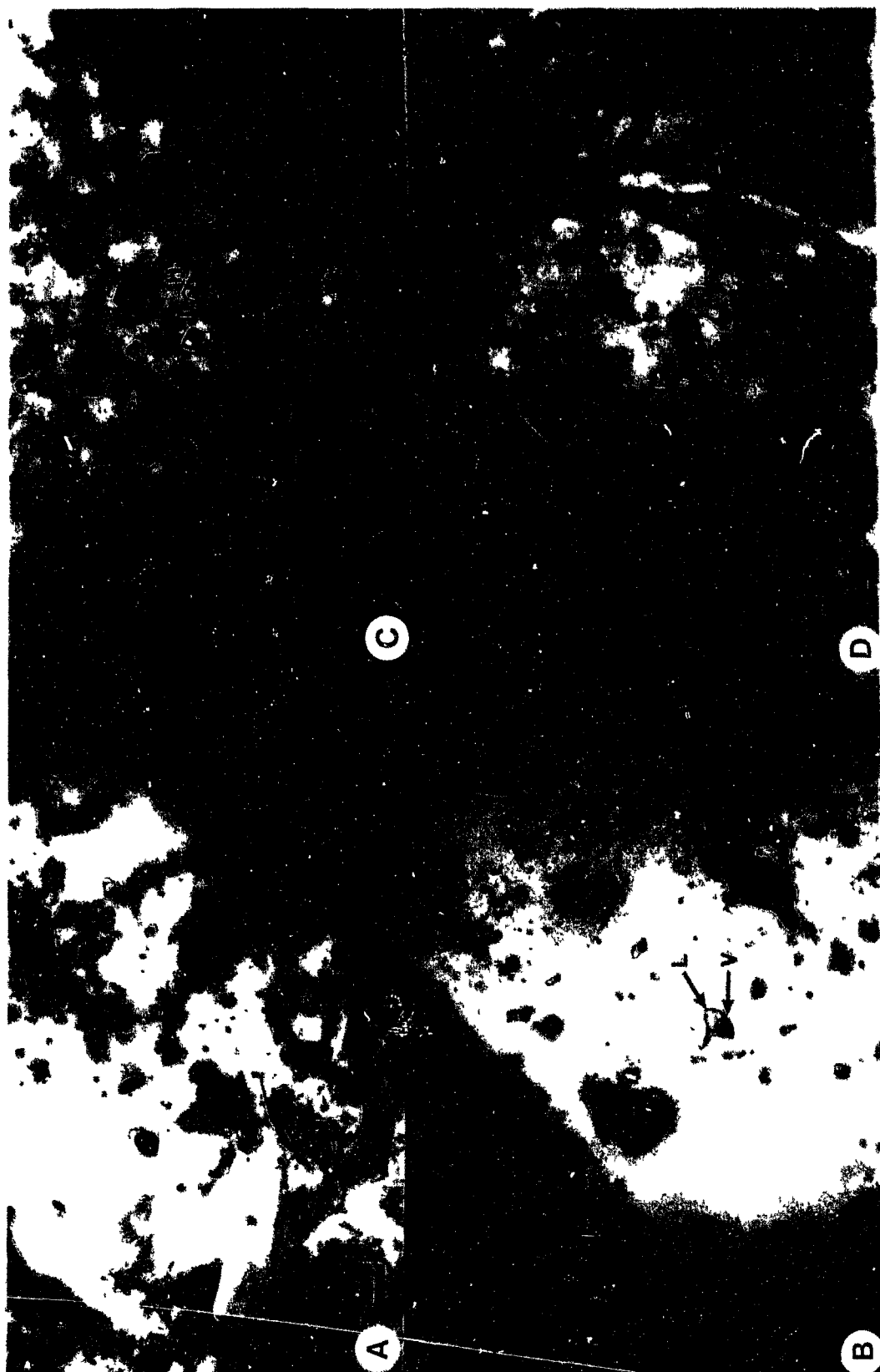


FIGURE 3.1

Figure 3.2 Microphotographs of fluid inclusions in clinopyroxene and amphibole grains. Scale bar in all photographs is equal to 25 microns. **A)** Vapor-dominated fluid inclusions in hydrothermal clinopyroxene in pegmatitic gabbro (Sample CY1181.75). The low-salinity inclusions are commonly elongate parallel to cleavage. Inclusions in hydrothermal clinopyroxene are extremely abundant. **B)** Amphibole-hosted inclusions in amphibole gabbro (Sample CY88-58). Note thin tubular inclusions and irregularly shaped inclusions in right portion of diagram. Highly variable vapor to liquid ratios are common in amphibole-hosted inclusions. **C)** Amphibole hosted inclusions along healed microfracture (Sample CY88-58). **D)** Liquid-dominated inclusion in amphibole (Sample CY88-58).

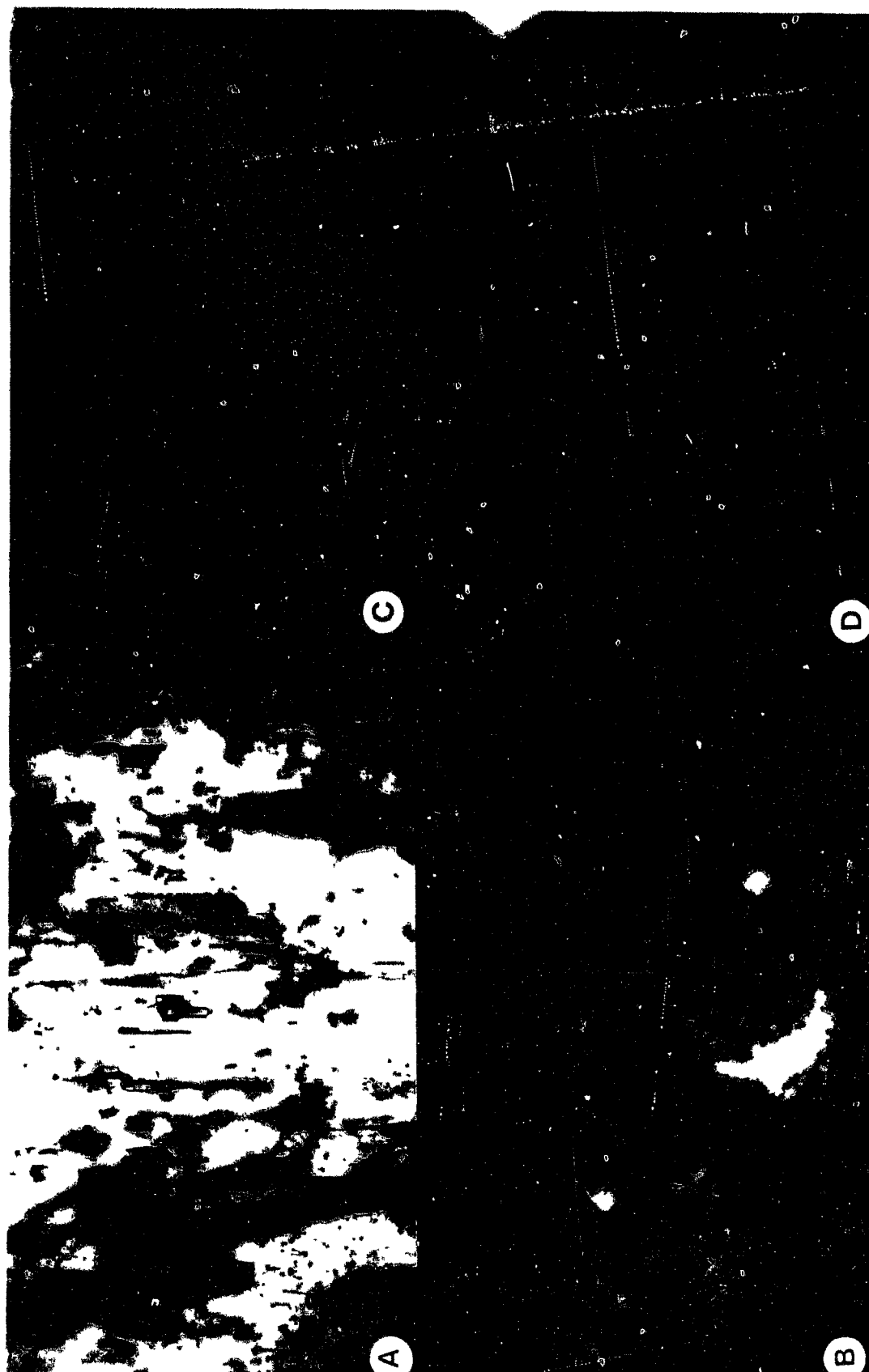


FIGURE 3.2

Figure 3.3 Microphotographs of fluid inclusions in plagioclase and epidote grains. **A)** Primary aqueous fluid inclusions, and glass inclusions in plagioclase (Sample CY1017.62). Inclusions are concentrated in cores of plagioclase grains and as bands which mimic grain boundaries. Scale bar is equal to 150 microns **B)** Liquid-dominated inclusions in plagioclase. Inclusions exhibit extremely constant vapor to liquid ratios (Sample CY1017.62). Scale bar in B-D is equal to 25 microns. **C)** Plagioclase-hosted inclusions containing an opaque daughter mineral and an elongate, whitish daughter mineral (Sample CY1017.62). **D)** Secondary, low-salinity inclusions in epidote (Sample CY88-9).



FIGURE 3.3

Figure 3.4 Microphotographs of fluid inclusions in epidote, quartz, and apatite. Scale bar in all photographs is equal to 25 microns. **A)** Secondary vapor-rich fluid inclusions in epidote (Sample CY8-9). **B & C)** Quartz-hosted, liquid-dominated inclusions containing a halite daughter mineral (H) and a red translucent daughter mineral, probably hematite (Ht) (Sample CY88-5). **D)** Apatite-hosted primary fluid inclusion (Sample ALV1011-1). The vapor-rich (V) inclusion contains a pale-green daughter mineral, thought to be amphibole (Amph), an opaque daughter (Opq) phase, and a whitish, elongate daughter mineral, possibly halite.

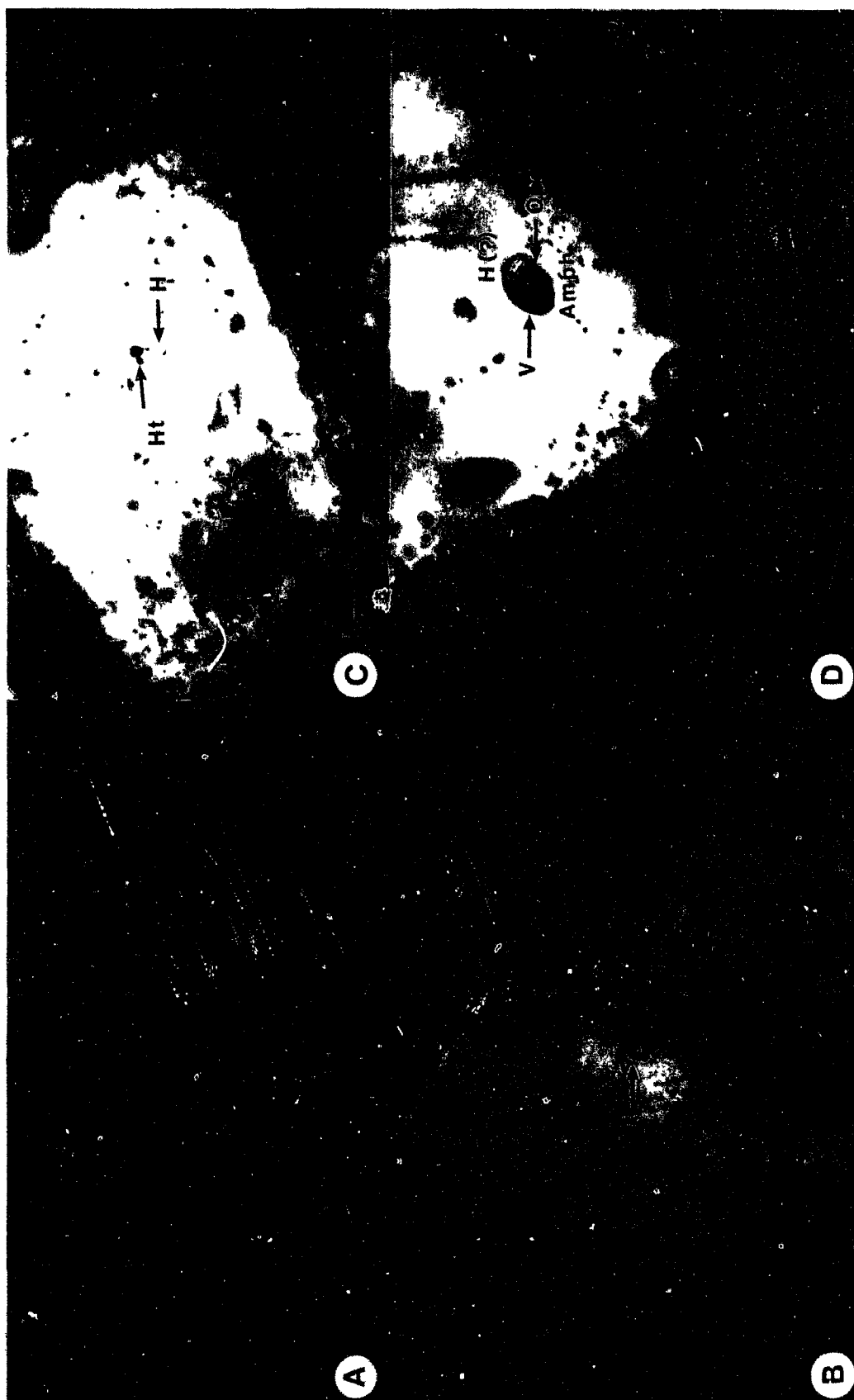


FIGURE 3.4

Figure 3.5 Quartz-hosted fluid inclusions in epidosite sample CY88-9. (A & C) Halite-bearing inclusions along crosscutting healed microfractures. (B & D) Inclusions contain halite daughter minerals (H) and less commonly daughter minerals of both halite (H) and sylvite (S). Trains of low-salinity inclusions crosscut arrays dominated by halite- ($\pm$ sylvite) bearing inclusions. Scale bar in all photographs is equal to 25 microns.

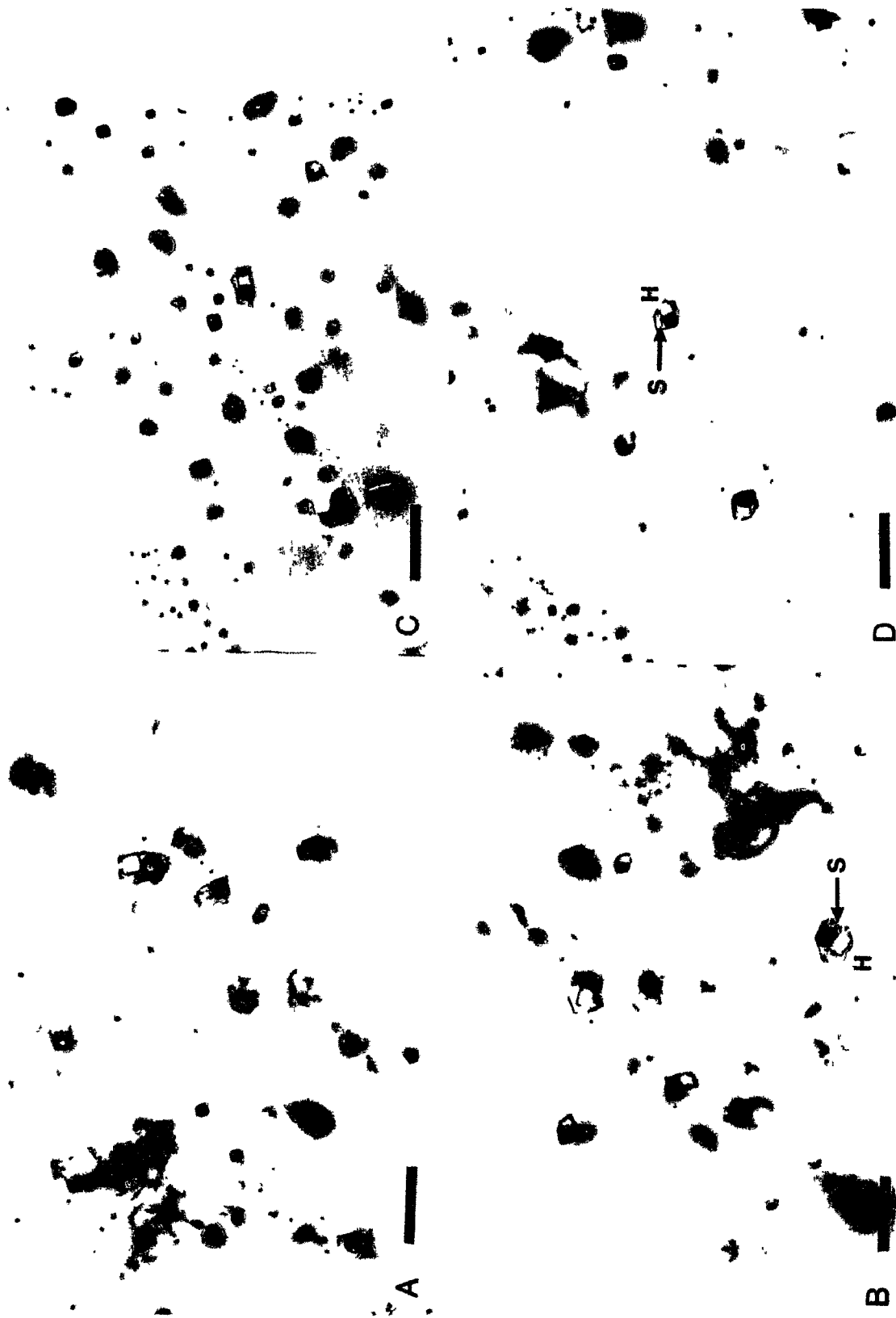


FIGURE 3.5

secondary (Fig. 3.6A). Their extreme abundance makes recognition of inclusions of unquestionably primary origin difficult. However, rare, seemingly isolated inclusions are observed and these are assumed to be primary (Fig. 3.6B).

Microthermometric analyses of fluid inclusions, along multiple generations of healed microfractures in primary and vein-filling minerals in the upper level plutonic rocks, provide information on evolving fluid compositions and thermal conditions in the submarine paleohydrothermal system of Troodos.

3.2 Methods

Microthermometric analyses of fluid inclusions were conducted on an adapted U.S.G.S. gas-flow heating and freezing stage according to procedures outlined by Roedder (1984). Replicate homogenization and freezing measurements were carried out on individual inclusions in order to obtain corresponding homogenization temperatures and fluid salinities. Homogenization and dissolution temperatures were measured during progressive heating of the sample in order to avoid decrepitation and phase changes associated with stretching. Thermocouple accuracy was evaluated by measuring phase transitions of synthetic fluid inclusions, at -56.6°C , 0.0°C , and $+374^{\circ}\text{C}$. Calibration temperatures obtained were always within 0.1°C at -56.6°C , 0.0°C at 0.0°C , and $\pm 1.0^{\circ}\text{C}$ at 374°C . All analyses reported were reproducible to within 0.2°C . Unsaturated and saturated solution salinities were obtained using the equations of Potter et al. (1977, 1978), and have an error of ± 0.2 wt% NaCl and ± 1.0 wt% NaCl, respectively. Homogenization temperatures of vapor-dominated inclusions may be several hundred degrees below actual filling temperatures. Experimental analyses of synthetic fluid inclusions entrapped under known P-T conditions, indicate that "apparent" homogenization temperatures of vapor-dominated inclusions may be 100 to 500°C below the actual homogenization temperature (Bodnar et al., 1985). As discussed by Bodnar et al. (1985), true temperatures of homogenization cannot be obtained on vapor-dominated inclusions due to the inability to detect optically when the

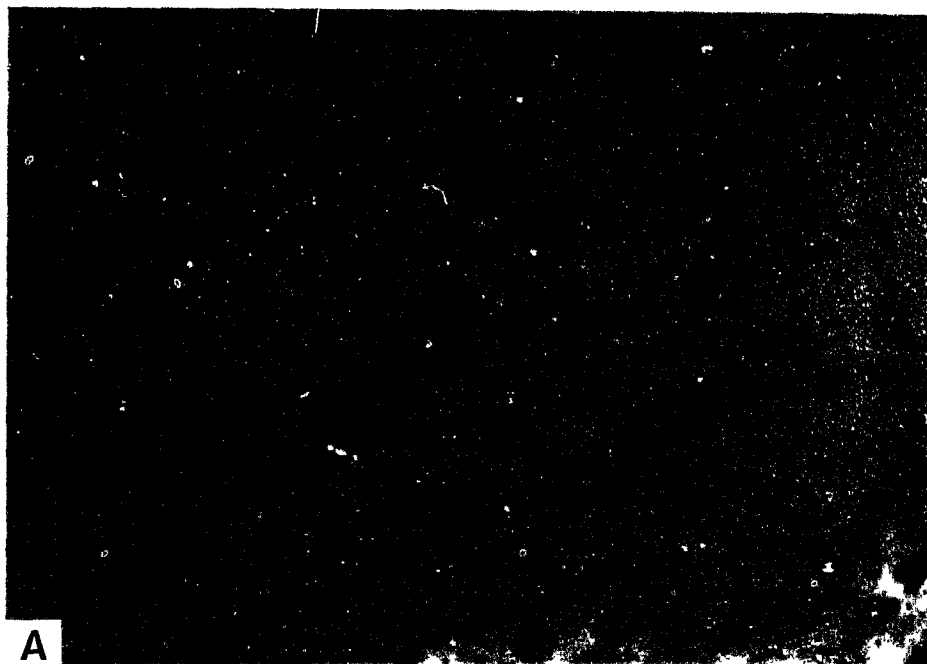


Figure 3.6 A) Microphotograph showing arrays of secondary fluid inclusions along healed microfractures in quartz. The liquid-dominated inclusions contain a small vapor bubble (V) rimmed by a low-salinity liquid (L). Scale bar is equal to 25 microns.

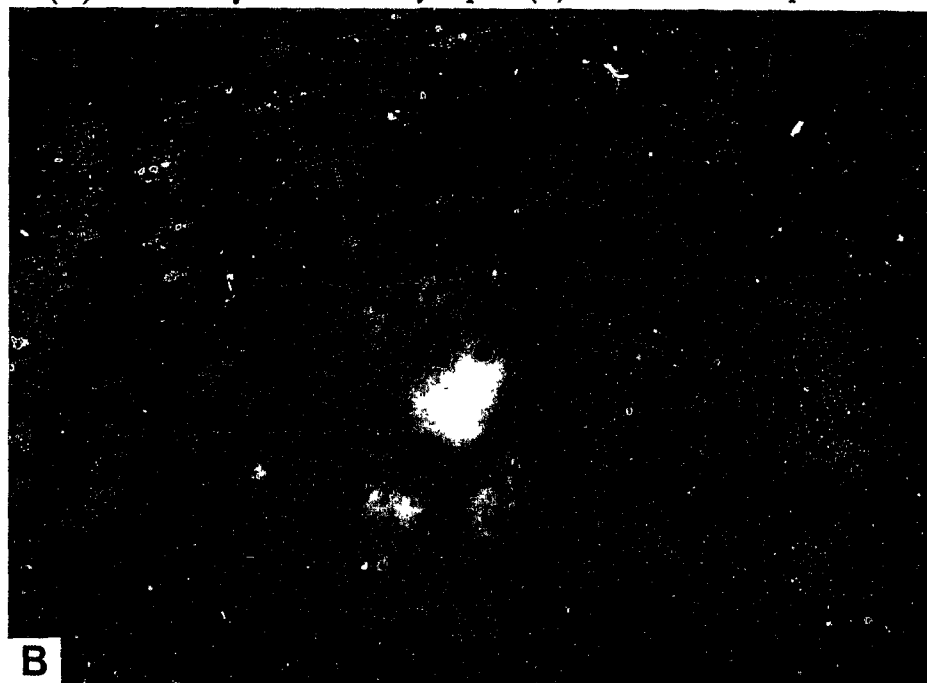


Figure 3.6 B) Primary (?) fluid inclusions in plagioclase. Scale bar is equal to 25 microns.

vapor phase completely fills the inclusion on heating (Fig. 3.7). Homogenization temperatures of these inclusions are, therefore, recorded as "apparent" temperatures of filling. Reported temperatures of homogenization have not been corrected for pressure effects, but corrections would range from +40°C to 100°C for the low-salinity fluids, at entrapment pressures of 470-1000 bars (Potter, 1977). The nomenclature used to describe inclusion behavior during heating and freezing runs (Table II) is that established by Roedder (1984).

3.3 Fluid Inclusion Types and Results

Fluid inclusion types, host minerals, and thermal-compositional information on entrapped fluids are summarized in Table III. Three types of fluid inclusions are recognized at room temperature within the gabbros and plagiogranites.

Type 1: Liquid-dominated, low-salinity inclusions.

Liquid-dominated, low-salinity fluid inclusions occur in quartz, epidote, amphibole, and plagioclase (Fig. 3.1-3.4, 3.6, 3.8). These low-salinity inclusions form anastomosing arrays along healed microfractures and are interpreted to be secondary in nature. In quartz, plagioclase, and epidote-hosted inclusions homogenization occurs in the liquid phase [Th L+V (L)] at uncorrected temperatures of 200-400°C (Fig. 3.9 & 3.10A). Freezing measurements indicate corresponding fluid salinities of 2-7 wt% NaCl equivalent (Fig. 3.9 & 3.10B). Type 1 inclusions are observed in all plutonic and dike samples studied (Fig. 3.11).

Type 2: Vapor-dominated, low-salinity inclusions.

Both primary and secondary vapor-dominated, low-salinity fluid inclusions occur in quartz, epidote, and hydrothermal clinopyroxene (Fig. 3.2, 3.5, 3.8B). Vapor-dominated inclusions in quartz and epidote homogenize in the vapor phase [Th L+V (V)] at apparent temperatures of 360-420°C and have fluid salinities of 1-5 wt% NaCl equivalent (Fig. 3.9 & 3.10). In sample CY88-9, vapor-rich inclusions are spatially

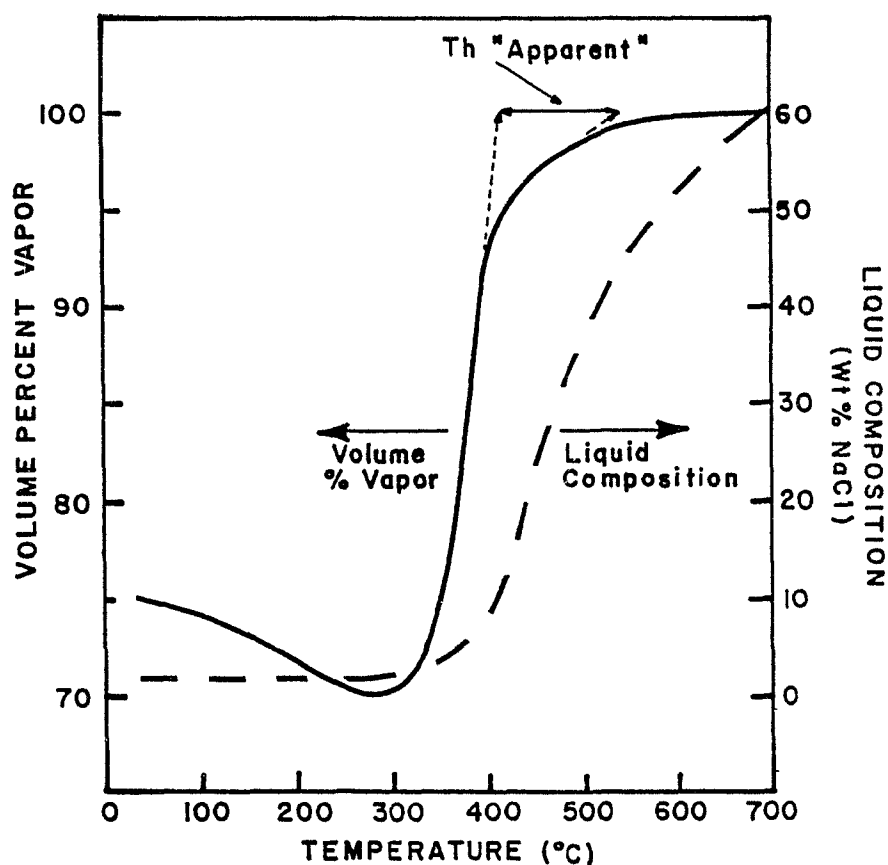


Figure 3.7 Change of volume percent vapor and liquid composition for a vapor-dominated inclusion entrapped at 700°C, and 700 bars (after Bodnar et al., 1985). Difficulty in detecting optically when the last bit of liquid disappears results in underestimation of actual homogenization temperatures by 100 to 500°C. At temperatures over 400°C, a gradual increase in the volume percent of the vapor phase occurs as the liquid composition approaches the composition of formation. The slope indicated by Th "apparent" reflects the temperature range over which the volume of the vapor phase may be large enough to appear to fill the entire inclusion.

TABLE II
FLUID INCLUSION NOMENCLATURE

LIQUID-DOMINATED INCLUSION	VAPOR-DOMINATED INCLUSIONS	HALITE+SYLVITE-BEARING INCLUSIONS
Th L+V (L)	Th L+V (V)	Tm > Th L+V (L)
Inclusions contain liquid and vapor phases. Homogenization occurs into the liquid phase by disappearance of the vapor bubble.	Inclusions contain liquid and vapor phases. Homogenization occurs into the vapor phase by expansion of the vapor bubble.	Inclusions contain salt daughter minerals + liquid + vapor phases. Vapor bubble homogenizes into the liquid phase, followed by dissolution of daughter phases.
Th - Temperature of homogenization L - Liquid phase V - Vapor phase L + V - Inclusion containing liquid and vapor phases (L) - Homogenization of inclusion into the liquid phase (V) - Homogenization of inclusion into the vapor phase Tm - Temperature of melting/dissolution of solid phase Tice - Final ice melting temperature Te - Eutectic temperature		Tm < Th L+V (L)
		Inclusions contain salt daughter minerals + liquid + vapor. Daughter phases dissolve prior to homogenization of the vapor phase. Vapor bubble homogenization occurs into the liquid phase.

SAMPLE	ROCK	HOST	#	T _h °C (min-max)	AVG	STD	T _m °C (min-max)	AVG	STD	NaCl wt%	AVG	STD
CY87-1	Plgrant	Quartz	46	238.2-635.0	317.0	70.8	348.0-537.0	441.0	38.9	41.6-60.6	50.2	3.9
		Quartz	17	248.6-390.5	317.3	52.2	-----	-----	-----	2.1-17.2	5.0	3.7
CY88-5*	Plgrant	Quartz	21	288.4-378.8	320.9	20.7	310.0-477.0	405.6	46.2	38.7-53.8	46.8	4.2
		Quartz	28	213.5-436.6	336.3	53.8	-----	-----	-----	2.2-20.7	5.2	4.0
CY88-9**	Epidosite	Quartz	55	305.0-402.0	362.2	22.0	258.6-411.0	357.9	40.8	35.1-47.0	42.5	3.2
		Quartz	68	255.0-402.6	388.1	21.8	-----	-----	-----	1.1-17.2	3.2	1.8
		Epidote	19	391.5-413.2	402.4	6.0	-----	-----	-----	2.2-4.7	3.8	0.7
CY88-17	Upper Gabbro	Quartz	18	184.0-260.7	197.0	16.5	-----	-----	-----	3.0-5.3	3.7	0.7
		Plag	7	182.9-264.2	207.1	27.8	-----	-----	-----	1.8-2.4	2.1	0.2
CY88-36	Plgrant Xenolith	Quartz	23	302.2-362.5	322.8	13.8	-----	-----	-----	1.8-5.5	4.2	1.1
		Quartz	37	238.2-317.8	295.7	18.2	-----	-----	-----	1.7-5.5	4.2	0.7
CY88-39 ⁺	Vein	Quartz	42	250.2-314.6	282.9	13.7	-----	-----	-----	1.8-5.5	3.8	0.6
CY88-54	Plgrant	Quartz	19	266.5-331.5	297.8	17.3	302.5-498.6	443.2	46.04	38.1-56.2	50.4	4.4
		Quartz	22	223.4-358.3	266.6	28.3	-----	-----	-----	2.8-14.2	4.5	2.9
CY88-58	Gabbro	Amphi	6	264.0-410.2	343.7	51.3	-----	-----	-----	0.5-12.4	6.2	4.2
CY88-77	Plgrant	Quartz	25	219.3-346.1	287.5	30.0	-----	-----	-----	2.9-7.0	3.9	0.9
CY88-78 ⁺⁺	Vein	Quartz	20	307.2-363.7	330.1	15.0	-----	-----	-----	2.1-4.4	3.2	0.6
CY1017.62	Gabbro	Plag	40	146.0-209.7	187.7	16.4	-----	-----	-----	0.0-2.4	1.2	0.6
CY1181.75	Gabbro Pegmatite	Quartz	2	225.8-296.6	261.2	36.2	378.6-397.7	388.1	17.2	44.1-45.6	44.8	0.7
		Quartz	13	219.2-328.4	276.6	35.2	-----	-----	-----	3.2-19.8	9.0	5.3
		Cpx	12	255.9-393.7	350.5	45.0	-----	-----	-----	2.4-4.6	3.7	0.7
CY10N.16	Diabase	Quartz	50	259.6-377.1	357.6	24.5	-----	-----	-----	2.0-5.4	3.5	0.6

#=Number of inclusions measured; T_h°C=vapor bubble disappearance temperature; T_m°C=halite dissolution temperature

Plgrant=plagiogranite; Plag=plagioclase; Amphi=amphibole; Cpx=hydrothermal clinopyroxene

AVG=average value of all measurements, STD=standard deviation

*Brines contain NaCl & KCl. See Table IV; **Some entrapped fluids contain NaCl-KCl-CaCl₂. See Table IV

⁺Felsic Vein cutting plagiogranite; ⁺⁺Quartz vein cutting upper level gabbros



Figure 3.8 Microphotographs of quartz-hosted fluid inclusions in plagiogranite samples. Bar scale in all photographs is 15 microns. A) TYPE 1: liquid-dominated, low-temperature, low-salinity inclusion. Inclusions homogenize in the liquid phase at 200-400°C [Th L+V (L)]. B) Type 2: vapor-dominated inclusion containing large vapor bubble rimmed by low-salinity fluid. Inclusions homogenize in the vapor phase [Th L+V (V)] at apparent temperatures of 360- 420°C. C) TYPE 3: high-temperature, brine inclusion containing cubic daughter mineral of halite. Inclusion homogenization occurs predominantly by halite dissolution [Tm NaCl >Th L+V (L)] at 400-500°C corresponding to salinities of 36-56 wt% NaCl.

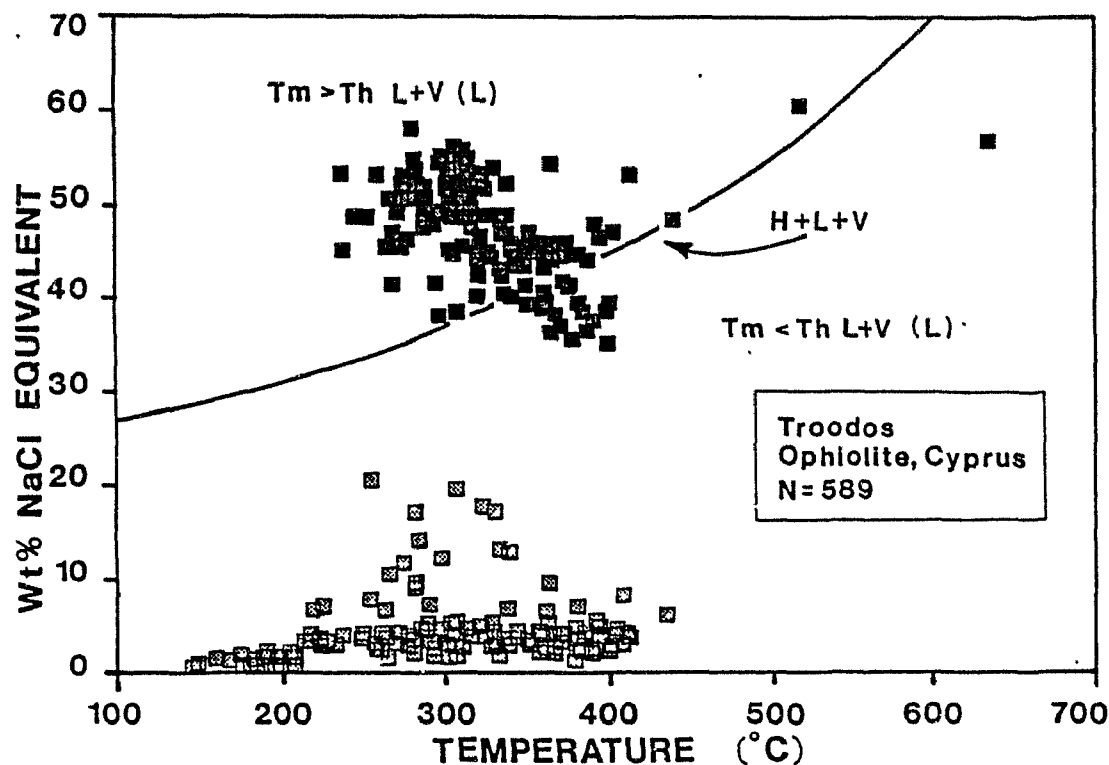


Figure 3.9 Temperatures of vapor bubble disappearance and corresponding equivalent fluid salinities for individual inclusions in quartz, plagioclase, epidote, and clinopyroxene. Secondary fluid inclusions homogenize in the liquid phase [Th L+V (L)] at temperatures of 200-400°C and contain salinities of 2-7 wt% NaCl. Primary and secondary vapor-dominated inclusions in quartz, clinopyroxene, and epidote, which homogenize in the vapor phase [Th L+V (V)], exhibit **apparent** homogenization temperatures of 360-420°C and contain salinities of 1-5 wt% NaCl equivalent. Brine-rich inclusions falling in the field above the halite solubility curve (H+L+V) homogenize by halite dissolution at 400-500°C [Tm > Th L+V (L)]: vapor bubble homogenization occurs at 230-400°C. Brine inclusions homogenizing in the liquid phase [Tm < Th L+V (L)] at 375-400°C contain fluid salinities of 36-40 wt% NaCl.

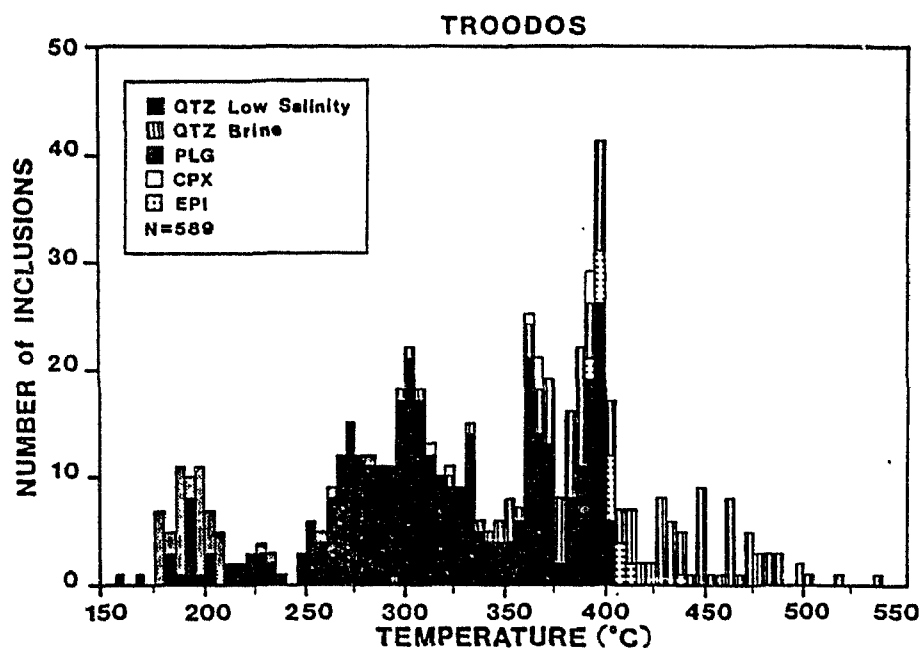


Figure 3.10 (A) Histogram of homogenization temperatures for gabbro, plagiogranite, and diabase-hosted inclusions. (Abbreviations indicate minerals hosting fluid inclusions: QTZ Low-Salinity indicates homogenization temperatures for quartz-hosted, low-salinity inclusions, QTZ Brine indicates high-salinity inclusions in quartz, PLG = plagioclase, CPX = clinopyroxene, EPI = Epidote)

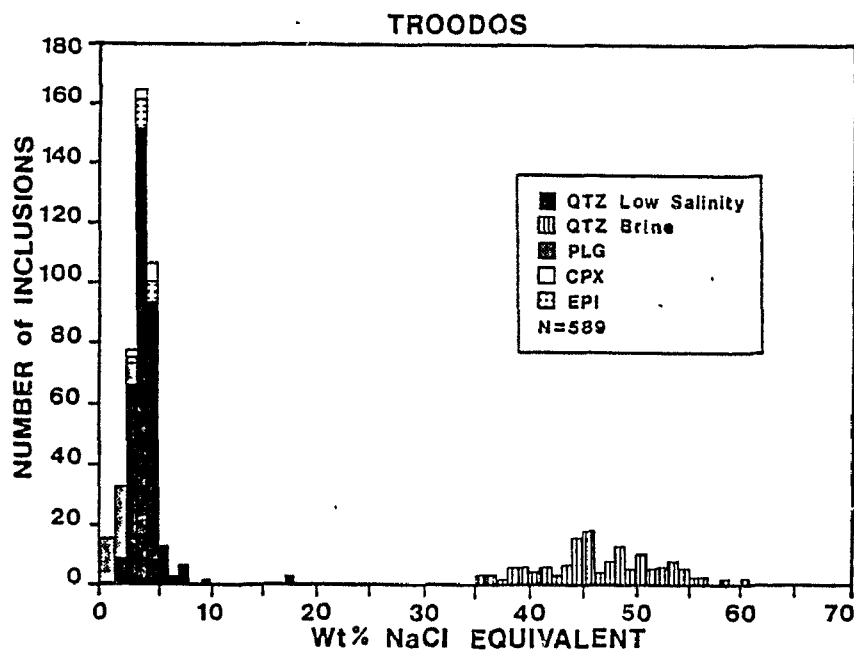


Figure 3.10 (B) Histogram of sodium chloride (NaCl) equivalent salinities for all samples used in this study. Abbreviations are the same as for Figure 3.10A.

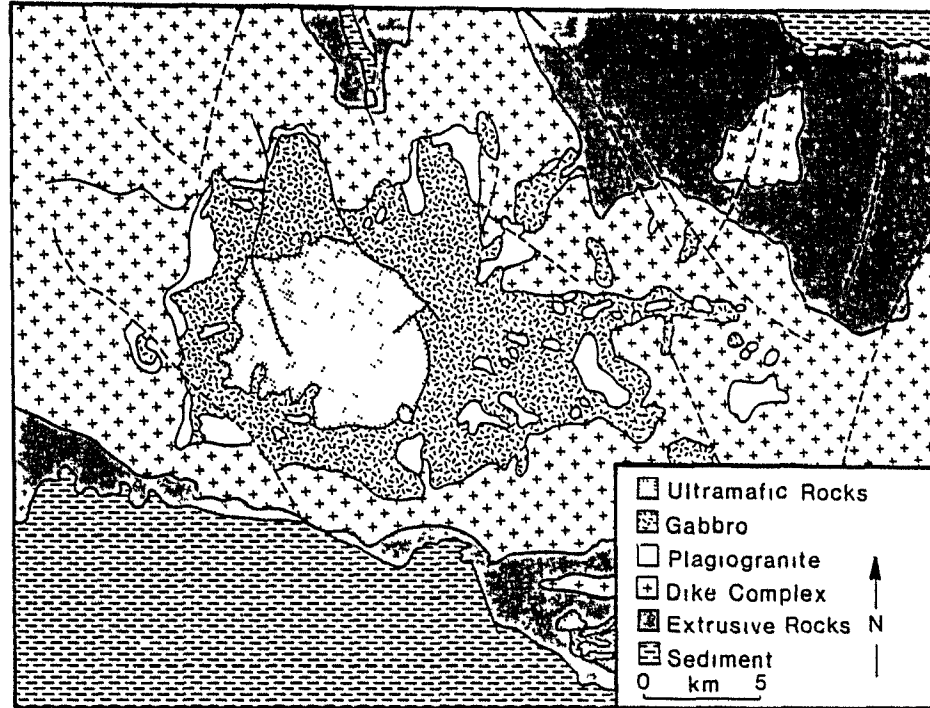


Figure 3.11 (A) Simplified geologic map of the Troodos ophiolite, Cyprus (After Constantinou and Panayiotou, 1982).

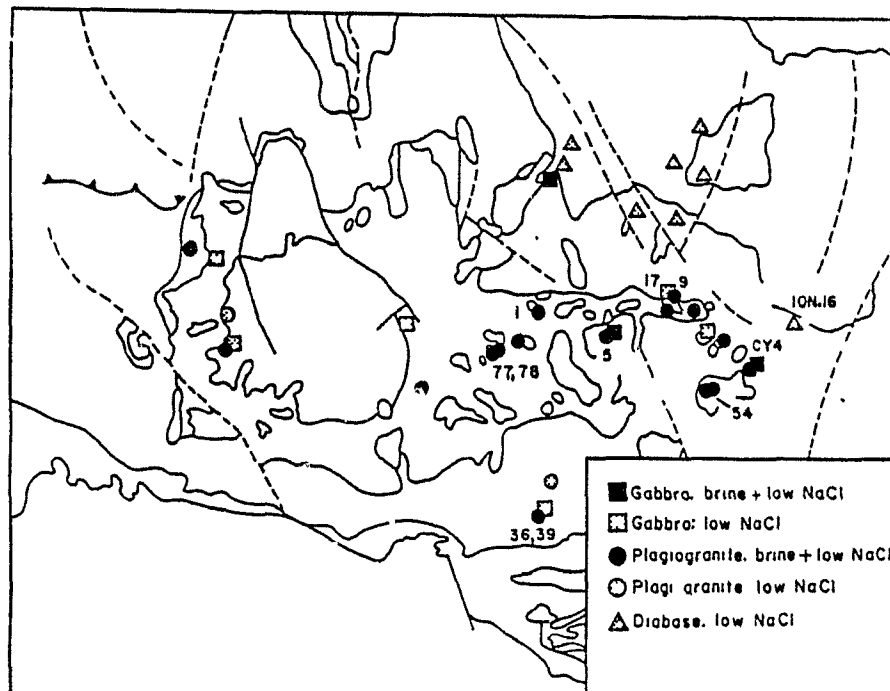


Figure 3.11 (B) Location of gabbro, plagiogranite, and diabase samples used in this study. Rock types hosting halite-bearing inclusions, and low-salinity inclusions are indicated by brine + low NaCl. Rock types containing low-salinity inclusions only, are indicated by low NaCl.

associated with conjugate brine inclusions (Fig. 3.12A), however, microfractures lined with exclusively vapor-dominated inclusions are observed as well (Fig. 3.12B).

Type 3: Liquid-dominated, high-salinity inclusions.

Liquid-dominated, high-salinity primary(?) and secondary inclusions occur in quartz and, more rarely, in epidote (Fig. 3.1, 3.5, 3.8C). The high-salinity inclusions always contain a sodium chloride daughter mineral. Less commonly an isotropic, cubic to subrounded, pale yellow daughter mineral is observed which exhibits a higher dissolution rate than halite, and which always dissolves before halite (Fig. 3.1D, 3.5B&D). These characteristics suggest that this second daughter phase is sylvite. A hexagonal, brown-red daughter mineral, common in samples CY87-1, CY88-5, and CY88-54 is probably hematite (Fig. 3.4B&C). Halite casts were not observed in any of the host minerals.

Halite-bearing inclusions which are not associated with vapor-dominated Type 2 inclusions homogenize by halite dissolution (i.e. vapor bubble disappearance occurs prior to dissolution of the halite daughter mineral [$T_m > T_h$ L+V (L)]); halite dissolution occurs at temperatures of 400-500°C corresponding to equivalent fluid salinities of 46-56 wt% NaCl (Fig. 3.13A and 3.13B). Inclusion homogenization by halite dissolution indicates these inclusions were entrapped in the absence of a vapor phase (Cloke and Kessler, 1979; Roedder, 1984). Due to high bulk densities of the fluids in sample CY88-54, it was not uncommon for decrepitation of the inclusions to occur before complete dissolution of the daughter phases; therefore, reported salinities for this sample are minimum total salinities.

The negative slope defined by halite dissolution temperatures vs temperatures of vapor bubble disappearance (Figure 3.13B) is a function of fluid density. Inclusions with the highest dissolution temperatures (i.e., highest NaCl concentrations) have correspondingly high fluid densities. During post-entrapment cooling a proportionally smaller vapor bubble will form from more highly saline and dense fluids. Under

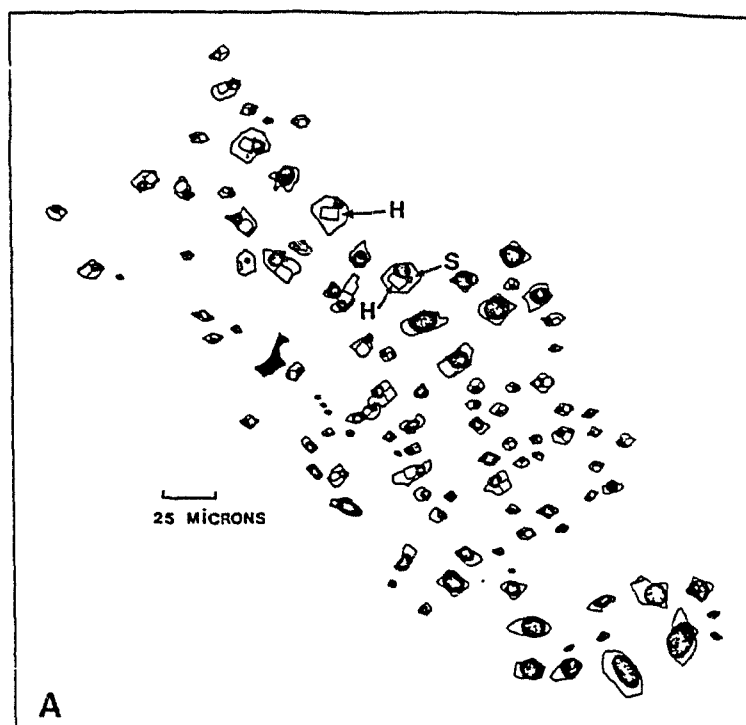
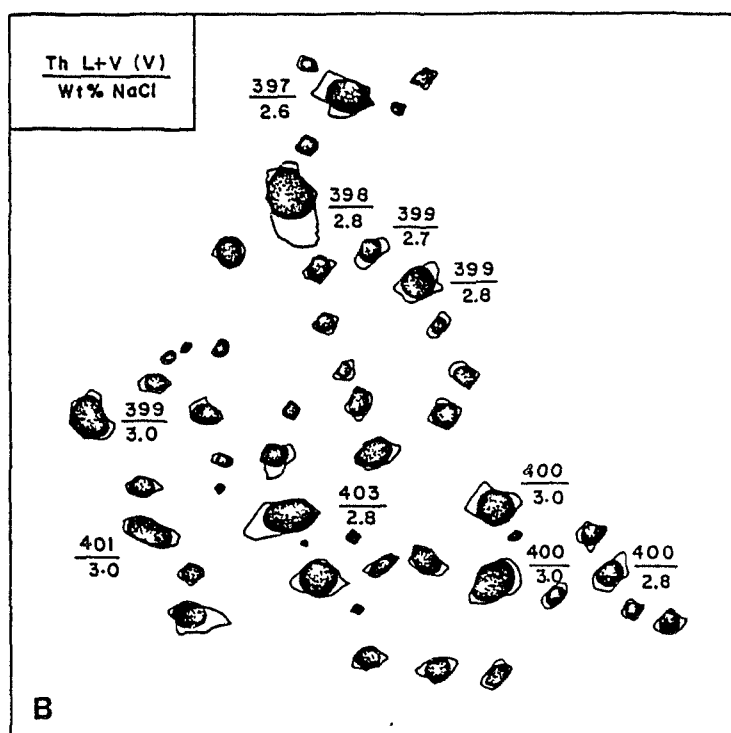


Figure 3.12 (A) Linear array of brine and vapor-rich fluid inclusions along a single healed microfracture in quartz (Epidosite sample CY88-9). Brine inclusions contain halite daughter minerals (H), and less commonly daughter minerals of sylvite (S). See Figure 3.15 for more detailed sketch. Scale bar is equal to 25 microns. (B) Array of vapor-dominated, low-salinity inclusions along healed microfracture in quartz.



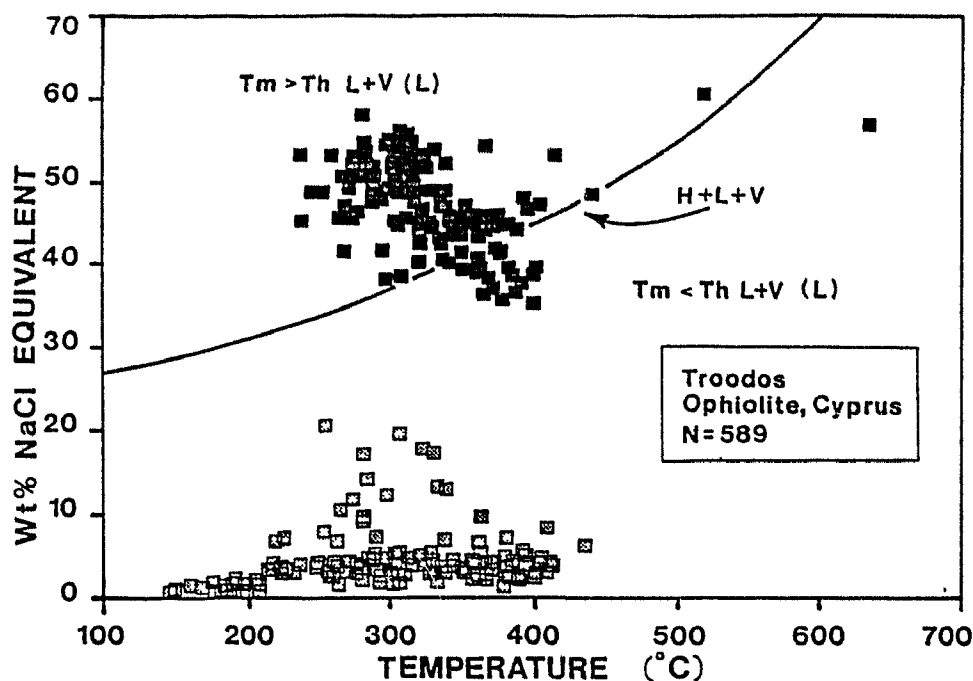


Figure 3.13 (A) Corresponding temperatures of vapor bubble disappearance and equivalent fluid salinities for measurements on individual fluid inclusions.

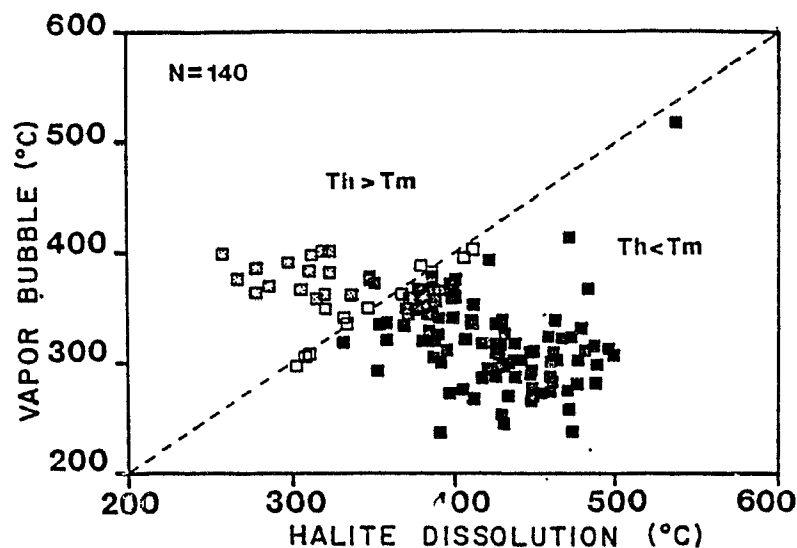


Figure 3.13 (B) Corresponding temperatures of halite dissolution and vapor bubble disappearance for halite-bearing fluid inclusions shown in Figure 3.12 (A). The 1:1 dashed line corresponds to inclusions in which halite dissolution and vapor bubble homogenization occurs at the same temperature (open squares). Inclusions which plot in the field $Th > Tm$ exhibit halite dissolution temperatures of 250-350°C. These inclusions homogenize in the liquid phase at temperatures of 330-400°C (lightly stippled squares). Homogenization by vapor bubble disappearance indicates fluids were entrapped in the presence of a vapor phase. Inclusions falling below the 1:1 line in the field $Th < Tm$, exhibit vapor bubble disappearance at temperatures of 230-400°C, followed by halite dissolution at temperatures of 320-500°C. Homogenization by halite dissolution indicates the inclusions were trapped in the absence of a vapor phase (Cloke and Kessler, 1979; Roedder, 1984).

identical entrapment conditions, a lower salinity, lower density inclusion of the same volume will form a larger vapor bubble and, therefore, will exhibit a higher temperature of vapor bubble disappearance.

Some quartz-hosted, halite-bearing inclusions, spatially associated with vapor-dominated, low-salinity inclusions, homogenize in the liquid phase [$T_m < T_h \text{ L+V (L)}$] at temperatures of 375-400°C. These inclusions contain fluid salinities of 36-45 wt% NaCl equivalent (Fig. 3.9 and Fig. 3.14).

In samples such as CY88-9 (Fig. 3.14), in which brine inclusions homogenize by either vapor bubble disappearance or halite dissolution, estimated fluid compositions may be somewhat greater or less than true total salinities, respectively. Accurate bulk fluid compositions are only recorded by inclusions which homogenize by simultaneous disappearance of the vapor bubble and halite daughter mineral (Sterner et al., 1988). Natural fluid inclusions may entrap fluids of similar bulk compositions, but of varying densities, which may result in calculation errors when computing fluid compositions. Due to the positive slope of the liquidus isopleth ($S + L/L$), a moderate salinity fluid which has a density (p^+) slightly higher than an inclusion having a density such that solid phase dissolution and vapor bubble disappearance occur simultaneously (p^0), will exhibit a slightly higher temperature of halite dissolution (Fig. 3.15). Therefore, an inclusion with density p^+ will record a salinity slightly in excess of the true salinity (p^0). An inclusion of the same bulk composition, but of lower density (p^-) will also exhibit a somewhat greater salinity than an inclusion of density p^0 , because water is strongly partitioned into the vapor phase. The magnitude of the error for inclusions which homogenize by solid dissolution is not known, but should be relatively small at pressures of 400-1000 bars. The error for inclusions containing 10% by volume of a vapor phase at halite dissolution temperatures of 350-450°C, is 0.3-0.6 wt% NaCl, respectively (Chou, 1987).

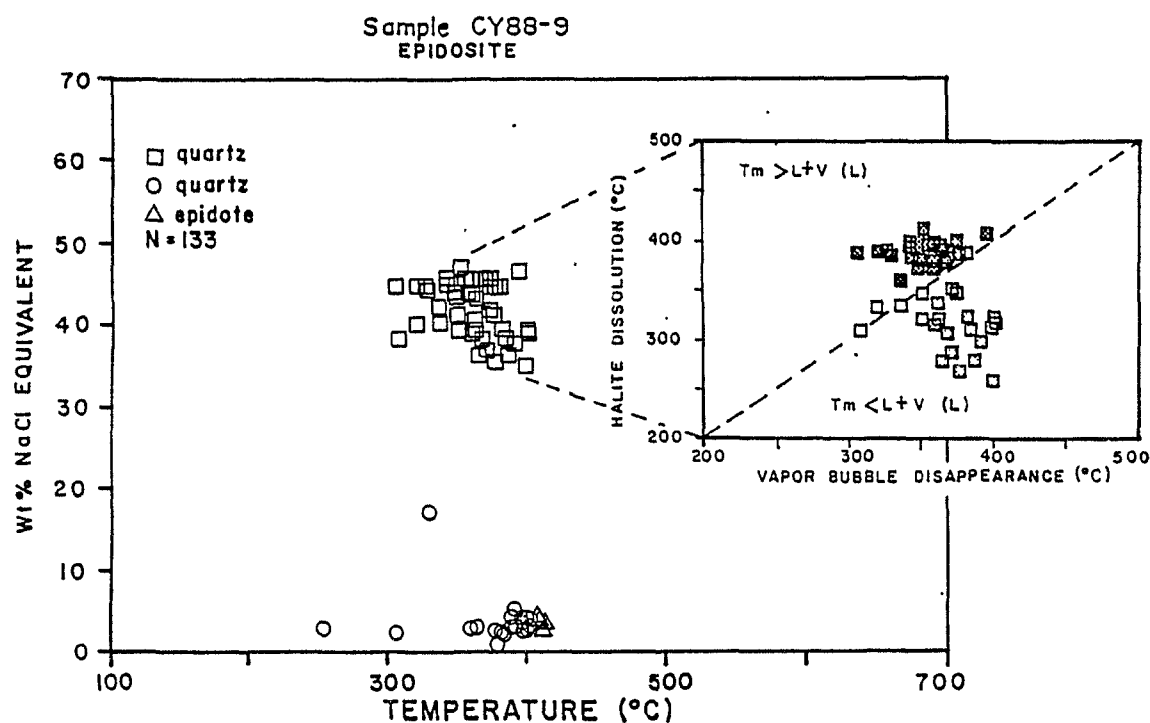


Figure 3.14 Corresponding vapor bubble disappearance temperatures and equivalent fluid salinities for individual inclusions in epidosite sample CY88-9. Open squares and circles indicate quartz-hosted inclusions. Inclusions hosted in epidote are indicated by open triangles. Detailed homogenization behavior of brine inclusions is shown in enlargement. Quartz-hosted brine inclusions homogenize by halite dissolution [darkly stippled squares in field $T_m > T_h \text{ L+V (L)}$], by homogenization in the liquid phase [lightly stippled squares in field $T_m < L+H \text{ (L)}$], and by simultaneous disappearance of the vapor bubble and halite daughter mineral (open squares).

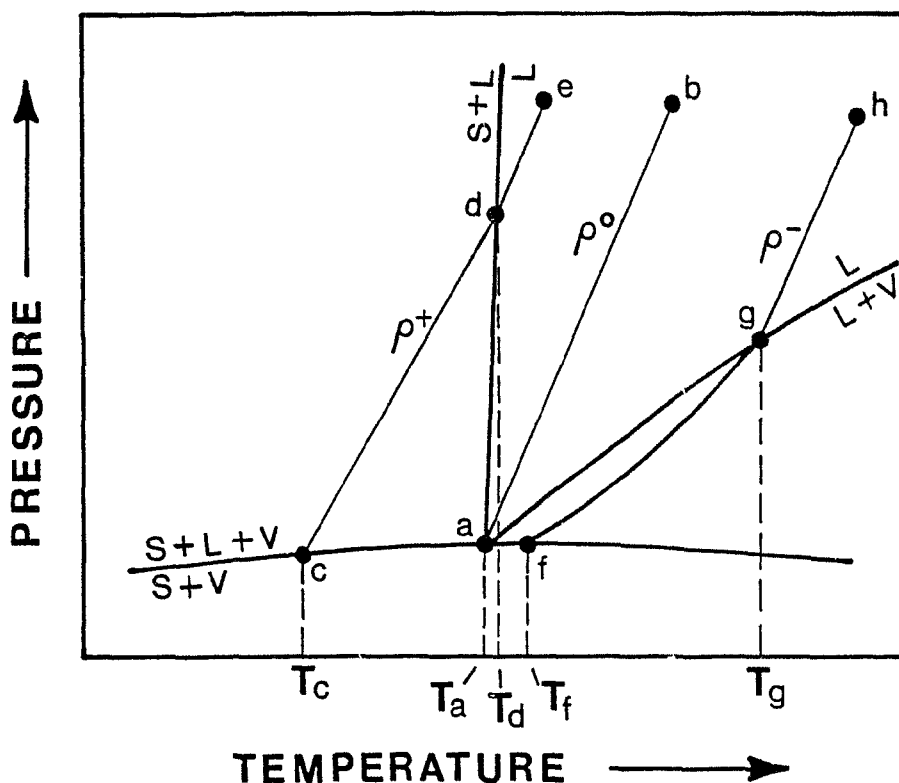


Figure 3.15 Schematic P-T projection of the high-salinity portion of NaCl-H₂O system (discussion and diagram after Sterner et al., 1988), showing the three phase curve (S + L + V), liquidus isopleth (S + L / L), vapor + solid field (S + L), bubble point curve for a fluid of fixed composition (L/L+V), and isochores for fluids with identical bulk compositions, but different densities (p^+ , p^0 , p^-). Accurate fluid compositions will be obtained from inclusions in which halite dissolution and vapor bubble homogenization occur simultaneously (isochore p^0 , at temperature T_a). Inclusions with the same bulk composition, but of slightly higher density (p^+) will exhibit vapor bubble disappearance at temperature T_c , and halite dissolution will occur at temperature T_d . For moderate to highly-saline inclusions, the liquidus isopleth has a positive slope (Chou, 1987): therefore, inclusions with density of p^+ will exhibit halite dissolution temperatures in excess of actual salt dissolution temperatures (temperature T_a) by an amount $T_d - T_a$. Inclusions of the same bulk composition, but of slightly lower density (p^-), will exhibit halite dissolution at a temperature of T_f and will homogenize in the liquid phase by vapor bubble disappearance at a temperature of T_g . The actual salinity of these lower density inclusions will be off by an amount $T_g - T_a$ (see Sterner et al., for further discussion). Maximum errors in calculation of fluid compositions occur near temperatures of 550°C [2.38 wt% for an inclusion containing 25% by volume of a vapor phase at halite dissolution (Chou 1987)]. With continued heating, inclusions will follow along the appropriate isochore to final entrapment temperatures indicated by e, b, and h, respectively.

Inclusions which contain both halite and sylvite daughter minerals exhibit halite dissolution temperatures of 359-460°C, and sylvite dissolution at 138-336°C (Fig. 3.16 & 3.17). Applying these temperatures to the ternary system $\text{H}_2\text{O}-\text{NaCl}-\text{KCl}$ [Fig. 3.17, after Sterner et al., (1988)] indicates $\text{H}_2\text{O}:\text{NaCl}:\text{KCl}$ fluid compositions of 43:32:25 wt% to 28:38:34 wt%, respectively. Vapor bubble disappearance occurs in these inclusions at 289-377°C.

Along an individual microfracture, phase ratios are consistent among halite-bearing inclusions and (halite + sylvite)-bearing inclusions; however, not all inclusions contain both daughter minerals (Fig. 3.16). Sterner et al. (1988) attribute this absence of daughter phases to metastable behavior of sylvite. They note that synthetically formed fluid inclusions, saturated with respect to NaCl and KCl, commonly fail to nucleate a sylvite daughter mineral at room temperature. In their studies, the metastable absence of daughter minerals was corrected for by nucleating the salts during supercooling of the inclusions. In this study, nucleation of sylvite was not observed upon supercooling of the inclusions to -180°C. It may be, however, that the nucleated daughter phases were too small to detect optically. Owing to metastable behavior in sylvite-absent inclusions, determination of bulk salinities may underestimate total salinities by 10-15 wt%, and overestimate NaCl concentrations by 10-14 wt% (Fig. 3.16).

In epidosite sample CY88-9 eutectic, ice melting, and dissolution temperatures indicate inclusion solutions may be complex $\text{NaCl}-\text{KCl}-\text{CaCl}_2$ brines (Table IV). Eutectic temperatures (T_e) of the four-phase inclusions (halite + sylvite + liquid + vapor) range from -76°C to -61°C, and final temperatures of ice melting are -42°C to -32°C (Table IV). It is not uncommon for some of these highly saline inclusions to remain unfrozen at temperatures of -180°C, even during repeated freezing cycles. Similar behavior has been observed in studies of brine-rich, synthetic fluid inclusions (Sterner et al., 1988), and in gabbro-hosted inclusions from the

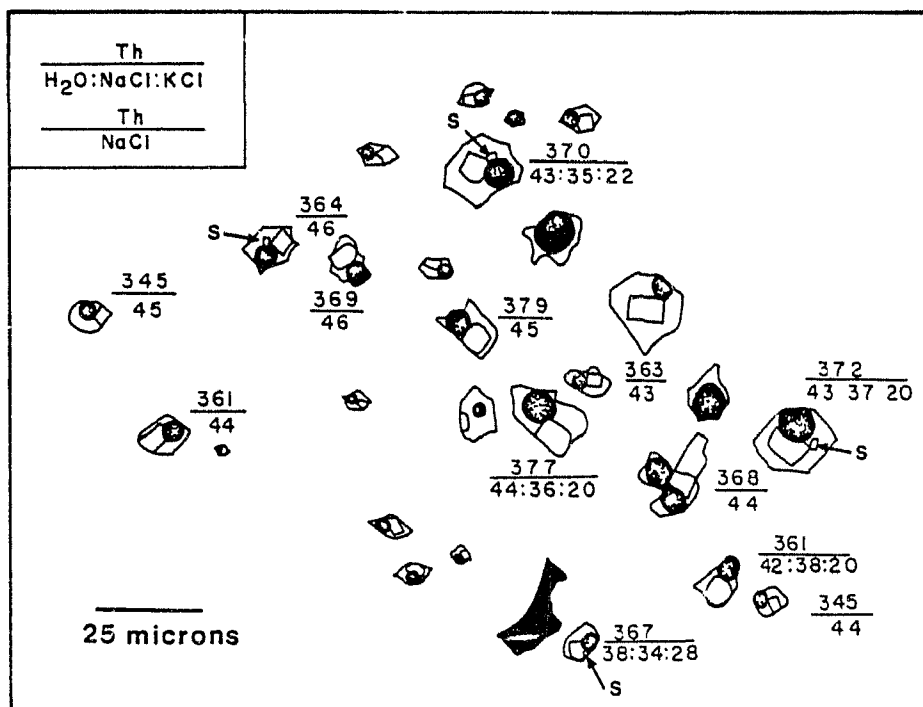


Figure 3.16 Detailed sketch of upper portion of Figure 3.12A. Along a single microfracture are inclusions which contain only halite daughter minerals, and inclusions which contain halite + sylvite (S) daughter phases. Temperatures of vapor bubble disappearance Th (°C) are shown as well as fluid compositions. H₂O:NaCl:KCl fluid compositions for the inclusions are calculated from Figure 3.17. Salinities of inclusions which contain only halite may be overestimated by 10-14 wt% NaCl due to salting out effects and bulk salinities may be underestimated by 10-15 wt% NaCl.

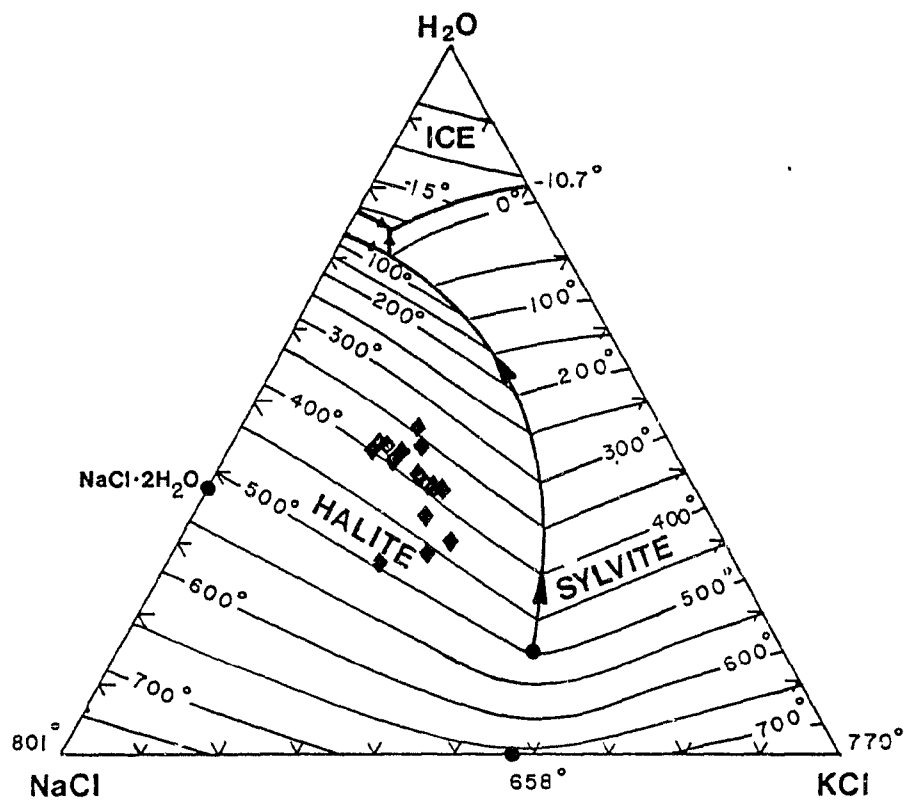


Figure 3.17 Vapor-saturated, polybaric solubility surface in the NaCl-KCl-H₂O ternary system (after Sterner et al., 1988). Solute concentrations for Troodos inclusions are indicated by solid diamonds. Fluid compositions are plotted by applying halite and sylvite dissolution temperatures for inclusions which contain both daughter phases. Inclusion compositions all lie within the halite + liquid + vapor field.

TABLE IV
SYLVITE- AND HALITE-BEARING FLUID INCLUSION ANALYSES

SAMPLE	Th°C	Te°C	Tice	Tm _H	Tm _S	H ₂ O:NaCl:KCl	TOTAL*
CY88-9	370	-67	---	384	173	42:35:23	58
	377	-61	-35	386	147	43:36:21	57
	367	---	---	390	240	37:33:30	63
	134	-63	-33	323	---	60:40	40
	356	---	---	397	142	42:38:20	58
	361	---	---	398	138	42:39:19	58
	379	-67	-49	386	---	55:45	45
	365	---	---	384	245	37:32:31	63
	363	---	---	388	203	39:35:26	61
	372	-72	---	398	170	41:37:22	59
	365	-72	---	397	---	54:46	46
CY87-1	301	---	---	460	317	28:38:34	72
	289	---	---	436	336	28:34:38	72
	336	---	---	389	232	38:34:28	62
	315	---	---	482	275	29:44:27	71
	320	---	---	428	274	33:36:31	67
	322	---	---	359	179	43:25:27	57

Th=vapor bubble disappearance temperature; Te=eutectic temperature;

Tice=final ice melting temperature

Tm_H=halite dissolution temperature; Tm_S=sylvite dissolution temperature

*Salinities in wt%

Mathematician Ridge (Vanko et al., 1988; Vanko, 1988). In these studies, the lack of ice nucleation is attributed to metastable behavior of the ice. The lower eutectic and final ice melting temperatures of inclusions in sample CY88-9 indicate that solution compositions cannot be characterized as simple NaCl-KCl brines. Dissolved species such as CaCl_2 and MgCl_2 act to depress eutectic minima (Crawford, 1981) and may be responsible for the values observed in the Troodos rocks. The compositions of submarine hydrothermal fluids, and experimental data on water/rock interaction indicate that mature hydrothermal fluids in oceanic systems are barren of magnesium. The epidiosites found near the base of reaction zones represent zones of extreme calcium metasomatism by evolved fluids at high water/rock ratios. It is doubtful, therefore, that MgCl_2 is responsible for the lower eutectic and ice melting temperatures. Although phase equilibria are not yet quantitatively determined for quaternary systems such as NaCl-KCl- CaCl_2 - H_2O under vapor-saturated conditions, it is known that CaCl_2 decreases the solubility of halite in the brines (Crawford, 1981; Sterner et al., 1988). The presence of CaCl_2 will result in calculation errors of total bulk salinities similar to those in the system NaCl-KCl; i.e., underestimation of the bulk salinity and overestimation of the relative amount of NaCl and, possibly, KCl.

3.4 Laser Raman Microprobe Spectroscopy (LRM) Results

Laser raman analyses were completed on a subset of 6 plutonic samples (Table V) to evaluate volatile components and solid phases of fluid inclusion Types 1-3. Raman microspectroscopic analyses were conducted by Dr. Jill Pasteris at Washington University, St. Louis, using a Jobin-Yvon RAMANOR U-1000 dispersive spectrometer interfaced with a modified NACHET microscope. A monochromatic continuous-wave 5W Ar-ion laser provided the excitation source for raman scattering. Spectra were obtained using variable step sizes and counting times: one to two scans were done per inclusion and total counting times ranged from 0.17 hr to 3.0 hr (Table V). Volatile species analyzed by LRM included CO_2 , CH_4 , N_2 , and SO_4 . In cases where small peaks were detected in the spectra of the inclusions, a scan of the matrix (at the same depth

TABLE V
RAMAN ANALYSES OF FLUID INCLUSIONS

SAMPLE	PHASE	SPECIES ANALYZED	# Scans	t (hr)	RESULTS
CY87-1 (PG) Quartz	(1) Vapor	CO ₂ ,CH ₄ ,N ₂ ,SO ₂ ,CO	1	0.5	BDL (1 bar)
	(2) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	BDL (1 bar)
	(2) Matrix	N ₂	1	0.17	Compared
	(3) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	CO ₂ suspect
	(3) Matrix	CO ₂	1	0.17	Compared
	(3) Vapor	CO ₂	1	0.17	BDL (1 bar)
	(4) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	BDL (1 bar)
	(5) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	BDL (1 bar)
CY88-5 (PG) Quartz	(1) Vapor	CO ₂ ,CH ₄ ,N ₂	2	0.5	BDL (2 bar)
	(2) Vapor	CO ₂ ,CH ₄ ,N ₂	2	0.5	BDL (2 bar)
	(3) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	BDL (2 bar)
	(4) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	N ₂ suspect
	(4) Matrix	N ₂	1	0.17	Comparison
	(4) Vapor	N ₂	1	0.17	BDL (2 bar)
	(5) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	BDL (2 bar)
	(6) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	N ₂ suspect
	(6) Matrix	N ₂	1	0.17	Comparison
	(6) Vapor	N ₂	1	0.17	BDL (2 bar)
CY1017.62 (GB) Plagioclase	(1) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	BDL (1 bar)
	(2) Solid	Anhy/Gyp	2	1.5	Carbonate (?)
	(2) Matrix	Plag	2	0.5	Comparison
	(3) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	BDL (1 bar)
	(4) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	BDL (1 bar)
	(5) Vapor	CO ₂ ,CH ₄ ,N ₂	2	0.5	BDL (1.5 bar)
	(6) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	BDL (1.5 bar)
	(7) Vapor	CO ₂ ,CH ₄ ,N ₂	1	0.5	BDL (1.5 bar)
ALV1011-1 (GB) Apatite	(1) Solid	OH Band	5	0.40	Decrepitated
	(2) Vapor	CO ₂ ,CH ₄ ,N ₂	1	Ab.	Fluorescence
	(3) Vapor	CO ₂ ,CH ₄ ,N ₂	1	Ab.	Fluorescence
	(4) Vapor	CO ₂ ,CH ₄ ,N ₂	1	Ab.	Fluorescence

(GB) = Gabbro; (PG) = Plagiogranite; BDL = Below detection limit

Ab. = Run aborted due to fluorescence; Anhy = Anhydrite; Gyp = Gypsum

of the inclusion) in the range of the suspect volatile was made to assess the importance of scattering from both the matrix and the air in the beam path. Detection levels are thought to vary between 1 and 2 bars partial pressure for each volatile species (Wopenka et al., 1990). For inclusions containing daughter phases, raman spectral bands were analyzed for anhydrite, gypsum, and amphibole (OH stretching band). Samples were prepared according to procedures outlined in Wopenka et al., (1990).

Results of laser raman analyses indicate that concentrations of the volatile species are below the limits of detection in **all inclusions** analyzed. Weak to substantial fluorescence was observed during analyses of plagioclase- and apatite-hosted inclusions, respectively. The resultant increase in background counting rates resulted in poor signal to noise ratios, therefore, distinct spectra could not be obtained on these samples.

Crystalline phases of the inclusions could not be identified unambiguously using raman spectroscopy. A bladed daughter mineral, thought to be amphibole, was analyzed in sample ALV1011-1 (Figure 3.4D). Absorption of laser energy by the red component of the mineral (in plane-polarized light) resulted in thermal decrepitation of the fluid inclusion as well as damage to the daughter phase. Weak raman spectra were observed for non-opaque solids in CY4-1017.62 indicating the presence of either magnesite or dolomite; however, this identification is very tentative.

3.5 Inclusion-Specific Mass Spectrometric Analyses and Results

Volatile contents of individual fluid inclusions were measured by mass spectrometric analyses on a replicate set of samples analyzed by LRM. Inclusion specific mass spectrometric analyses were conducted by Dr. Colin Barker and Bill Underwood at University of Tulsa, Oklahoma, using a UTI 100C mass spectrometer controlled by an external Apple IIe computer. Sample chips (1-2 grams each) were progressively heated under vacuum until inclusion decrepitation occurred. An inclusion burst is indicated by a rapid pressure rise or when any or all of the masses increase significantly from one

mass spectrum to the next (Fig. 3.18; Barker and Smith, 1986; Barker et al., 1987; Barker and Sullivan, 1989). This rapid pressure rise is recognized by the computer program, which then triggers the mass spectrometer to retain the previous spectra as background and sample the following spectra for analytical data. An initial calibration run is carried out with part of the sample to obtain optimum attenuation factors for each mass sampled. The UTI 100C scans from mass 1-64 in 20 ms, followed by 5 ms of dead time for each scan during which time the computer organizes previously collected spectra, resets the scan to mass 1, and initiates another scan. Data are collected throughout the entire heating process. These operating procedures permit analysis of trace components present at levels below 1 part in 10,000 (Barker and Smith, 1986).

Figure 3.18 illustrates the mass spectrometer response (Sample ALV1011-1) for a portion of the collected data for water at mass 18, and carbon monoxide at mass 28. The horizontal axis is spectrum number which correlates approximately linearly with temperature, increasing to the right. Rupture of large inclusions (A) are easy to detect, where as smaller inclusions (B) are impossible to detect with any accuracy because of their size relative to noise (N). The difference between each peak and the immediately preceding trough is the amplitude plotted for individual inclusions.

Detectable inclusion ruptures in the Troodos samples were rare and contained water with little or no carbon dioxide, or other volatiles, confirming results from LRM and microthermometric analyses. Three samples (CY87-1, CY88-5, CY1017.62) contained no detectable inclusions. Sample CY88-9 contained 1 inclusion, CY88-4 had 3, and CY1181.75 had 12 inclusions. Spectra from sample CY1181.75, a gabbro-hosted pegmatitic vein, indicate the inclusions are dominated by water with little or no other volatiles detected (Fig. 3.19 and 3.20). Scattering between amu's 17 and 18 (Figure 3.20) is due to noise. Inclusions all fall close to the 17-18 axis indicating the absence of CO₂.

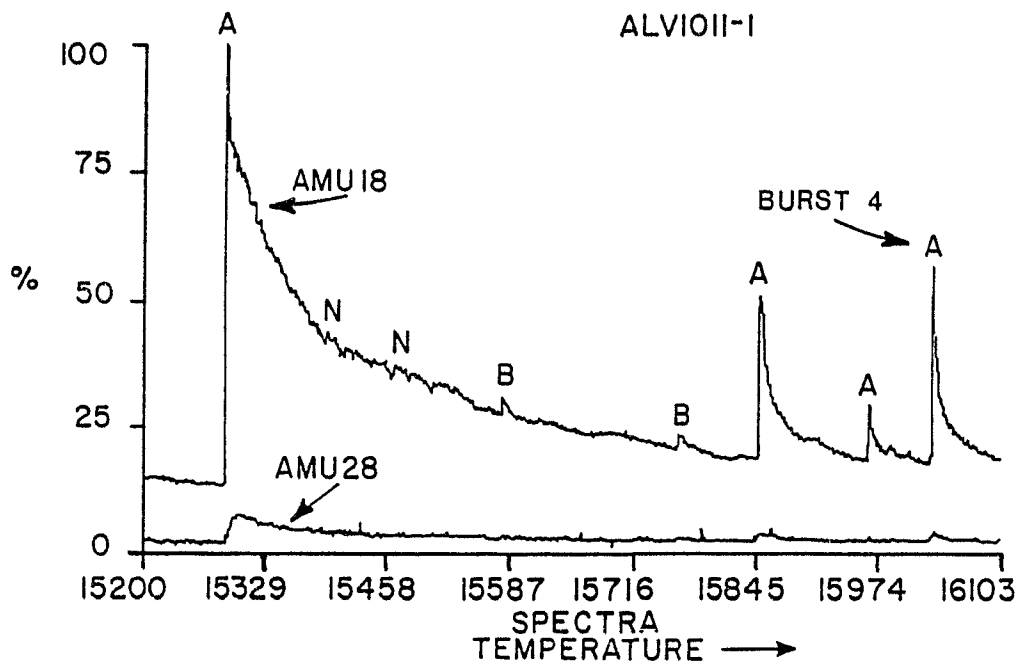


Figure 3.18. A portion of the collected data for amu's 18 (H_2O) and 28 (CO) for sample ALV1011-1. The horizontal axis is spectrum number which correlates approximately linearly with temperature. Each sharp peak represents an inclusion rupture. Decrepitation of large inclusions is indicated by A, those labelled B are small inclusions and background noise is indicated by N. The difference between each peak and the immediately preceding trough is the amplitude plotted for individual fluid inclusions. Burst 4 at $400^\circ C$, corresponds to mass spectrum 16031 shown in Figure 3.21.

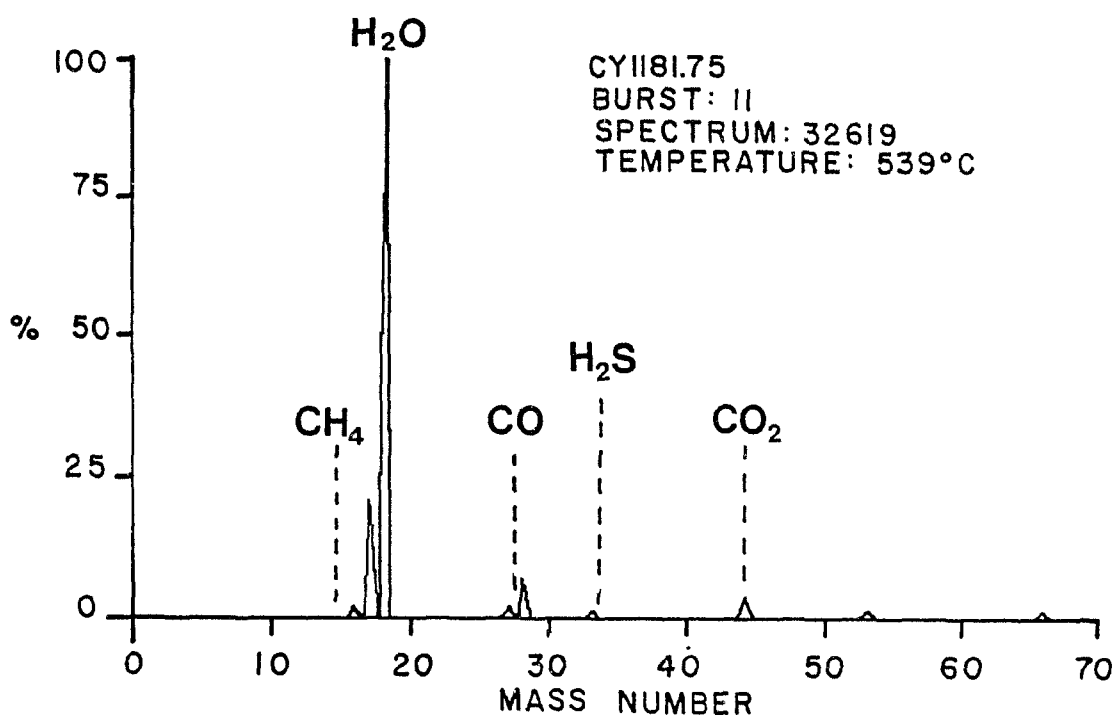


Figure 3.19. Sample mass spectrum for sample CY1181.75. Spectra indicate the inclusions are dominated by water and contain little or no carbon dioxide. Peaks represent bursts of vapor-dominated inclusions hosted in hydrothermal clinopyroxene and/or quartz-hosted, brine-rich inclusions.

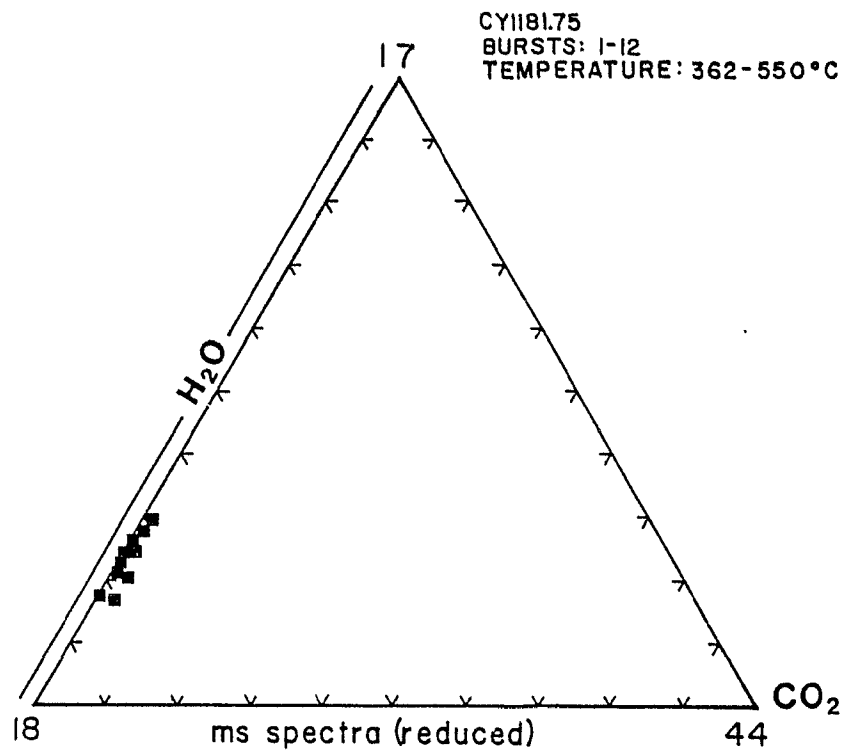


Figure 3.20. Ternary diagram for water (amu 17 and 18) and carbon dioxide (amu 44). Squares indicate inclusion compositions measured during 12 inclusion bursts upon heating of the sample from 362-550°C. The data show a scattering between amu's 17-18 due to noise, but do not indicate the presence of CO₂

Fluid inclusions hosted in a gabbro sample from the Mid-Atlantic Ridge (ALV1011) were analyzed in order to compare volatile compositions between the two spreading systems. Fluid inclusions in the Mid-Atlantic Ridge sample are dominated by water (amu's 16, 17, 18; Fig 3.18 and Fig. 21-23) with a trace of carbon dioxide (amu 44). Twenty six inclusion ruptures were detected between 379-701°C. The inclusions contain a small, but detectable amount of CO₂, as illustrated in Figure 3.23.

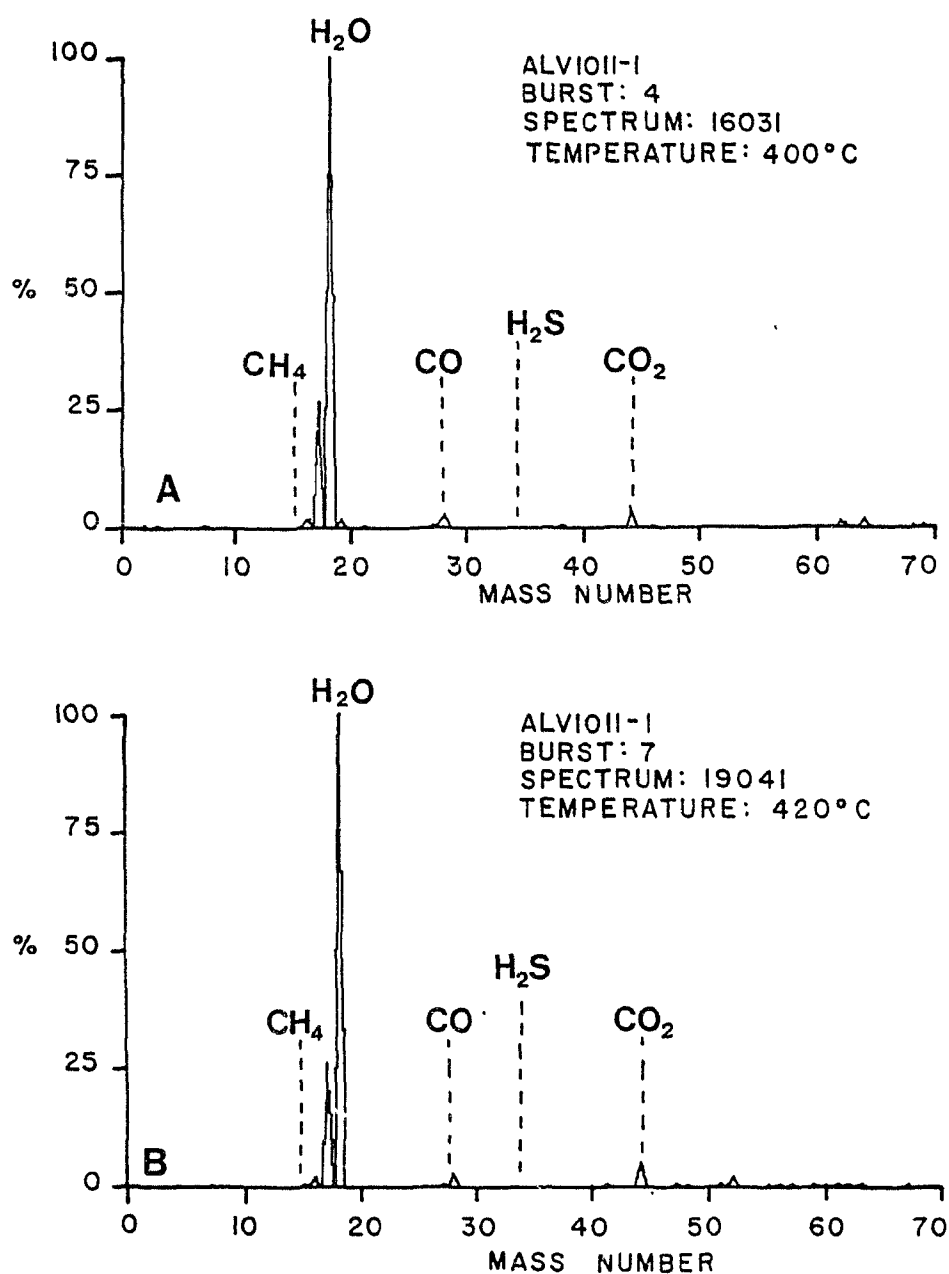


Figure 3.21. Sample mass spectrum for sample ALV1011-1. (A) Spectrum 16031, inclusion burst number 4 at 400°C. Inclusions are dominated by water (H_2O) and contain small amounts of carbon dioxide (CO_2). (B) Spectrum 19041, inclusion burst number 7 at 420°C.

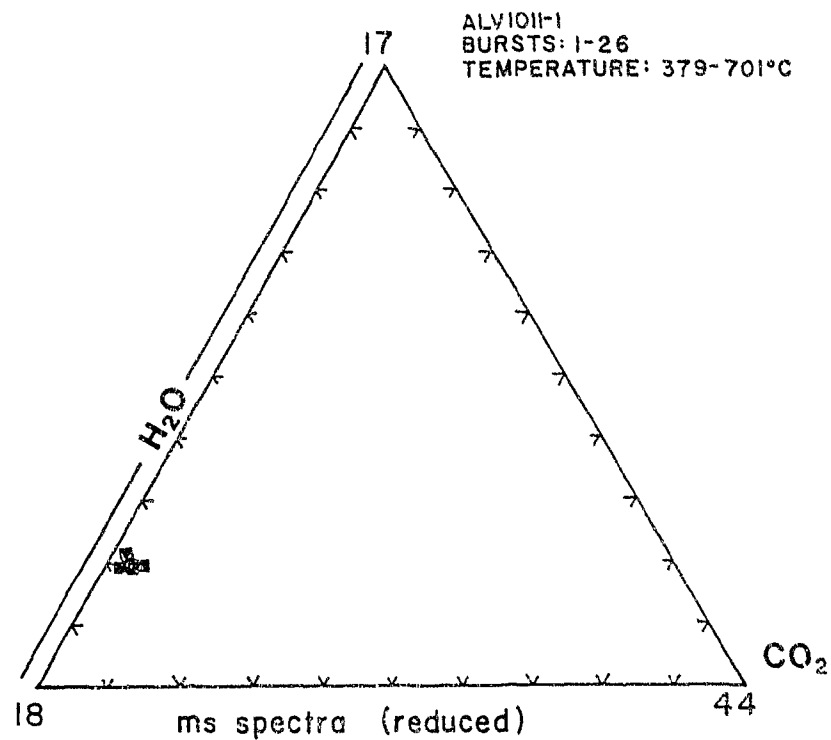


Figure 3.22. Ternary diagram for amu's 17 (H_2O), 18 (H_2O), and 44 (CO_2). Analyses of volatiles released during decrepitation of 26 inclusions (solid squares) in sample ALV1011 indicate the inclusions are dominated by water, but contain some carbon dioxide.

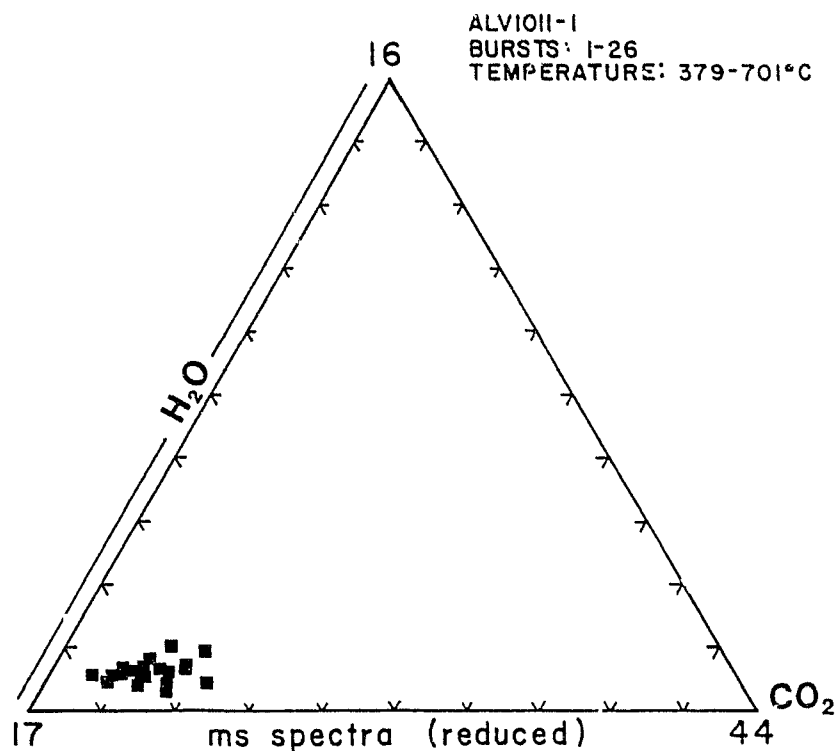


Figure 3.23 Ternary diagram for water (amu's 16 and 17) and carbon dioxide (amu 44) showing fluid inclusion compositions for sample ALV1011-1. Amu's 16 and 17 are fractions of the main water peak at amu 18. Noise is relatively increased, causing scattering of the points. The data indicate inclusions are dominated by H₂O, and contain a small amount of CO₂.

CHAPTER IV

DISCUSSION

4.0 INTRODUCTION

Microthermometric analyses of aqueous fluid inclusions in fresh and epidotized plagiogranites and gabbros from the Troodos ophiolite indicate that circulation of high-temperature, Fe-rich brines was common at crustal depths of 2-3 km (Fig. 3.11). Anastomosing networks of fluid inclusion arrays in rocks of the upper intrusive sequence are believed to record episodic fracturing events. The earliest fracturing event, at temperatures greater than 400-500°C, resulted in pervasive entrapment of brine-rich aqueous fluids, the compositions of which vary spatially throughout the complex by as much as 23 wt% NaCl [33 to 56 wt% NaCl equivalent (Table III & Fig. 3.11)]. Homogenization of the high-temperature inclusions by halite dissolution indicates the fluids were entrapped in the absence of a vapor phase at minimum temperatures of 400°C to 500°C (Cloke and Kessler, 1979; Roedder, 1984). Arrays of low-temperature, low-salinity inclusions, which cut fractures dominated by brine inclusions, indicate that subsequent fracturing occurred at uncorrected temperatures of 200-400°C. Salinities of the low-temperature inclusions (1-7 wt% NaCl equivalent) vary from 70% below to 200% above seawater concentrations (Fig. 4.0 and Fig. 4.1; Table VI). Conditions of brine generation and fluid circulation models are discussed below.

4.1 Generation of High-Salinity Fluids in the Oceanic Crust

Brine-rich fluids have been noted for many years in fossil hydrothermal systems associated with porphyry ore deposits (e.g., Gustafson and Hunt, 1975; Ahmad and Rose, 1980; Reynolds and Beane, 1985). Fluid inclusion analyses of these systems indicate that the earliest fluids to circulate through the plutonic host rocks are very high-temperature (>700-800°C), complex chloride brines which contain high metal concentrations (Bodnar and Beane, 1980; Reynolds and Beane, 1985; Roedder, 1984). Only recently, however, have highly saline fluids been recognized in the oceanic crust

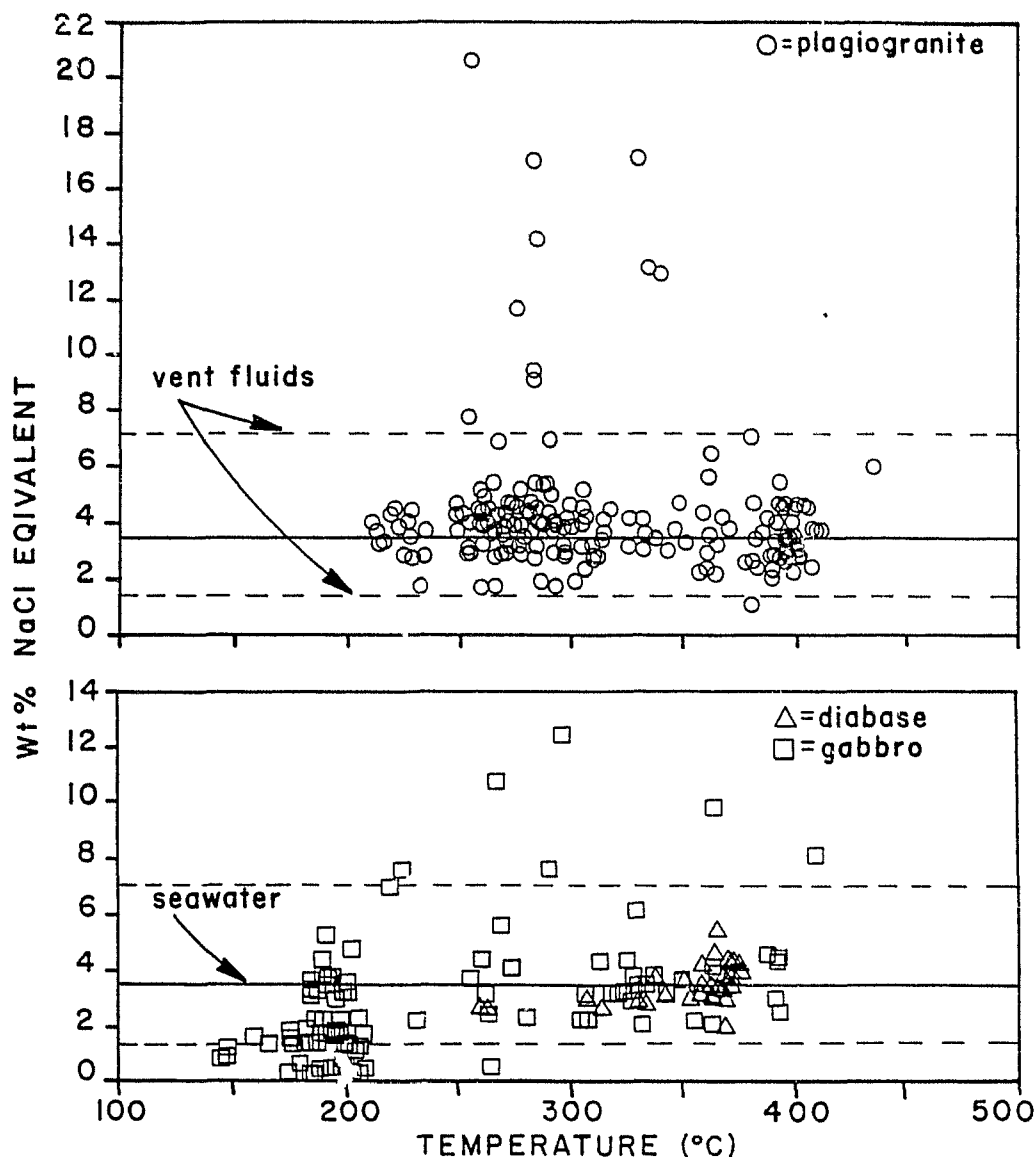


Figure 4.0 Temperatures of vapor bubble disappearance and corresponding equivalent fluid salinities for low-temperature fluid inclusions in quartz, epidote, hydrothermal clinopyroxene, and amphibole. Fluid inclusions hosted in plagiogranite rocks (open circles), diabase (open triangles), and gabbroic rocks (open squares), exhibit uncorrected homogenization temperatures of 200-400°C, and contain fluid salinities of <1.0-7.0 wt% NaCl equivalent. Salinities of the inclusions are close to seawater (solid line) and closely overlap the salinity field measured for fluids exiting active submarine hydrothermal vents (dashed lines); therefore, the inclusions are interpreted to represent fluids entrapped during circulation of modified seawater at depth.

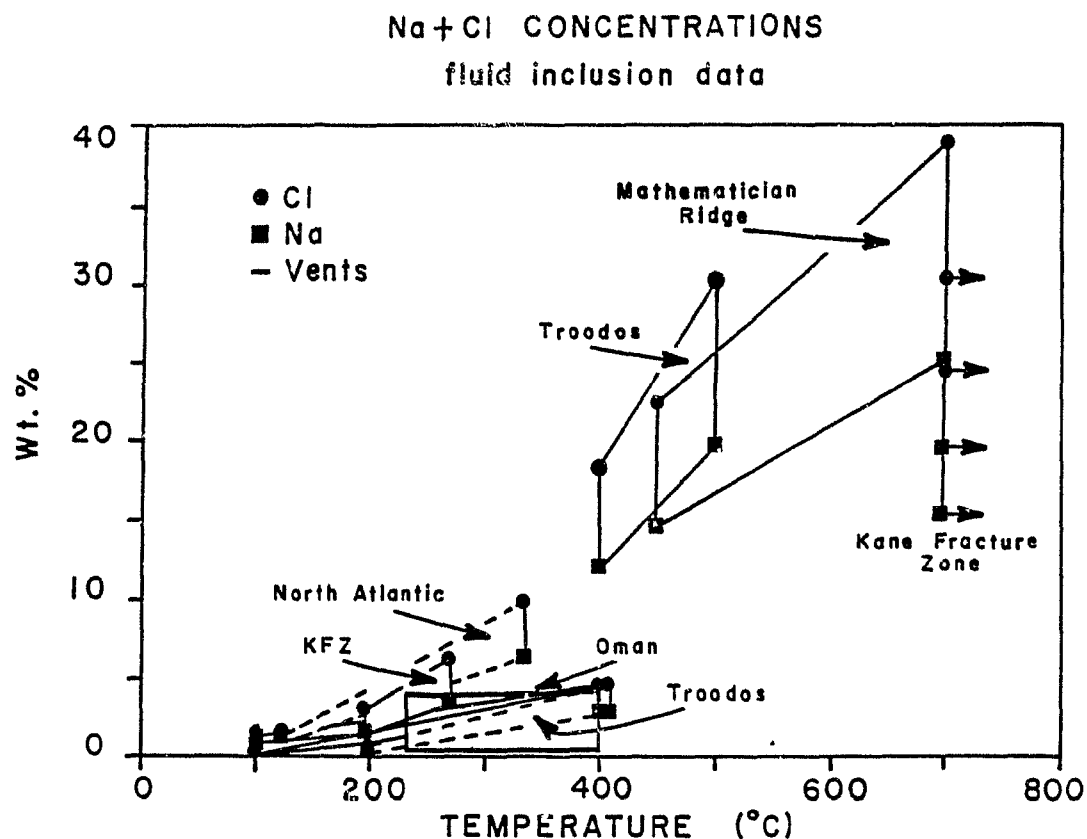


Figure 4.1. Ranges of chlorine (Cl) and sodium (Na) contents of fluids exiting hydrothermal vents (open rectangle at base of diagram), and of inclusions in submarine extrusive and plutonic rocks. Submarine samples hosting fluid inclusions include: quartz-bearing, greenstone breccias from the Kane Fracture Zone [(KFZ) Delaney et al., 1987], basalts to gabbros from the North Atlantic (Jehl et al., 1977), quartz veins in metagabbros from the Mathematician Ridge (Vanko, 1988), gabbro-hosted inclusions from the Kane Fracture Zone (Kelley and Delaney, 1987), and basalt to diabase-hosted inclusions from Oman (Nehlig and Juteau, 1988). Measured fluid compositions indicate dramatic increases in chlorine and sodium contents of fluids at temperatures $>400^{\circ}\text{C}$.

TABLE VI
CHLORINE AND SODIUM CONCENTRATIONS IN
SUBMARINE HYDROTHERMAL FLUIDS

Authors		Area	T°C	Cl	Na	Cl	Na
				mmol/kg	mmol/kg	wt%	wt%
		Seawater	2.42	539	510	1.91	1.06
Butterfield et al., (1990)	JdF	Inferno	326	624	501	2.21	1.15
		Hell	301	550	446	1.95	1.02
		Mushroom	283	520	417	1.84	0.96
		Hillock	323	482	391	1.71	0.90
		Crack	217	258	209	0.91	0.48
		Virgin	299	176	151	0.62	0.35
Von Damm (1985)	EPR	21°N-NGS	273	573	510	2.03	1.81
		21°N-OBS	350	494	432	1.75	0.99
		21°N-SW	355	500	439	1.77	1.01
		21°N-HG	351	496	443	1.76	1.02
Bowers (1988)		13°N-2	354	712	551	2.52	1.27
		13°N-3	380	760	596	2.69	1.37
		13°N-4	347	563	472	2.00	1.08
Campbell (1988)	KFZ	23°N-1	350	559	510	1.98	1.17
		23°N-2 335	559	509	1.98	1.17	
Kelley This Study	CYP	Troodos	600	8555	8555	30.33	19.67
	CYP	Troodos	500	5133	5133	18.20	11.80
Kelley (1987) & Delaney	KFZ	23°N	700	8555	8555	30.33	19.67
		23°N	700	6848	6848	24.28	15.72
Delaney et al., (1987)	KFZ	23°N	237	959	959	3.40	2.20
		23°N	270	1675	1675	5.94	3.85
		23°N	196	787	787	2.79	1.81
		23°N	240	1027	1027	3.64	2.36
Jehl (1977)	N. Atlantic		124	409	409	1.45	0.94
			335	2742	2742	9.72	6.30
Vanko (1988)	Math. Ridge		450	6329	6329	22.44	14.55
			700	10950	10950	38.82	25.18

JdF=Juan de Fuca Ridge, *EPR*=East Pacific Rise, *KFZ*=Kane Fracture Zone
CYP=Cyprus, *N.Atlantic*=North Atlantic, *Math. Ridge*=Mathematician Ridge

[Table VI, VII, Fig. 4.1 and references therein]. High-temperature ($>700^{\circ}\text{C}$), sulfide-bearing brine inclusions (48-50 wt% NaCl equivalent), similar to those in porphyry systems, have been observed in metagabbros from the Mid-Atlantic Ridge (Kelley and Delaney, 1987). Brine-rich inclusions have also been documented in plagiogranites from the Semail ophiolite (Nehlig, 1989) and in gabbro-hosted quartz veins from the Mathematician Ridge (Vanko, 1988). An important feature of all these high-temperature brine inclusions is their close spatial association with very low-salinity, vapor-dominated inclusions. Such extreme NaCl concentrations have not been observed in hydrothermal vent solutions, where salinities vary from 70% below to 200% above seawater concentrations (Table VI).

This sodium chloride variability in submarine hydrothermal solutions has been attributed to hydration reactions under rock-dominated conditions (Cathles, 1983; Ito and Anderson, 1983; Vanko, 1986; Vibetti et al., 1989), retrograde dissolution of ephemeral chloride-bearing mineral phases (Edmond et al., 1979; Seyfried et al., 1986; Berndt and Seyfried, 1990) and supercritical two-phase separation of hydrothermal solutions (Kelley and Delaney, 1987; Vanko, 1988; Von Damm, 1988; Bischoff and Rosenbauer 1989).

4.1.1 Hydration Reactions

In the deep levels of submarine hydrothermal systems where permeability is low, hydration reactions are likely to occur under rock-dominated conditions. Formation of hydrated phases may result in modified chlorine and sodium concentrations of the residual fluids. Solutions with elevated salt concentrations may form as water is preferentially incorporated into hydrated mineral phases (Cathles, 1983). Under certain P-T-X conditions, however, hydration reactions may also act to reduce chlorine concentrations in the solutions, as indicated by secondary amphiboles containing up to 4 wt% chlorine (Vanko, 1986). Chlorine has been detected in actinolitic hornblende

TABLE VII
FLUID INCLUSION STUDIES ON SUBMARINE SAMPLES

AUTHOR	LOCATION #	ROCK TYPE	HOST	Th (°C)	Tf (-°C)	NaCl (wt%)
Jehl (1977)	North Atlantic N=639	Basalt- Gabbro	Quartz	237-324	2.3-4.8	3.8-7.6
			Flspar	136-335	1.4-11.0	2.4-15.0
			CC	124-246	1.9-12.0	3.2-16.0
Delaney ⁺ et al., (1987)	MARK N=123	Quartz Breccia	Quartz	237-270	3.4-6.4	5.6-9.8
			Quartz	196-240	2.8-3.7	4.6-6.0
Kelley & Delaney ⁺ (1987)	MARK N=362	Gabbro	Flspar	230-330	0.4-3.7	0.7-6.0
			Epi	370-430	2.4-3.7	4.0-6.0
			Cpx	370-430	2.1-4.0	3.5-6.5
			Apt	240-310	2.4-4.4	4.0-7.0
			Apt	360-410	0.3-1.8	0.5-3.0
			Apt	>700	—	38.0-47.0
Nehlig & Juteau (1988)	OMAN N=391	Basalt	Quartz	128-409	1.8-4.8	3.0-7.6
			CC	100-228	0.7-2.1	1.2-3.5
		Diabase	Quartz	149-393	0.6-5.8	1.0-8.9
		Plgran-	Quartz	106-372	1.6-2.5	2.7-4.8
		Gabbro	Flspar	121-191	1.9-2.1	3.2-3.5
			Amph	320-390	0.9-3.7	1.6-6.7
			CC	109-198	0.4-3.7	0.7-6.0
Vanko (1988)	EPR N=342	Gabbro	Quartz	138-550		0.0-22.0
			Quartz	330-430	0.6-4.4	1.0-7.0
			Quartz ⁺⁺	409->700	---	36.0-64.0
Cowan & Cann ⁺ (1988)	Troodos N=38	Plgran	Quartz	330-410	0.0-1.2	0.0-2.0
			Quartz	330-430	---	37.0-48.0
Kelley ⁺⁺	Troodos N=540	Plgran- Gabbro	Quartz	270-420	0.8-4.4	1.0-7.0
			Quartz	400-500	---	33.0-56.0
			Cpx	370-430	2.4-4.4	4.0-7.0
			Epi	370-430	2.1-4.5	3.5-7.2

Host=mineral host, Th=homogenization temperature, Tf=freezing temperature

Flspar=feldspar, CC=calcite, Epi=epidote, Cpx=clinopyroxene

Apt=apatite, Amph=amphibole, ⁺=corresponding homogenization and salinities measurements on individual inclusions

⁺⁺Some inclusions contain NaCl-KCl-CaCl₂-H₂O, ⁺⁺Inclusions contain NaCl-CaCl₂-H₂O

from the CY4 drillcore, but never or rarely in hornblende or fibrous actinolite (Thy et al., 1989).

How important hydration reactions are in modifying ionic strengths of hydrothermal solutions is a function of rock permeability and whether fluids interact with fresh rock. In high flow-through zones where crack apertures are large, fluids may become insulated from wall rock reaction as minerals precipitate and line fracture walls. Hydration reactions may be of considerable importance, however, in zones containing small aperture cracks and where fluids are continually exposed to fresh rock.

Although mineral hydration may play a limited role in generating low-salinity fluids in Troodos (salinities from 70% below to 200% above seawater concentrations), hydration is unlikely to have been responsible for generation of the highly saline brines. To double the salinity of the parental fluids, assuming perfect partitioning of sodium and chlorine into the aqueous phase, 50% of the gabbros and plagiogranites would have to be hydrated. Generation of the highly saline brines from a seawater source would require a minimum of 93% of the plutonic rocks to be hydrated. Although epidosite zones indicate there are localized areas of extreme alteration, such widespread alteration is not present in the upper or lower plutonic sequence. Therefore, rock hydration is not a viable method for brine formation.

Hydration during serpentinization, however, was suggested as a mechanism to produce calcium chloride brines observed in quartz veins hosted in diabase and gabbro samples from hole CY4 (Vibetti et al., 1989). The quartz veins, 2 to 5 cm wide, are located at depths of 983, 1058, and 1196 m, and occur 600 to 800 m above concentrated zones of ultramafic rocks. Primary, quartz-hosted inclusions exhibit depressed eutectic temperatures similar to those observed in this study (Te -55 to -43°C); homogenization temperatures of the brines range from 135 to 280°C (Table VII). Some of these inclusions contain daughter minerals, suggested to be halite and

antarticite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$), however, neither dissolution temperatures nor salinities of the inclusions are reported. These brine inclusions are interpreted to result from multistage calcium metasomatism and serpentinization of the underlying ultramafic rocks by seawater-derived fluids; the resultant brines were presumably injected into the overlying roof rocks along fractures induced by serpentinization. Although partial serpentinization of the ultramafic rocks is common, it is highly unlikely that this process can generate the 400-500°C brines hosted in the upper plutonic sequence.

4.1.2 Retrograde Solubility

Chlorine variations of some hydrothermal vent solutions [Galapagos 83°W, Edmond et al. (1979); EPR 13°-11°N, Bowers et al. (1988)] have been attributed to the formation or retrograde dissolution of a transient Fe- or Mg-hydroxychloride mineral phase. The presence of chlorine-bearing minerals in ultramafic rocks (Early, 1958; Rucklidge and Patterson, 1977), and experimental data (Poty et al., 1972; Seyfried et al., 1986; Berndt and Seyfried, 1990) provide limited support for this suggestion. Microprobe analyses of fine-grained serpentine bordering olivine and orthopyroxene in ultramafic rocks indicate chlorine contents of 970 ppm to 7000 ppm (Early, 1958; Rucklidge and Patterson, 1977). The absence of chlorine in adjacent coarser-grained serpentine led Rucklidge and Patterson to suggest that compounds like $\text{Fe}_2(\text{OH})_3\text{Cl}$ or $\text{Mg}_2(\text{OH})_3$ may undergo retrograde dissolution during migration of lower temperature fluids.

Hydrothermal fluid/rock experiments, under rock-dominated conditions, may lend support for this hypothesis. Seyfried et al. (1986) noted chlorine depletion of up to 20% in model hydrothermal seawater solutions (starting fluid composition of 3.2 wt% NaCl) at temperatures of 425°C and 400 bars pressure. Chlorine depletions in the experiments were not observed, however, in all samples and appeared to be rock specific. A re-evaluation of these experiments by Bischoff and Rosenbauer (1989), under similar run conditions and using similar rock types, failed to reproduce the results

of Seyfried's lab. Chlorine depletions were not observed in any of Bischoff's experiments, and in fact chlorine concentrations actually increased 1.5 to 2.0%. Additional experimental work is needed to determine the effective magnitude of this process on fluid chemistry variation in natural submarine hydrothermal systems. Although transient retention or dissolution of chlorine-bearing mineral phases may affect chemistry of low-salinity fluids, these processes do not appear to be capable of generating high levels of brine enrichment.

4.1.3 Two-Phase Separation

The importance of two-phase separation in generation of brines at depths of 2-3 km in the oceanic crust, and the effect this process has on determining the upper temperature limit and composition of vent fluid chemistry, is currently under intense debate (Bischoff, 1980; Seyfried et al., 1986; Delaney et al., 1987; Bowers et al., 1988; Campbell et al., 1988; Von Damm, 1988; Bischoff and Rosenbauer, 1989; Berndt and Seyfried, 1990). Within the last 5 years compelling evidence for phase separation has been provided by the discovery of brine-rich fluid inclusions in gabbros from the Kane Fracture Zone (Kelley and Delaney, 1987), Mathematician Ridge (Vanko, 1988), ODP Hole 735B in the Indian Ocean (pers observation), Semail ophiolite (Nehlig, 1989) and the Atlantis II and Oceanographer Fracture Zones (Vanko, pers comm.). Observations of plutonic-hosted brine inclusions, to date, are limited to high-temperature paleohydrothermal systems associated with slow-spreading environments and to ophiolites; it is difficult to evaluate the degree to which deep crustal brines may be generated in medium- to fast-spreading environments due to the paucity of submarine samples collected from these areas.

Brine-rich fluid inclusions in many of the metagabbros from these areas are spatially associated with low-salinity (1-2 wt% NaCl), vapor-dominated aqueous inclusions. Because most of these rocks have been affected by multiple hydrothermal pulses and fracturing events, it is difficult to determine whether the two disparate

inclusion populations are cogenetic. The coexistence of low-salinity, vapor-dominated fluid inclusions and brine inclusions along single healed microfractures in gabbros from the Mid-Atlantic Ridge (Kelley and Delaney, 1987) provided the first unambiguous evidence for supercritical two-phase separation of saline fluids at depth in submarine systems. Spatial and compositional relationships of the disparate inclusions are difficult to account for in terms of hydration or retrograde reactions and are **most reasonably** explained by **two-phase separation**, whereby high temperature, dilute to moderately saline fluids circulating at depth impinge the two phase field, resulting in equilibrium separation of the fluid into coexisting saline liquid and dilute vapor phases.

Although brine-rich solutions have not been observed in rocks from shallow crustal levels (i.e. pillow lavas and stockwork systems), the compositions of submarine hydrothermal vent fluids indicate phase separation may play an important role in determining vent fluid chemistry (Von Damm, 1988; Butterfield et al., 1990). Salinity variations of hydrothermal vent solutions, which exhibit covariant depleted and enriched gas phases, respectively, are postulated to result from subsurface mixing of modified seawater with gas-enriched vapor phases and gas-depleted brines; the vapor- and brine-rich phases are generated during previous phase separation events at deeper crustal levels. Vent solution chemistries from the Galapagos spreading center, 21°N and 13°N on the East Pacific Rise, and the Southern Juan de Fuca Ridge, indicate salinity variations resulted from mixing of seawater with 20 wt% brines, in the proportions 15-20% brine with 80-85% seawater (Von Damm, 1988). Although dissolution and alteration of chlorine-bearing mineral phases can account for the observed salinity variations, the covariation in volatile phases with fluid salinity is difficult to reconcile with these processes and again points to phase separation as the most likely mechanism for the observed salinity variations.

Because these vents are found at moderate- to fast-spreading ridges, phase separation may not be unique to slow-spreading environments and paleohydrothermal

systems associated with ophiolites, but rather may be an integral process of submarine systems common throughout the ocean ridges. Therefore, evaluating P-T-Depth relationships in the generation of phase-separated brines in Troodos can provide important insight into deep crustal hydrothermal process acting on many of the ridge crest systems today.

4.2.0 The System NaCl-H₂O

Solution chemistry of submarine hydrothermal vents, and freezing measurements of fluid inclusions associated with plutonic environments, indicates that the ionic compositions of the fluids are dominated by NaCl. Thus, the conditions of fluid generation and evolution in these high-temperature systems can be approximated by phase relationships in the system NaCl-H₂O. P-T-X relationships in the system NaCl-H₂O were initially determined by Sourirajan and Kennedy (1962); however, recent experimental studies (Bischoff and Rosenbauer, 1985, 1987, 1988; Bodnar et al., 1985; Sterner et al., 1985) and thermodynamic modelling of NaCl in steam (Pitzer, 1983; Pitzer and Pabalan, 1986) indicate the early results are in considerable error at high temperatures. Therefore, this study uses the more recent phase determinations in modeling brine generation in Troodos. Because NaCl concentrations in brines generated by two-phase separation are independent of the ionic strength of the parental fluid, fluid sources for the inclusions are discussed later in the chapter.

The boiling point curve for pure water terminates at the critical end point, where vapor and liquid phases become indistinguishable (Fig. 4.2). Adiabatically rising fluids which intersect this univariant curve undergo boiling, separating out a vapor from the liquid phase. As long as vapor and liquid coexist, the rising fluids are restricted to temperature and pressure conditions along the boiling curve. The addition of NaCl to the system extends the boiling curve, and shifts the critical point to higher temperatures and pressures. At temperatures and pressures greater than the critical point, the two-phase curve extends as a condensation curve, terminating at the liquid

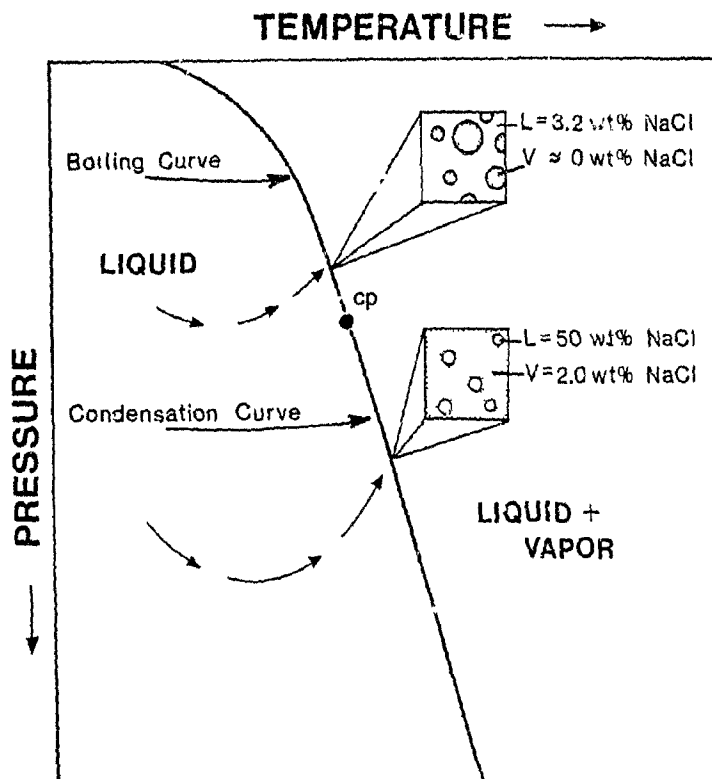


Figure 4.2. Generalized P-T relationships for the NaCl-H₂O system with pressure (depth) increasing downward and temperature increasing to the right. The boiling curve for the pure water system terminates at the critical point (cp). Fluids circulating at shallow crustal levels which intersect the two-phase curve at T-P conditions less than the critical point will undergo "boiling", separating out a vapor from the liquid phase. Deeply circulating saline fluids which intersect the two-phase curve at temperatures and pressures greater than the critical point will condense out droplets of brine from a relatively dilute vapor phase. A 3.2 wt% NaCl fluid (seawater) which intersects the boiling curve will separate out a very dilute vapor phase from the fluid. In order to double the salt concentration of the parental fluid, 50% of the initial fluid must be boiled off. In contrast, a fluid which intersects the condensation curve at 1200 bars pressure and 700°C will separate out a 50 wt% NaCl brine and a vapor phase containing 2.0 wt% NaCl.

saturation curve (Fig. 4.3). The two-phase curve defines a saddle-shaped field boundary in P-T-X space, which separates the one-phase field from the two-phase vapor + liquid field (Fig. 4.3 and Fig. 4.4). Low-temperature, shallow-level fluids whose P-T-X evolution intersects the two-phase surface at P-T conditions less than the critical point undergo "boiling", causing separation of a relatively dilute vapor phase from the fluid (Fig. 4.2). In contrast, high-temperature, deep-seated fluids whose P-T-X evolution intersects the two-phase surface under pressure-temperature conditions greater than the critical point will condense small amounts of brine from a vapor-like fluid (Fig. 4.2). In both cases, end-member vapor-brine compositions are determined by the pressure and temperature conditions of phase separation; mass ratios of the separated phases are governed by the salinity of the parental homogeneous fluid (Fig. 4.3).

Recent experimental work on metal mobilization in rock-dominated, seawater hydrothermal systems indicates that leached metals are enriched in both the brine and the vapor phases relative to seawater during phase separation (Bischoff and Rosenbauer, 1987). This result is not surprising in light of the common occurrence of sulfide daughter minerals in coexisting vapor- and brine-dominated fluid inclusions associated with porphyry copper systems (Bodnar and Beane, 1980; Reynolds and Beane, 1985).

Brine-rich fluids should be common in the deep-seated portions of submarine paleohydrothermal systems, yet, few studies document their existence. At mid-ocean ridges, shallow levels of magma emplacement (1-3 km below the seafloor), coupled with high hydrostatic pressures, provide favorable conditions for two-phase separation and the generation of brine-rich fluids. How extensive brine generation is, however, depends to a large extent upon the permeability structure at depth. In zones of high permeability it may be difficult for circulating fluids to extract enough heat to intersect the two-phase curve at temperatures and pressures above the critical point (Fournier, 1987; Goldfarb and Delaney, 1988). Under these conditions rising fluids would retain

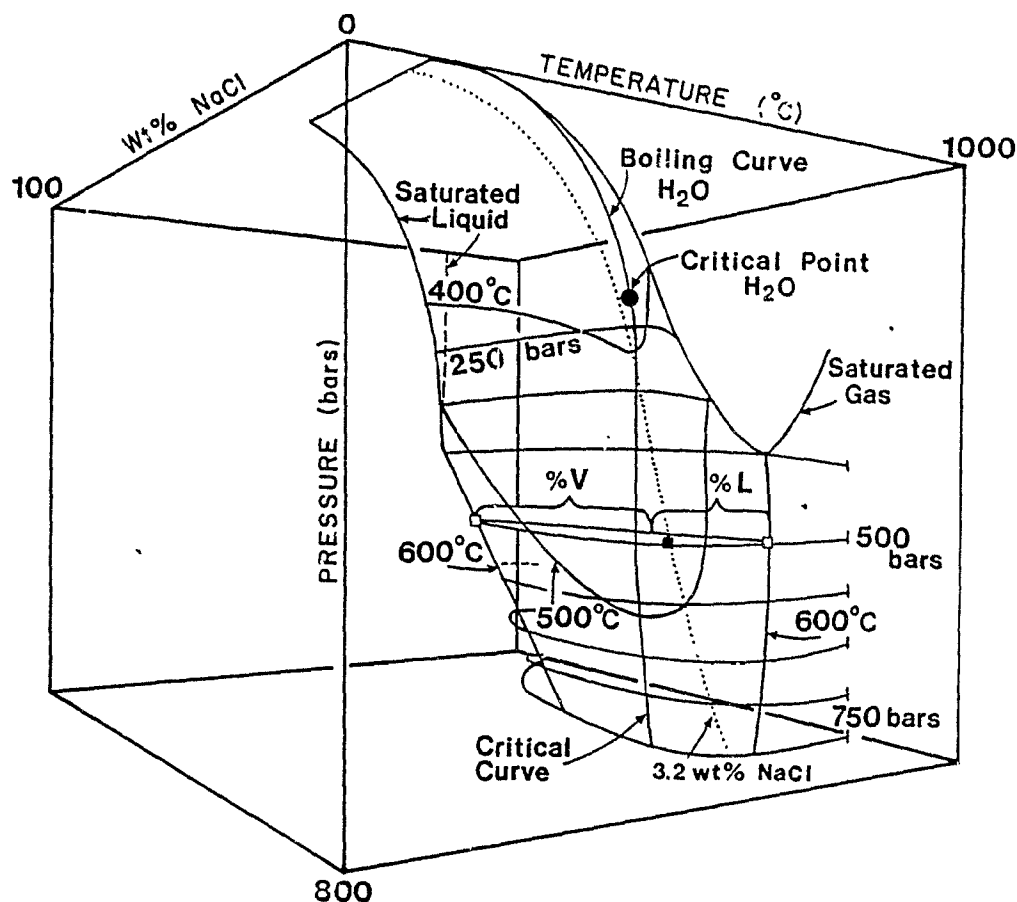


Figure 4.3. Pressure-temperature-composition relationships for the NaCl-H₂O system (after Goldfarb and Delaney, 1988). Isotherms define a saddle shaped field boundary which separates the 1-phase field from the two-phase (vapor + liquid) field. Brackets mark relative proportions of vapor (%V) and liquid (%L) generated by phase separation of a fluid with 3.2 wt% NaCl (dotted line) which intersects the two-phase curve at 600°C and 500 bars (solid square). Open squares mark end-member fluid compositions of phase separated brine and vapor phases. End-member vapor-brine compositions are determined by the pressure and temperature conditions of phase separation; mass ratios of the separated fluids are governed by the salinity of the parental homogeneous fluids.

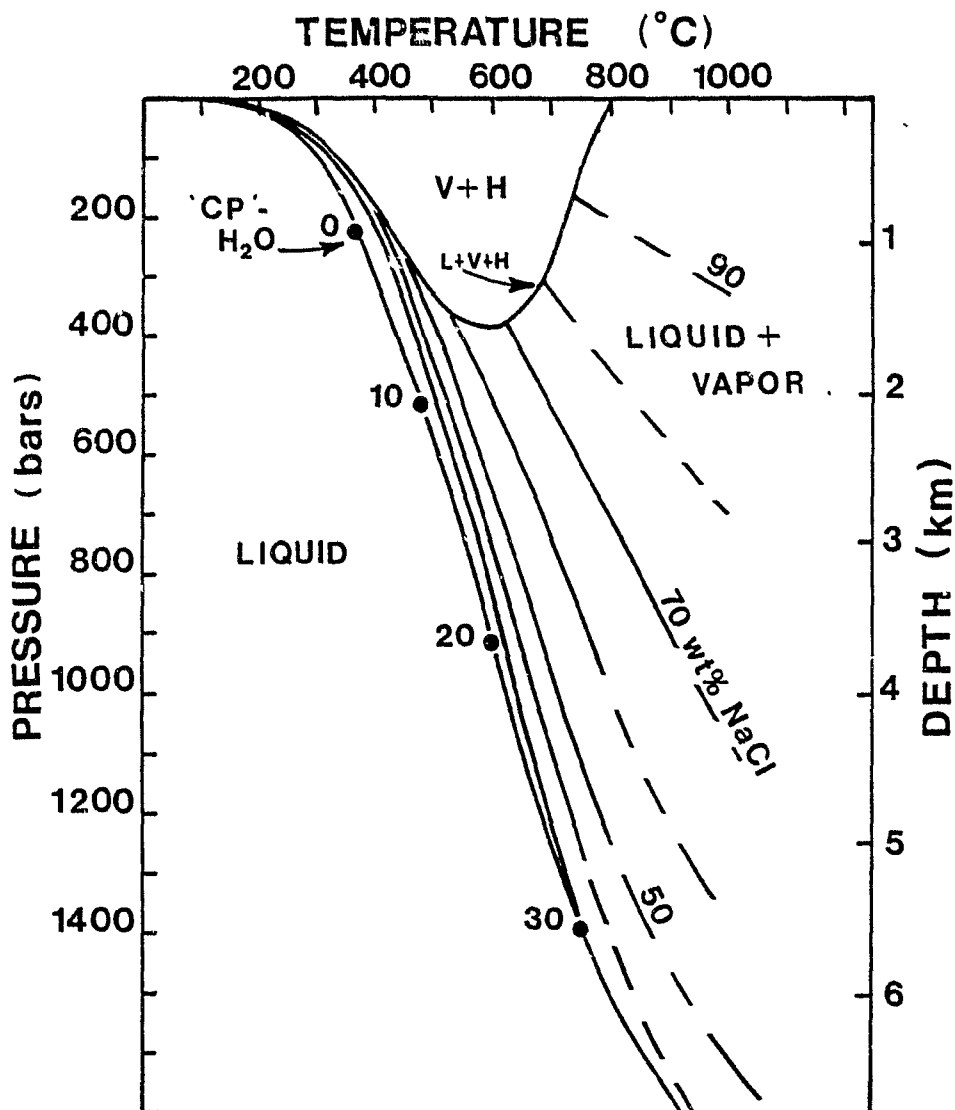


Figure 4.4. Isopleths on a P-T-depth projection in the system NaCl-H₂O (after Fournier, 1987). Curved isopleths define the position of the two-phase curve for fluids of different bulk salinities. The two-phase boundary separates the one-phase liquid field from the two-phase (vapor + liquid) field. Isopleths terminate at the halite (H) saturation curve (L+V+H). Increasing fluid salinities result in migration of the critical point (CP) to higher pressures and temperatures (solid circles). The depth relationship to pressure assumes lithostatic conditions (P_l^f) and a rock density of 2.85 gm/cm³.

their initial seawater-like composition and would follow a path parallel to the boiling curve. In zones of low permeability and/or repeated magma injection, however, temperatures may be high enough that migrating fluids intersect the two-phase curve at temperatures above the critical point, resulting in formation of a brine-rich fluid.

Because the sodium chloride content of fluids generated by phase separation depends only on the pressure and temperature at time of formation, and not on chlorine concentrations in parental fluids, constraints on fluid circulation in Troodos should be applicable to other submarine systems as well.

4.2.1 Pressure-Depth Relationships

In the simplest case, the question of whether pore fluid pressures in any rock approximate hydrostatic or lithostatic pressure depends on the mechanical properties of the rock. If open fractures in the area of interest extend to the seafloor, then pore fluid pressures within those fractures approach hydrostatic pressure, defined as the pressure exerted at any depth by an overlying water mass. The expression for hydrostatic fluid pressure is:

$$P_h^f = \int_{sl}^z \rho_w g dz$$

where P_h^f is the hydrostatic pore fluid pressure, ρ_w is the density of water, g is the acceleration due to gravity, sl is sealevel, and z is any depth within the water column or within the openly fractured upper crust. The slope of the hydrostatic curve is 1:1 reflecting the average density of water (Fig. 4.5A).

If the rock is molten or ductile, the pressure exerted on an enclosed fluid by the surrounding material may more closely reflect the combined load of the overlying rock and seawater. Predicting the transition depth between brittle and ductile deformation at any point in the evolution of a magma-hydrothermal system is a complex problem.

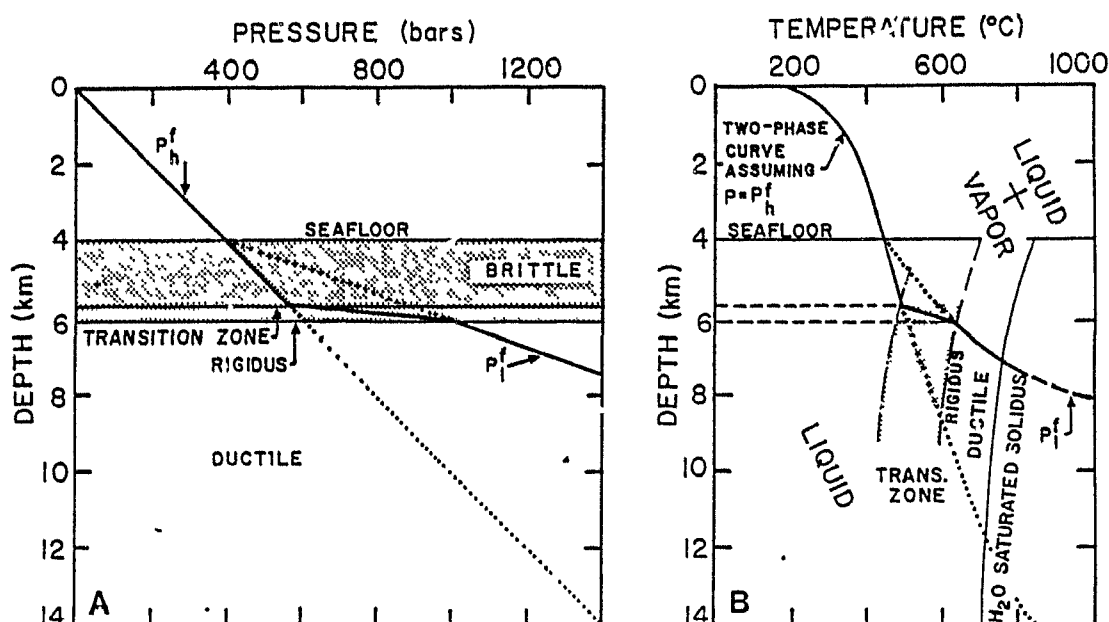


Figure 4.5 (A) Schematic relationship between pore fluid pressure and depth as a function of the deformational regime within the oceanic crust (after Kelley and Delaney, 1987). The upper portion of the crust is depicted as well-fractured; the lower portion (on axis) is represented as being partially molten or too ductile to sustain significant amounts of stress. These two regions are separated by a transition zone in which fracturing begins. The rigidus (Lister, 1986), is the temperature above which material creeps freely without developing significant stress. The line with the 45° slope labeled P_h^f represents the pressure-depth curve for hydrostatic fluid conditions. The more gently sloping line labeled P_l^f represents pressure-depth relationships assuming 4.0 km seafloor depth and a rock density of 3.0 g/cm³. The gently sloping pressure-depth curve connecting the two idealized lithostatic and hydrostatic curves represents the pore fluid pressure gradient expected in the vicinity of the transition zone. (B) Generalized two-phase, liquid vapor curve for a relatively dilute saline solution under the pressure-depth conditions identified in A. The portion of the curve labeled P_h^f is the position in T-P space of the "boiling curve" under hydrostatic conditions. The portion labeled P_l^f is the position of the two-phase curve under lithostatic conditions. The gentle slope between the two end-member curves reflects the pore fluid pressure gradient expected in the transition zone between brittle and ductile deformation regimes. Because the strain rates are poorly constrained for real systems, the actual temperature/pressure portions of the brittle/ductile field and the transition between them is strictly schematic and not intended to depict actual conditions [see Norton et al. (1984) for a similar development]. As the transition zone shifts downward during waning of magmatic activity, fluids which had existed in the one-phase field would be in the two-phase field and would undergo phase separation.

The position of the transition zone depends on temperature distribution, pressure, fluid and rock composition, and the strain rate ($\dot{\epsilon}$), but probably occurs within the lower crust or upper mantle. To a first approximation, the thickness of this zone will be inversely proportional to the spacing of the relevant geotherms. In the margin of an active, hydrothermally cooled magma chamber, the transition between brittle and ductile deformation is probably narrow. Lister (1986) has referred to a threshold condition on the high temperature side of this transition as the "rigidus", defined as the temperature above which material creeps freely without developing significant stress. Below the rigidus the material behaves elastically and for appropriate strain rates will experience brittle failure. The lower bound on the transition zone represents the conditions under which fractures may stand open or connected to the seafloor. For estimating the confining pressure on a pore fluid under P/T/ $\dot{\epsilon}$ conditions greater than those of the "rigidus", the following expression may be used:

$$P_1^f = \int_{sf}^z p_w g dz + \int_{sf}^z p_{rock} g dz,$$

where P_1^f is the submarine lithostatic pressure, z refers to any depth below the "rigidus", sf refers to seafloor, and p_{rock} is the density of the rock.

The 3:1 pressure-depth slope of the lithostatic curve reflects the approximate density of rock and although the curve may be computed at any point below the seafloor, the effective pore pressure does not achieve lithostatic conditions unless the enclosing rock is subjected to conditions on the high temperature side of the rigidus. The solid heavy line in Fig. 4.5A traces idealized pressure-depth relationships in a sub-seafloor system with a brittle-ductile transition zone at a depth of about 6 km below sealevel. Wherever the transition zone occurs, the pore fluid pressure gradient is likely to be steeper than in either a purely hydrostatic or a purely lithostatic pressure gradient. Furthermore, this transitional pressure gradient must ultimately connect the

two pressure-depth curves on either side of the transition zone. These curves will diverge by an increasing amount as the brittle-ductile transition deepens.

The influence of this steep pressure gradient on the shape of the pressure-temperature projection of the two-phase curve for NaCl-H₂O is depicted in Fig. 4.5B. The two-phase surface indicated by the solid heavy curve has a significant offset, corresponding to the steep pressure gradient near the rigidus zone. As a result of this shift in slope, phase separation near magma chamber margins should occur at much shallower depths than if only hydrostatic pressures are exerted. In any active magma-hydrothermal system, the position of the rigidus zone will not be stable. A downward shift in the rigidus, with encroachment of a cracking front, would result in substantial decompression of pore fluids formerly at lithostatic pressure. If the initial temperature/pressure conditions of the fluid had been on the one-phase side of the curve, the decompression from local fracturing could induce two-phase separation without significant vertical migration of the fluid. In a spreading environment repeated injections of magma could induce multiple phase separation events during thermal reheating and refracturing of the host rocks. The onset of phase separation may aid fracture development, enlarging areas of phase separation. As NaCl has a large negative partial molar volume, and the low salinity vapor phase is much less dense than the homogeneous fluid, the total volume of the two-phase mixture is much greater than the one-phase fluid. For example, a one-phase fluid entering the two-phase field at 450°C and 414-420 bars would undergo a 160% increase in volume (Goldfarb and Delaney, 1988). This effect should be most extreme at shallow levels and where the brittle-ductile transition zone occurs over a broad depth interval. Irreversible isenthalpic expansion of the fluids in these zones should induce significant cooling of the fluids (Toulmin and Clark, 1967); resulting mineral precipitation would counteract further crack development.

Decompression of solutions in the two-phase field, during intermittent fracturing could generate hypersaline brines (Fig. 4.6). Seawater at 600°C and 790 bars would separate into a brine containing 40 wt% NaCl and a vapor phase of 2.0 wt% NaCl; the volume percent of the vapor and brine generated would be 86% and 14%, respectively. Segregation, followed by isothermal decompression to 650 bars would induce separation of the 40 wt% brine and 2.0 wt% vapor into even higher salinity fluids containing 52 wt% NaCl and a vapor phase 0.45 wt% NaCl in composition; vapor and brine ratios of the solutions would be 9:91, and 69:31 respectively.

4.3 Models of Brine Generation and Fluid Circulation in the Upper Plutonic Sequence of Troodos

Few studies examine fluid flow in the deep-seated, high temperature portion of submarine hydrothermal systems hosted in plutonic rocks. The paucity of submarine plutonic rocks sampled, in conjunction with poor control on spatial relationships of dredge or submersible samples, make this zone inherently difficult to study. In this respect, the Troodos ophiolite is an ideal place to obtain quantitative data on spatial-temporal variations of fluid flow in an evolving hydrothermal system. The pressure-temperature-depth relationships discussed above, which govern conditions of brine generation in the oceanic crust, in conjunction with fluid inclusion analyses and models of fluid flow in submarine hydrothermal systems, provide insight into the paleohydrothermal system developed in Troodos.

4.3.1 Fluid Sources

Sources of the high-temperature brines include compositionally modified seawater, fluids incorporated into melts during assimilation of stopped, hydrothermally altered roof rocks, or primary magmatic fluids derived by exsolution from plagiogranitic and gabbroic melts.

4.3.1.1 Seawater Source Model

Although it is widely accepted that seawater is the overwhelmingly dominant source for hydrothermal solutions venting on the seafloor, little is known about fracture-fluid evolution and distribution of these fluids in the deep-seated, high-temperature portions of the system. Assuming that seawater is the source for the high temperature brine inclusions provides some rate limiting controls on temperatures of cracking and conditions of fluid flow in this dynamic zone.

Experimental studies indicate the thermochemical and physical properties of hydrothermal seawater can be approximated using a 3.2 wt% NaCl solution (Bischoff and Rosenbauer, 1985, 1987). The position of the two-phase curve for this solution in P-T-Depth space is shown in Figure 4.7. Assumptions involved in placement of the two-phase boundary include a water column of 2.0 km (Bednarz et al., 1987), 2.7 km of dikes and volcanic rocks (Heaton and Sheppard, 1977), and a crustal density of 2.85 g/cm³. Seawater-derived fluids which intersect the two-phase curve at temperatures and pressures greater than the critical point (CP = 407°C, 298 bars; Bischoff and Rosenbauer, 1988), will undergo two-phase separation and condense a small amount of brine from a vapor.

As discussed above, generating brine-rich fluid inclusions in the plutonic rocks from a seawater source requires that deeply circulating hydrothermal fluids must have entered the two-phase (vapor + liquid) field and undergone phase separation. However, inclusion homogenization by halite dissolution necessitates that fluid entrapment occurred in the **absence** of a vapor phase at **minimum** temperatures of 400-500°C (Fig. 4.7; field to the right of the liquid + halite/liquid curve). This apparent discrepancy in entrapment conditions can be accounted for by deep-seated, limited migration of hydrothermal seawater into the two-phase field at temperatures greater than 400-500°C, separation of brine and vapor phases, and subsequent phase **segregation** of the brine and vapor along the microfracture networks (Fig. 4.7). The

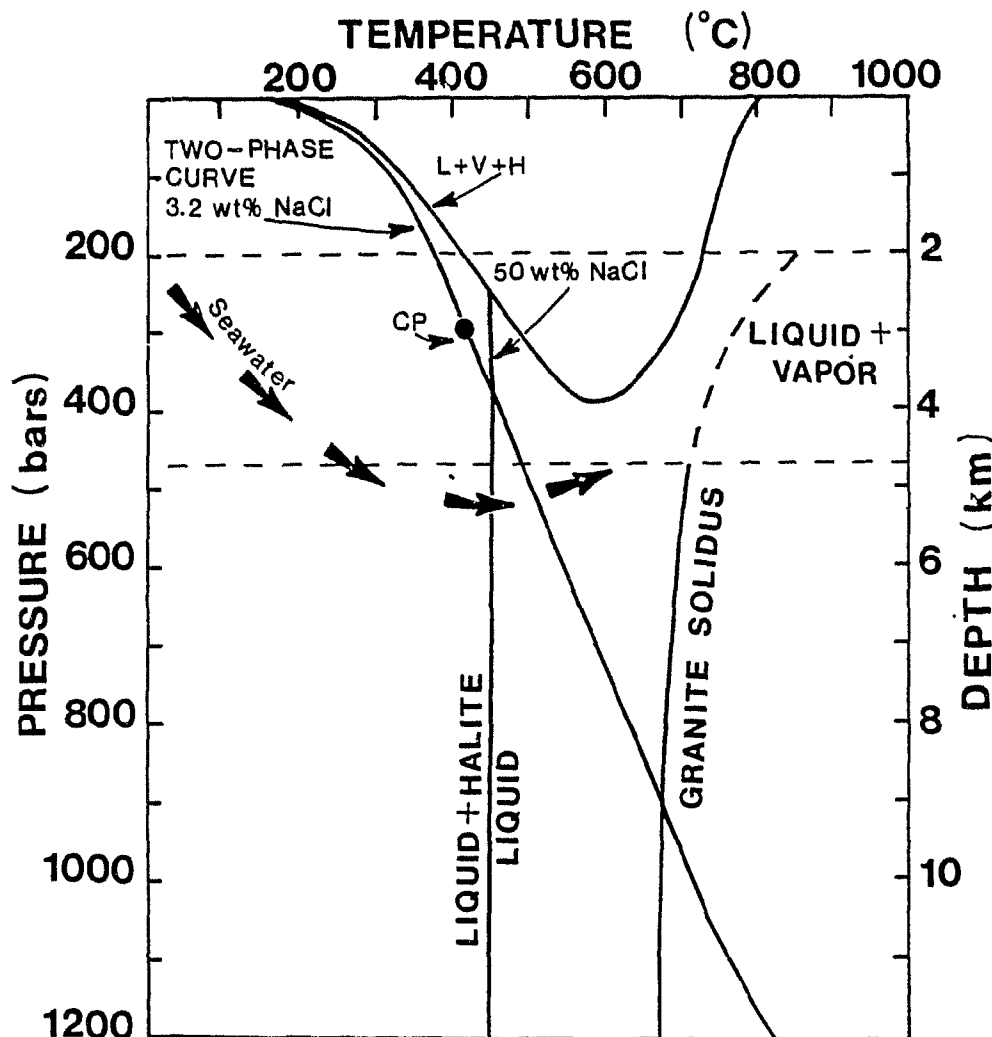


Figure 4.7. T-P-depth relationships in the NaCl-H₂O system for a hydrothermal seawater (3.2 wt% NaCl) solution. The two-phase curve separates the one-phase liquid field from the two-phase (vapor + liquid) field, under hydrostatic conditions (P_h^f). Pressure-depth relationships assume a 2 km water column, 2.7 km of lavas and sheeted dikes, a water density of 1.0 gm/cm³, and a rock density of 2.85 gm/cm³. The nearly vertical line labeled liquid + halite/liquid shows the position of the saturation curve for a 50 wt% NaCl solution. Fluids intersecting the two-phase curve at T-P conditions greater than the critical point (CP at 407°C and 298 bars) will condense a brine from vapor. Fluid inclusion homogenization by halite dissolution at temperatures greater than 450°C indicates inclusion entrapment occurred in the field to the right of the liquid + halite/liquid curve. The highly saline inclusions may have formed as a result of limited seawater migration into the two-phase field, which resulted in generation of brine and vapor phases. Density stratification and isolation of the brine and vapor phases resulted in preferential entrapment of the 36-56 wt% NaCl brines in rocks of the upper plutonic sequence.

absence of detectable volatile species in the inclusions lends support for this model (Table V).

Flow of brines in the plagiogranitic and gabbroic rocks occurred predominantly along anastomosing systems of microfracture networks, which probably did not exceed 200-400 microns in width. This provides a favorable environment for isolation of the vapor and brine phases. In large aperture, high flow-through fractures, flow is likely to be turbulent and it would be difficult for brine and vapor phases to remain immiscible. In contrast, in small aperture, less continuous fracture networks flow is more likely to occur under laminar conditions and the vapor and brines may coexist as discrete phases. Preferential wetting of fracture walls by brines, coupled with preferential movement of the brines into small fractures and vapors into larger aperture fractures promotes isolation of brine and vapor phases (Fig. 4.8) (Goldfarb and Delaney, 1988; Fox, 1990). Intermittent release of such brine- and vapor-rich pools at depth during transient fracturing events, and subsequent mixing with upwelling hydrothermal fluid, would result in highly varying vent fluid chemistries (Butterfield et al., 1990). Although the fracture networks may have allowed pervasive penetration of seawater into the hot rocks, flow along a single fracture was probably short lived, as micron-scale cracks seal quickly (Brantley et al., 1990).

Fluid inclusion results from a single epidotized plagiogranite sample from Cyprus (N=38, Table VII) led Cowan and Cann (1988) to suggest that mixing between seawater and a phase-separated fluid may be an important process in generation of coexisting brine and liquid-dominated, low-salinity inclusions in the plagiogranite. Their analyses on quartz-hosted fluid inclusions indicate two disparate populations of **primary** inclusions: a low salinity (0-2 wt% NaCl equivalent) generation of inclusions which homogenize in the **liquid** phase at 330-410°C, and a high-salinity (37-48 wt% NaCl equivalent) population which homogenize predominantly by vapor bubble disappearance at 330-430°C. They interpreted their data to indicate that the inclusions entrapped

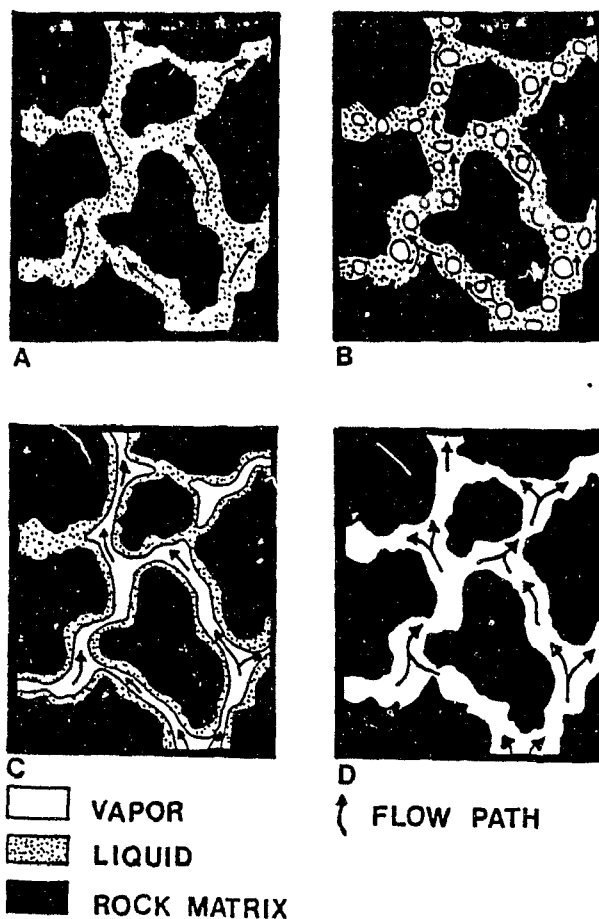


Figure 4.8 Schematic illustration of the effect of the presence of two phases on fluid flow in a fracture network (after Fox, 1990). (A) and (D) If only one phase is present fluid flow occurs at the full permeability of the rock. (B) If a vapor phase is present, fluid flow may be restricted by gas bubbles. (C) As the proportion of bubbles to brine increases, the vapor bubbles may coalesce in the centers of channels, while the brine phase preferentially wets the fracture walls. Increased vapor pressure within the conduits may force the liquid into surrounding fractures resulting in segregation of the vapor and brine phases.

varying mixtures of seawater undergoing phase-separation at 500-525°C and 400 bar pressure, with unmixed seawater at 0-20°C. Their data are difficult to reconcile with this model in light of phase equilibria in the NaCl-H₂O system. It is difficult to envisage under what physical conditions it is possible to mix 0-20°C seawater (at 2-3 km depth) with 500°C phase-separated fluid, and still retain discrete low salinity **fluids** and droplets of **brine**. As these inclusions are hosted in an epidosite, it is also unclear why freezing measurements of the inclusions fail to show any evidence of CaCl₂.

In the plagiogranites it is clear, however, that interaction of rock with high-temperature fluids resulted in localized zones of extreme alteration and epidosite formation. On the basis of mass balance calculations, these metal-depleted, epidote- and quartz-rich zones, have been inferred to represent the fossilized heat sources and reaction zones for seawater-derived fluids feeding hydrothermal vents (Richardson et al., 1987; Cowan and Cann, 1988; Schiffman and Smith, 1988). Alternatively, Berndt et al. (1989) concluded that these zones are regions of concentrated upflow in which little modification of fluid chemistry occurs. They suggested that reaction zones in the upper level gabbros control chemistry of hydrothermal vent solutions, and that most of the metals in solution are leached from the reaction zones subjacent to the epidosite bodies.

Both of these models infer conditions and chemistry of altering fluids from a single pass flow model and do not allow for alteration effects based on multiple hydrothermal events, nor do they address the effect brine generation may have on alteration mineralogy. The crosscutting arrays of fluid inclusions in the Troodos rocks clearly show that multiple pulses of high temperature fluid flow affected the plagiogranites. Temperatures of the brine inclusions are 100-200°C above those inferred for reaction zone temperatures in these studies (400-450°C; Schiffman and Smith, 1988; Campbell et al., 1988). The fluid inclusion results indicate caution should

be used when attempting to infer conditions of fluid flow at depth based on extrapolations of vent fluid chemistry and mineral phase equilibria.

4.3.1.2 Magmatic Source Model

Abundant, partially assimilated, hydrothermally altered mafic xenoliths in the plagiogranites (Fig. 4.9), and more rarely in the gabbros, indicate that substantial amounts of fluid may have been added to the melt by enclave incorporation (Taylor, 1983; Malpas et al, 1987; Malpas et al., 1989). However, distinction between fluids incorporated at magmatic temperatures and truly magmatic fluids is difficult. It is probable that under magmatic conditions the large fluid volumes derived from volatile exsolution from melts would swamp most chemical signatures of fluids associated with enclave incorporation; therefore, in the absence of isotopic data, the two sources are treated together in terms of a magmatic fluid.

Volatile evolution and formation of hydrothermal mineral assemblages associated with silicic melts have been well documented, primarily because of their association with mineral deposits (Henley and McNabb, 1978; Bodnar and Beane, 1980; Reynolds and Beane, 1985). Similar models, however, have only recently been proposed for more mafic systems, and still require substantiation by field studies (Norton et al., 1984; Fournier, 1987; Goldfarb and Delaney, 1988). Differences in magmatic and hydrothermal fluid evolution between these two systems arise predominantly because basaltic melts are emplaced at higher temperatures and contain less water, exsolved and circulating fluids are subject to greater hydrostatic pressure, and oceanic systems are recharged by an abundant supply of saline fluids (Fournier, 1987).

A magmatic source model for the brine inclusions requires that either the 33-56 wt% NaCl fluids were exsolved directly from the melts, or that phase separation of exsolved fluids occurred. Mass spectrometric analyses of glasses from the upper extrusive sequence indicate dissolved water contents of 2.11-2.30 wt.% (Muenow et al.,

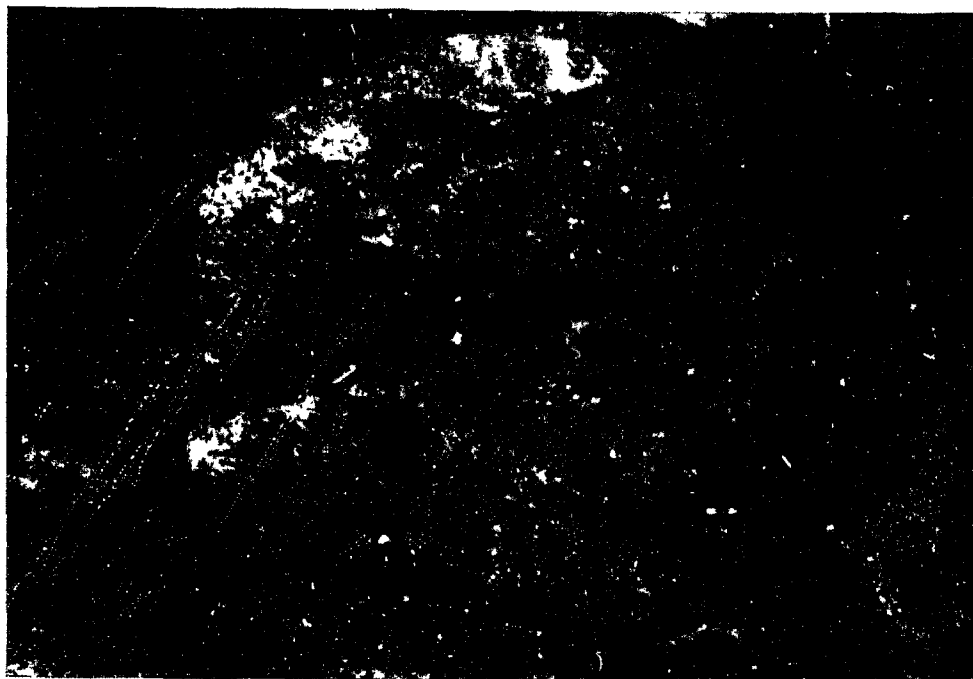


Figure 4.9 Plagiogranite with abundant diabase xenoliths. Road cut near Zoopiyi.

1990); extensive vesiculation in the extrusive rocks is consistent with such elevated volatile contents. Progressive low-pressure fractionation of these melts, coupled with CO_2 degassing, would further increase H_2O in the residual melt; fractionation could eventually lead to melt saturation with respect to H_2O . However, as the primary Cl content of these rocks is quite low [0.11-0.13 wt%, (Muenow et al., 1990)] it is unlikely that even extensive low-pressure fractionation would lead to exsolution of a 50 wt% NaCl fluid directly from the melt (Burnham, 1979; Fournier, 1987). This again leads to phase separation as the most likely mechanism for generating the brine-rich, metal-bearing inclusions.

At the shallow level of intrusion (2-3 km) represented by the upper level gabbros and plagiogranite bodies in Troodos, evolved melts would likely be saturated with respect to water (Burnham, 1979). Figure 4.10 shows the position in P-T-depth space of the condensation curves for a 50 wt% NaCl solution assuming hydrostatic (P_h^f) and lithostatic (P_l^f) fluid pressure conditions, and their relationship to the minimum melting curve for H_2O -saturated granite. The heavy line connecting the two condensation curves reflects the extreme pressure gradients that must exist in the brittle-ductile transition zone near magma chamber margins (Lister, 1986).

Whether the parental solutions were exsolved from the melts as homogeneous or heterogeneous fluids is dependent upon the pressure-depth relationships at the time of exsolution. Aqueous fluids exsolved from melts at depths greater than the two-phase boundary labeled P_1^f , would be exsolved as homogeneous fluids. Attendant hydrofracturing associated with exsolution of the volatile phases (Burnham, 1979), or fracturing due to emplacement of magma could have resulted in phase separation and segregation of the pore fluids along microfracture networks. Alternatively, in shallower intrusions, fluids may have been exsolved directly as brines and vapors. Migration of the $\text{NaCl-KCl-(}\pm\text{CaCl}_2\text{)}$ fluids into the fractured margins of the intrusions, and subsequent phase segregation, would preserve the temperature-composition relationships

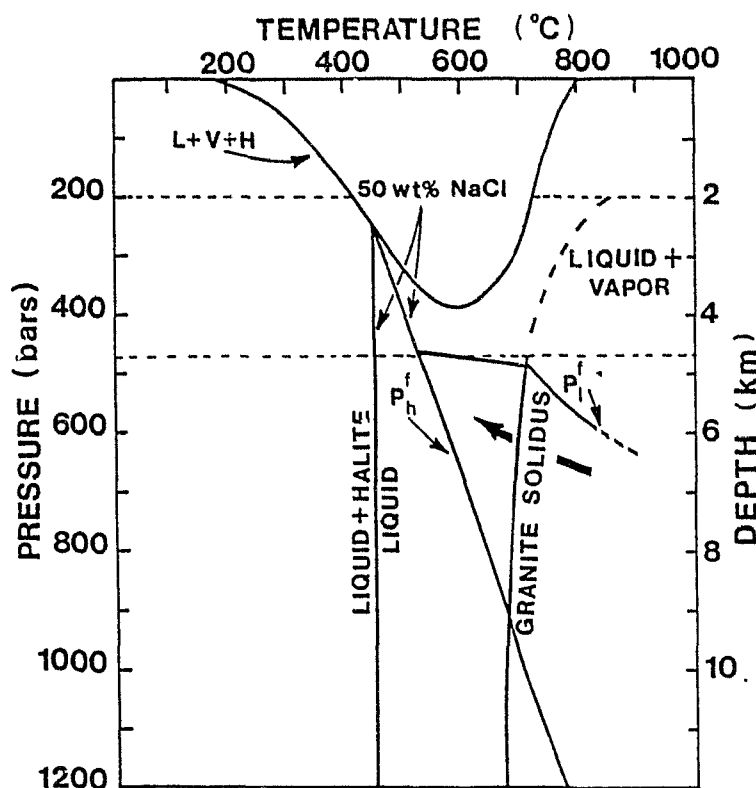


Figure 4.10 T-P-depth relationships in the NaCl-H₂O system for a phase-separated 50 wt% NaCl magmatic aqueous phase. The line with a 60° slope labeled P_h^f is the two-phase curve in P-T space for a 50 wt% NaCl solution under hydrostatic pressure conditions. The portion labeled P_l^f is the position of the liquid-vapor curve under lithostatic conditions. The gently sloped solid line connecting the liquid-vapor curves reflects the transition between the two end-member pressure regimes. The gradient of the slope depends on the P-T-stress conditions under which rock deformation changes from brittle to ductile behavior. Intersection of the two-phase curves and the H₂O-saturated granite solidus define the regions in which a 50 wt% NaCl exsolved magmatic aqueous phase would undergo phase separation. Fluid inclusion homogenization by halite dissolution at temperatures greater than 450°C indicates that the fluids were entrapped in the absence of a vapor phase. Lack of halite casts in the quartz host minerals implies the fluids were not saturated with respect to NaCl prior to fluid entrapment. This restricts the field of inclusion entrapment to the region to the right of the liquid + halite/liquid curve. The 50 wt% NaCl inclusions may have entrapped a magmatic aqueous phase exsolved in the two phase region from the plagiogranitic melts. Migration of the exsolved vapors and brines into the fractured margins of the crystallizing gabbroic and plagiogranitic bodies, in conjunction with phase segregation and isolation along the microfracture networks, would preserve the temperature-composition relationships observed in the brine inclusions.

observed in the plutonic-hosted inclusions. Primary, vapor-dominated fluid inclusions hosted in veins containing hydrothermal clinopyroxenes, which cut upper level gabbros, indicate subsequent formation of pegmatite veins at temperatures $>400^{\circ}\text{C}$.

Localized circulation of the NaCl and KCl acid-rich brines may have resulted in extreme deuteric alteration of the plagiogranite bodies and in the formation of the podiform epidiosites (Fig. 2.22). Release of K, Rb, Ba-rich volatiles from the plagiogranite melts into the circulating fluids would account for the characteristic depleted values of hygromagmatophile elements in the plagiogranite (Malpas et al., 1987).

It is difficult to evaluate, from the fluid inclusion compositions alone, whether brines hosted in the plutonic rocks of Troodos are of seawater or magmatic origin. Microthermometric analyses of highly saline inclusions from the Mathematician Ridge indicate the fluids contain Na:Ca ratios similar to hypothetical end-member hydrothermal fluids, suggesting a seawater origin (Vanko, 1988). Similar constraints, however, cannot be placed on origin of the Troodos brines because equilibrium phase relations in the NaCl-KCl-CaCl₂-H₂O under vapor-saturated conditions are not well known. The preliminary fluid inclusion data indicating high KCl values of the fluids may support the suggestion that potassium depletion in the plagiogranites is a result of deuteric alteration. However, the ambiguous secondary/primary origin of the inclusions, combined with the fact the inclusions are commonly hosted in recrystallized quartz, makes exact determination of fluid sources difficult. Future work, applying detailed petrography and mapping of inclusion arrays on oriented thin sections, in concert with cathodoluminescence of the quartz grains, may allow delineation of inclusion origin (Sprunt, 1979; Boiron et al., 1990).

4.3.2 Fluid Flow Models for Seawater-Derived Fluids

Models of hydrothermal circulation have recently been developed in an effort to characterize the conditions of fluid flow at depth. These models include: simple slot convection (Cann et al., 1986), flow through porous medium (Fehn and Cathles, 1979; Fehn et al., 1983), and flow driven by an advancing cracking front (Lister, 1974, 1983). Although all three models produce results which are consistent with thermal measurements of exiting vent fluids, they are less successful in describing the chemical effects imposed by their implied fracture geometry.

The slot convection model may apply to fluid flow in large aperture, ridge-parallel fractures which shallow out at the base of the sheeted dikes (Fig. 4.11), however, this model does not explain the limited range of compositions measured for vent fluids (Campbell et al., 1987). In the slot convection model, fluids migrating along mature flow channels are insulated from fresh rock by the previous interaction of passing fluids. In a mature system, unreacted fluids would be high in magnesium, which is contrary to the low magnesium concentrations measured in all vent systems studied so far. This model may be useful in describing the upflow portions of hydrothermal systems at shallow crustal levels, but does not seem to be applicable to fracture configurations in the roots of the system.

A more plausible model is that developed by Lister (1974, 1983) in which small, fluid-filled cracks continually propagate downward into a cooling magma body as a result of thermal contraction, allowing high temperature circulation of seawater at depth (Fig. 4.12). This model has the advantage, with respect to generation of vent fluid chemistries, in that it allows fluids to continually be in contact with previously unreacted rock. In Lister's model, the velocity of the cracking front is proportional to the thermal gradient in the fluid boundary layer, which itself is a function of the flow rate, the temperature at which the rocks crack, and the flow length along the heated boundary. Fluid density and kinematic viscosity are assumed to be constant with temperature,

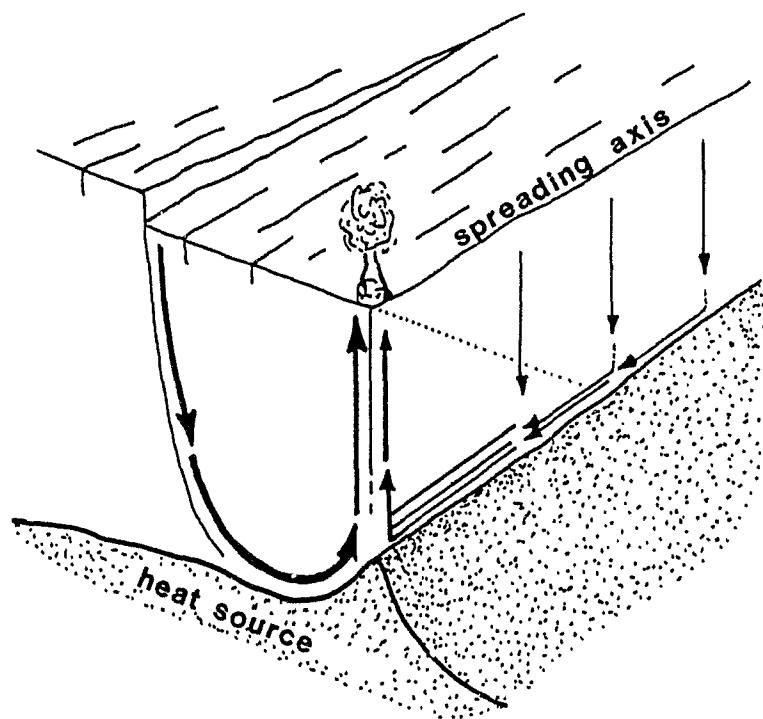


Figure 4.11 Circulation model of Cann et al. (1986) in which fluid flow is modelled assuming discharge occurs through bundles of pipes 3 cm in diameter. Fluid flow in the pipes extracts heat from crystallizing magma near the ridge axis. Fluid in the upflowing limb is assumed to follow an adiabat.

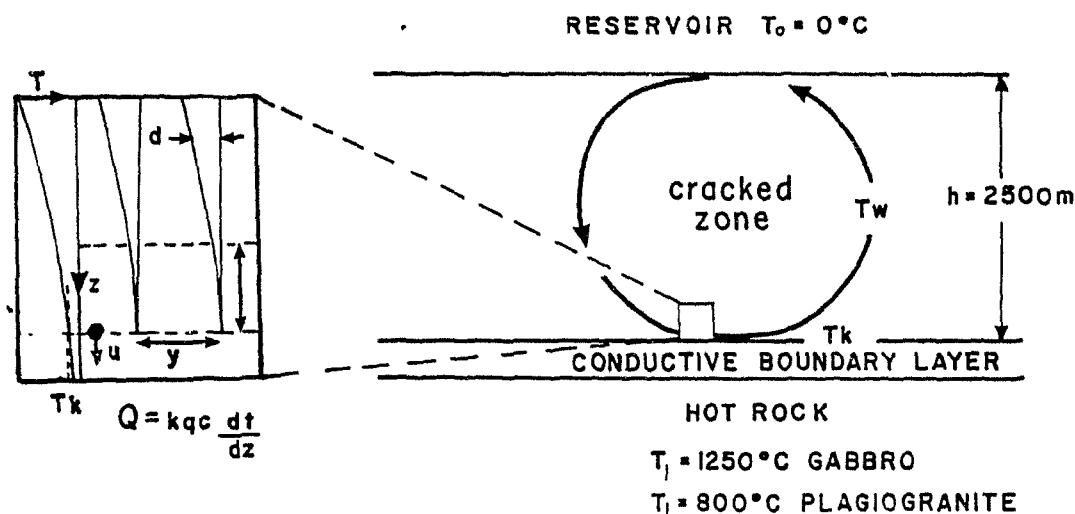


Figure 4.12 Circulation model of Lister (1974, 1982, 1983) in which water penetration into hot rock occurs by advancement of a cracking front moving downward (z) at velocity u . The model is one-dimensional, where rock is treated as uniform infinite layers that cannot shrink without cracking. Thermal shrinkage at temperatures below the cracking temperature (T_k) allows fractures of width d to form at crack spacing y . The thermal boundary layer is a function of the cracking front velocity, which in turn is a function of the crack spacing (y). Cracking temperatures necessary to generate fluid temperatures (T_w) similar to those in Troodos were calculated iteratively using the fluid inclusion homogenization temperatures as T_w in the cracks. Boundary conditions assumed a fluid reservoir temperature (T_0) of 0°C , initial temperatures (T_1) of 1250°C for gabbro and 800°C for plagiogranite, and depth of convection (h) equal to 2500 m (See Appendix B for specific calculations and results). A schematic temperature curve is shown adjacent to the cracks. The heat flux out of the system (Q) is equal to the product of the thermal conductivity of the rock and the change in temperature with depth. The calculations indicate cracking temperatures of 600 – 800°C are needed to generate water temperatures of 400 – 600°C . During high temperature circulation, front velocities are on the order 10 to 176 m/yr (implying cracking occurs intermittently) and permeabilities are high (10^{-10} cm^2). The heat flux out of the system (q) by hydrothermal convection is high, ranging from 971 to 4423 w/m^2 .

whereas the ratio of fluid expansibility to compressibility is allowed to vary with temperature. Fluid within the cracks is assumed to be under hydrostatic pressure and cracking temperatures are inferred to be around 500°C. In zones of lower permeability, however, fluid pressure may be higher and fluid migration impaired. This would result in a lowering of the thermal gradient and slowing of the cracking front velocity. Precipitation of secondary mineral phases also hinders crack growth.

A recent study of the Semail ophiolite provides field evidence which may support this model. An extensive vertical network of subparallel, millimetre-wide amphibole veins in the layered gabbros is interpreted to represent the fossil trace of a cracking front at temperatures of 500°C (Nehlig and Juteau, 1988). Indirect support for this model in modern hydrothermal systems is provided by a recent study on the relationship between seismic events and fluid flow in submarine hydrothermal vents on the Juan de Fuca Ridge (McClain et al., 1989; Leflamme et al., 1989). Variation in fluid velocity and temperatures of hydrothermal vent solutions, coincident with the onset of microearthquake swarms, are interpreted to indicate a pervasive microcracking event at depth, which may represent pulsing of a cracking front.

The ubiquitous fracture networks in the plagiogranite to diorite rock may represent the remnants of a paleocracking front. Applying the cracking front model to the plutonic rocks in Troodos suggests that cracking temperatures of 600-800°C were needed in order to generate the 400-600°C brines [Fig. 4.13 (Appendix B)]. These temperatures are reasonable by comparison with other hydrothermal systems: fracturing temperatures greater than 700°C are recorded by secondary fluid inclusions in gabbros from the Mid-Atlantic Ridge and cracking temperatures of 600-800°C are inferred from high temperature mineral assemblages in hydrothermal veins from the Skaergaard Intrusion (Norton et al., 1984). Permeabilities during this period of high temperature flow in Troodos were on the order of 10^{-10} cm² (Fig. 4.14A), resulting in high heat flux out of the system (Fig. 4.14B). Implied front velocities are on the order of 7 to 177

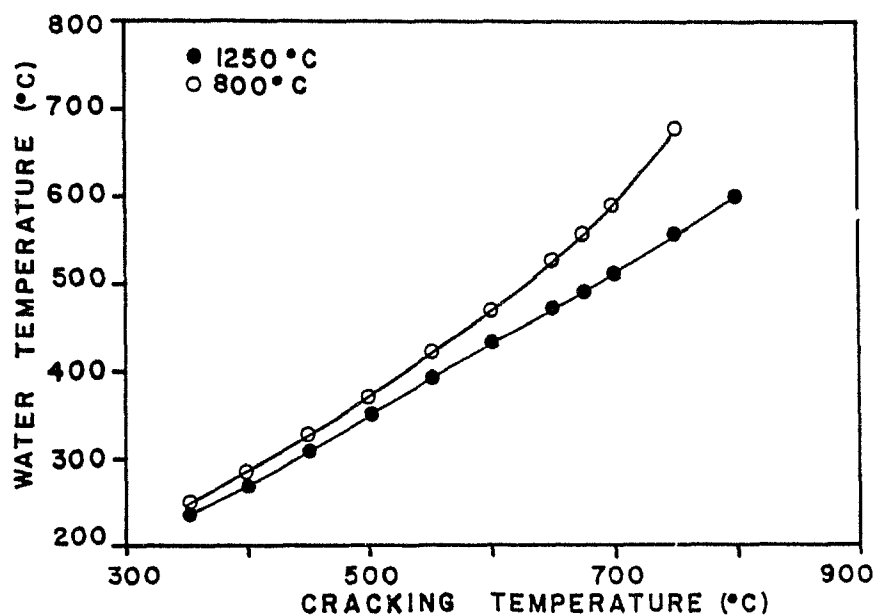


Figure 4.13 Cracking temperatures necessary to generate temperatures (T_w) obtained from fluid inclusion results. The model assumes that the convective boundary layer will control the crack spacing (y) by the relationships $y = h/2N$ where h is the height of the convecting slab and N is the Nusselt number. Cracking temperatures of 600-800°C are necessary to generate water temperatures of 400-600°C. Solid circles indicate results assuming initial temperatures of 1250°C. Open circles indicate results assuming initial temperatures of 800°C.

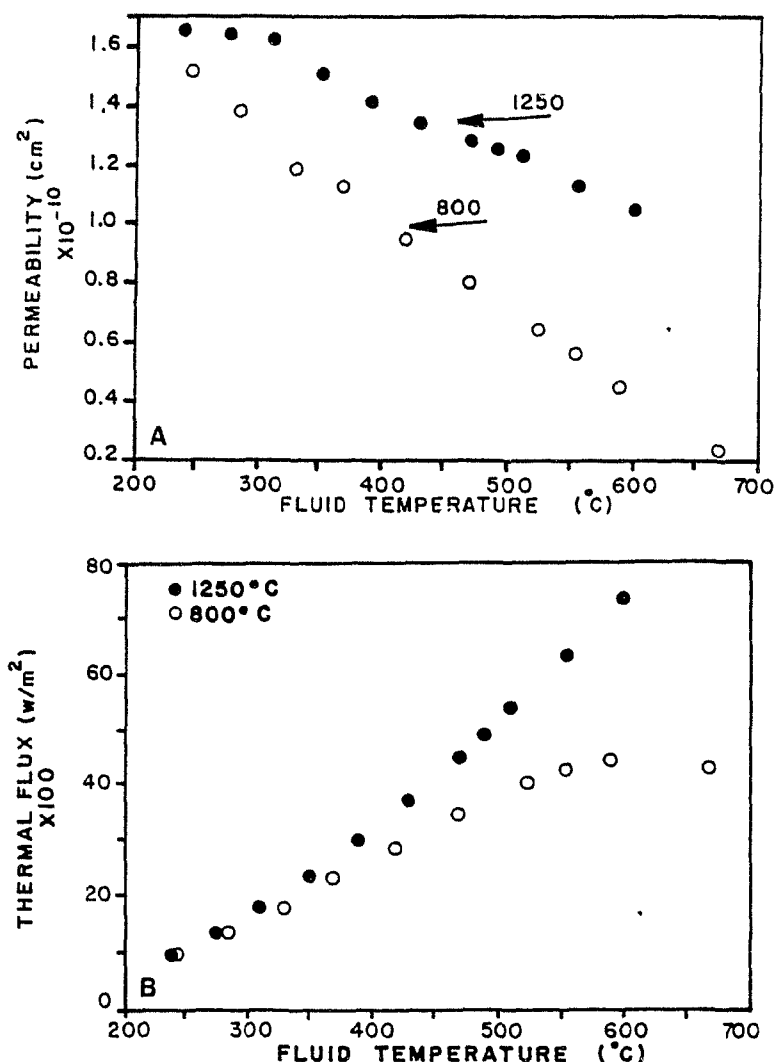


Figure 4.14 (A) Calculated permeabilities (D) of the hydrothermal system in Troodos applying the relationship $D = 2/12 \alpha^3 y^2 (T_k - T_w)^3$ where α is equal to the linear expansion of rock, y is equal to the crack spacing, T_k is equal to the cracking temperature and T_w is equal to the water temperature. Initial rock temperatures are 1250°C (filled circles) for gabbro and 800°C for plagiogranite (open circles). The model predicts that permeabilities were initially highest in the gabbros, but with cooling approached those of the plagiogranite rocks. Calculated permeabilities are higher than normally quoted for in situ studies (10^{-13} to 10^{-17} ; Anderson et al., 1985). This is not surprising, however, in that the calculated permeabilities are generated for a single fracturing event, and do not reflect the integrated "permeability history" of the rock. (B) Thermal flux as a function of fluid temperature. Heat transport becomes less efficient at very high fluid temperatures due to turbulent and unstable convection in the plume. Aspect ratios of the circulation cells decline and may eventually break into multi-tiers at very high Rayleigh numbers (Lister, 1983).

km/year. As these cracking rates are much faster than spreading rates, fracturing must occur intermittently. Although uncertainties regarding the mechanical properties of rocks at high temperature and the absence of experimental data on the efficiency of heat transfer at high Rayleigh numbers make one wary of applying these results too strictly, the calculations are useful in providing order of magnitude results for modeling conditions of fluid flow at depth.

Although the cracking model uniquely produces conditions compatible with generation of high temperature, low magnesium fluids, it is unclear how fluids migrate to depth at such elevated temperatures. Transport processes in the pure water system are governed by extrema in fluid density, viscosity, heat capacity, and the ratio of thermal expansion to compressibility of the fluid near temperatures of 350°C and 300 bars pressure [Fig. 4.15 (after Norton, 1984)]. Clustering of these extrema near the two-phase curve results in a zone of maximum efficiency for fluid transport (Fig. 4.16). Temperatures greater than 350°C are generally not attained in fluids exiting hydrothermal vents (Campbell et al., 1988), indicating that physical properties of the fluid may limit maximum achievable fluid temperatures in zones of submarine hydrothermal upflow.

Fluid temperatures may also be controlled by quartz solubility in the reaction zones at depth. Because the maxima in SiO_2 solubility falls below the two-phase curve, deeply circulating fluids will first increase and then decrease in quartz solubility at T-P conditions near the two-phase curve (Von Damm and Bischoff, 1987). Resultant quartz precipitation in the fracture networks decreases permeabilities and hinders fluid flow at higher temperatures. Quartz saturation may be an important constraint on fluid flow at shallow crustal levels, as indicated by the common occurrence of quartz veins. Seawater-derived fluids may gain access to deeper crustal levels by migration along low angle listric faults, which probably terminate near the brittle-ductile boundary (Harper, 1985).

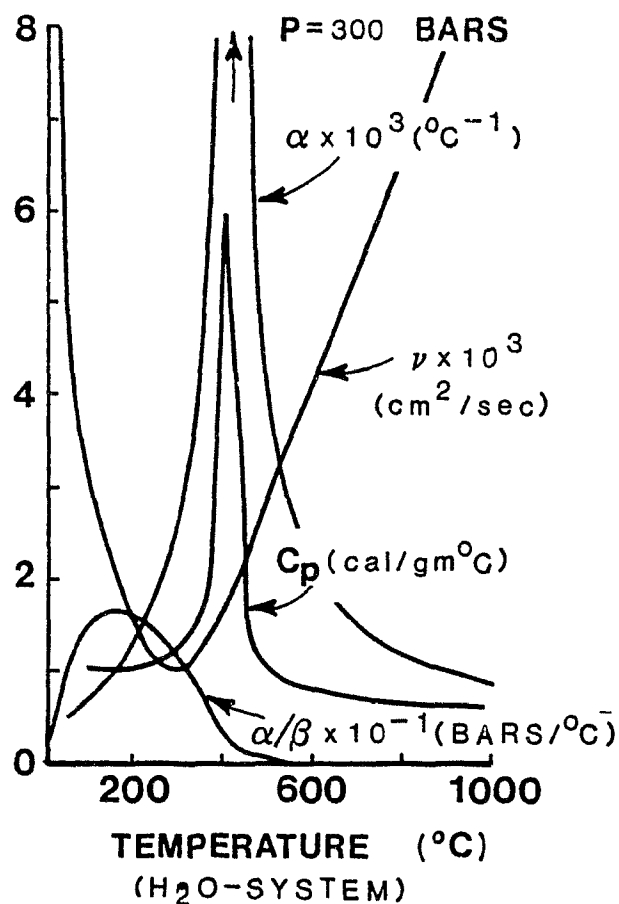


Figure 4.15 Properties of H₂O as a function of temperature at 300 bars pressure (after Norton et al., 1984). Transport properties reach extrema at 350°C resulting in a zone of optimum transport efficiency. C_p = heat capacity, α/β = ratio of thermal expansibility to compressibility, ν = kinematic viscosity.

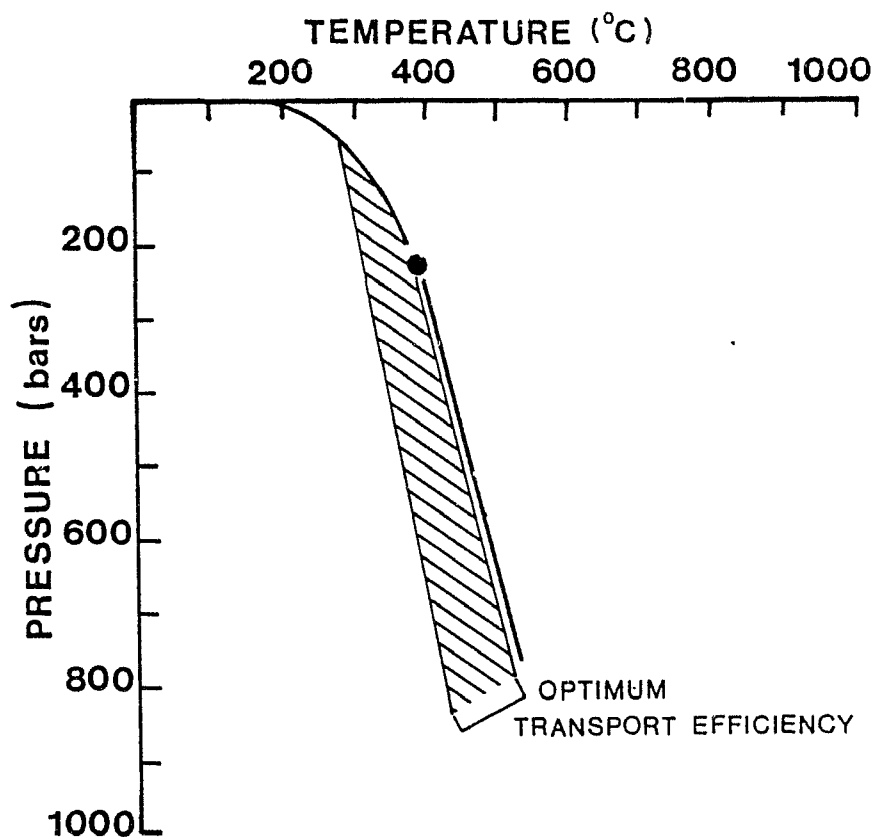


Figure 4.16 Zone of optimum transport efficiency as a function of temperature and pressure. Thermal measurements of fluids exiting submarine hydrothermal vents rarely indicate temperatures rarely over 350°C. This suggests transport properties of dilute saline fluids, similar to those of the pure water system, may limit maximum achievable temperatures in zones of submarine hydrothermal upflow.

Although there is evidence of pervasive fracturing in the plagiogranites and diorites, fractures are not as common in the gabbros. An alternative to the cracking front model to generate high temperature brines involves phase separation of trapped pore fluids. Steep pressure and temperature gradients, coupled with rapid changes in stress imposed by multiple episodes of magma injection, may cause extensive fracturing in the surrounding crystalline host rocks (Burnham, 1979; Fournier, 1987) and rapid decompression of pre-existing pore fluids. Under the appropriate P-T conditions, this will result in phase separation of the fluids. During passage of a thermal front in the crystalline rocks, differential expansion of the pore fluids and enclosing rock may promote increased crack development (Knapp and Knight, 1977) and phase separation. The complex intrusive relationships in the plutonic rocks are compatible with multiple magma chambers beneath the paleosspreading axes of Troodos (Malpas et al., 1989). In such a dynamic environment, the brines may have been generated as relatively dilute to saline pore fluids underwent multiple phase separation events (Fig. 4.6).

Although it is clear that some fluid migration must have occurred in order for the brine and vapor phases to have become physically isolated from each other, intuitively and from the arguments presented above, it is difficult to envisage how extensive migration of seawater occurred in the two-phase field at minimum temperatures of 400-500°C (and up to 600°C if fluids are pressure corrected). This in conjunction with the absence of evidence for an extensive cracking front in the upper level gabbros, suggests that a pore fluid model or a magmatic source model more accurately depicts conditions of brine generation in Troodos.

4.4 Generation of Low-Temperature, Low-Salinity Fluids

Salinities of the low-temperature fluids (2-7 wt% NaCl equivalent) in the upper-level plutonic rocks are close to those of submarine hydrothermal vent solutions, where salinities range from 70% below to 200% above seawater concentrations [Fig. 4.0 (Von Damm and Bischoff, 1987; Von Damm, 1988; Bowers et al., 1988; Butterfield et al.,

1990)]. Hence, these fluids probably represent seawater slightly modified by circulation to depth.

Variations in Na and Cl concentrations in the low-salinity fluids may have resulted from either limited mixing of fluids with seawater-like salinities (3.5 wt% NaCl) and phase-separated vapors and brines, or from hydration reactions under greenschist facies conditions. Offsets in homogenization temperatures of the fluid inclusions hosted in xenoliths and plagiogranitic-host rocks indicate that fracturing occurred early in the thermal history of the rocks before enclaves and plagiogranite hosts reached thermal equilibrium (Fig. 4.17).

The ubiquitous occurrence of low-salinity fluid inclusions in all plutonic rocks and dike samples studied, indicates that migration of modified seawater along small aperture fractures was pervasive in the upper plutonic and lower extrusive sections of Troodos (Fig. 3.14B.). Microfracture networks containing low-salinity inclusions which cut fractures dominated by brine-rich inclusions indicate that subsequent migration of seawater occurred at minimum temperatures of 200-400°C. In concentrated zones of high water-rock interaction in the epidiosites and epidotized shear zones temperatures were 50-100°C higher than in surrounding rocks (Fig. 4.18).

Results of modeling indicate cracking temperatures ($T_k=350-600^\circ\text{C}$; Fig. 4.13) and permeabilities remained high (Fig. 4.14A), although heat flux dropped significantly ($4423-971 \text{ w/m}^2$; Fig. 4.14B) during the waning stages of hydrothermal circulation. The extensive fracture networks may represent the distal, deep-seated feeder system for zones of more concentrated hydrothermal upflow.

4.5 A Comprehensive Model of a Brine-Dominated Hydrothermal System in Troodos

Microthermometric analyses of brine-dominated secondary fluid inclusions, in conjunction with thermal modeling, suggest the onset of fluid flow in the upper plutonic

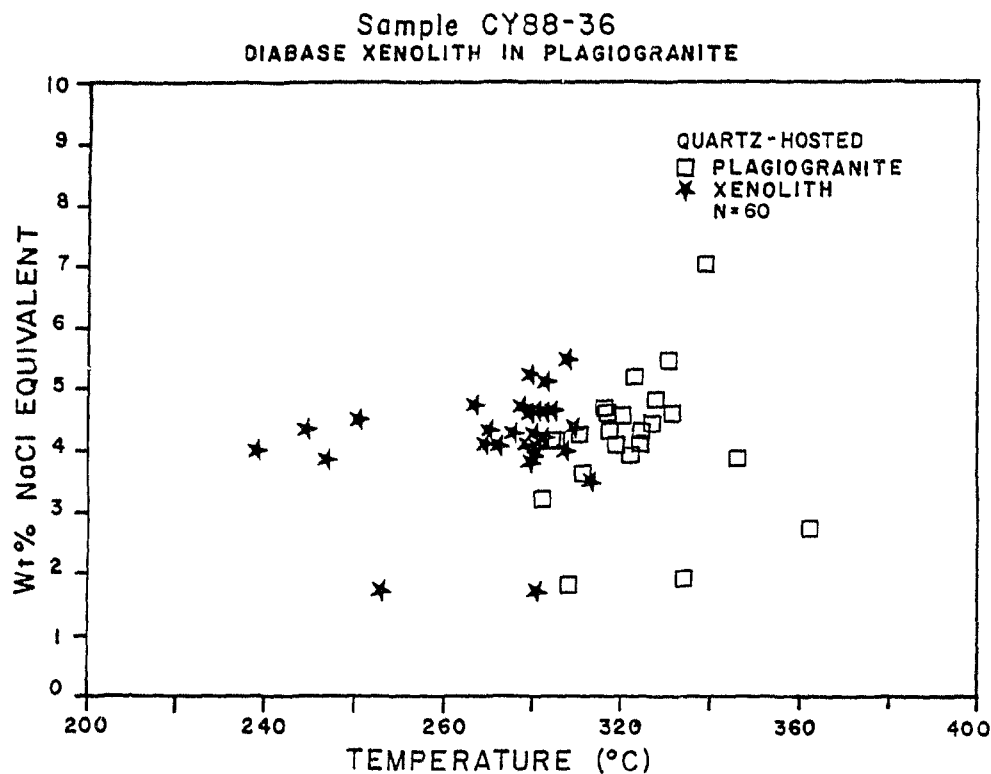


Figure 4.17 Temperatures of homogenization and corresponding equivalent fluid salinities for secondary, quartz-hosted fluid inclusions. Fluid inclusions hosted in an amphibolitized diabase xenolith exhibit homogenization temperatures 20-30°C lower than inclusions hosted in the plagiogranitic host rock. The lowered temperatures may reflect a localized relict temperature gradient between the xenolith and plagiogranitic host.

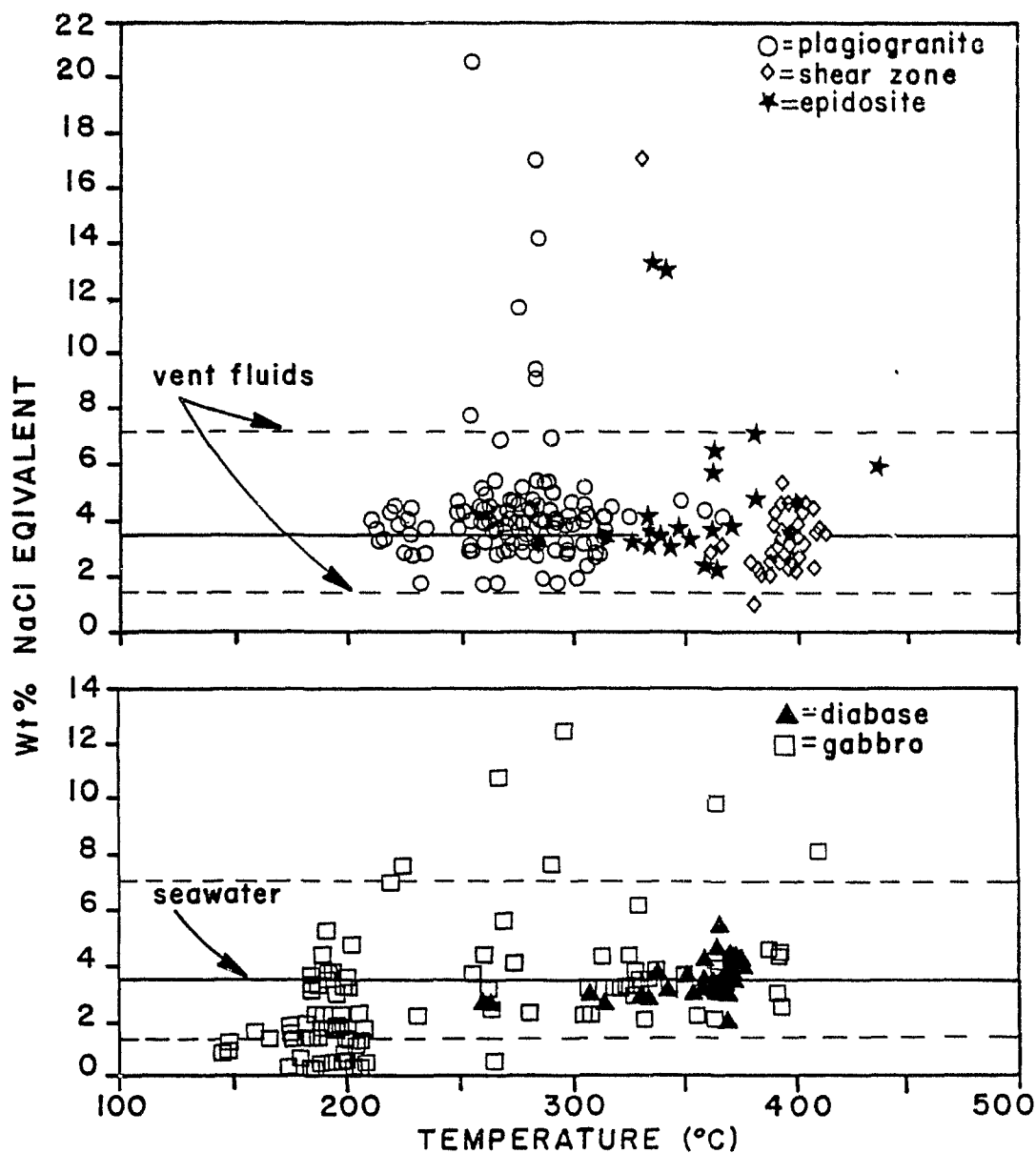


Figure 4.18 Corresponding temperatures of homogenization and fluid salinities for epidosite- and shear zone-hosted inclusions. Inclusion homogenization temperatures in these zones of high flow through are 50-100°C higher than inclusion temperatures in zones of lower permeability.

sequence of Troodos resulted from fracturing events at temperatures of 600-800°C. The pluton-hosted microfractures lined exclusively with high-temperature brine inclusions are most reasonably interpreted in terms of two-phase separation at near solidus temperatures of either pore waters or magmatic fluids. The complex intrusive relationships within the upper plutonic sequence provide strong evidence for the presence of multiple magma chambers beneath the paleospreading axes of Troodos. Rapid stress changes and thermal pulses associated with emplacement of these bodies likely induced episodic fracture propagation in the crystalline host rocks and expansion of trapped pore fluids. These intermittent cracking events resulted in transient increases in permeability and heat flow out of the system, enhanced brine generation as pore fluids underwent multiple phase separation events, and promoted isolation and segregation of the brine and vapor phases.

In localized areas, circulation of the high-temperature fluids resulted in extreme alteration of the plagiogranite bodies and in the formation of podiform epidiosites. Brine-rich fluid inclusions in these pervasively altered rocks indicate circulating fluids were enriched in $\text{NaCl-KCl} \pm \text{CaCl}_2$ (4.19). Exsolution and upward migration of these KCl-enriched fluids may account for the observed K-depletions of oceanic plagiogranites. Subsequent density stratification of the phase-separated fluids and preferential migration of the brines along fine-scale fractures resulted in formation of a brine-dominated hydrothermal system in the upper level plutonic sequence of Troodos. The extremely fine nature of the fractures indicates that brine migration at any one locality was probably short-lived. Vapor-dominated fluid inclusions in hydrothermal clinopyroxenes indicate injection of gabbro pegmatites following or coincident with circulation of the brine-rich fluids.

Arrays of low-temperature, low-salinity fluid inclusions, which crosscut fractures dominated by brine inclusions indicate that penetration of seawater during subsequent fracturing events in the upper level plutonic sequence and sheeted dike complex

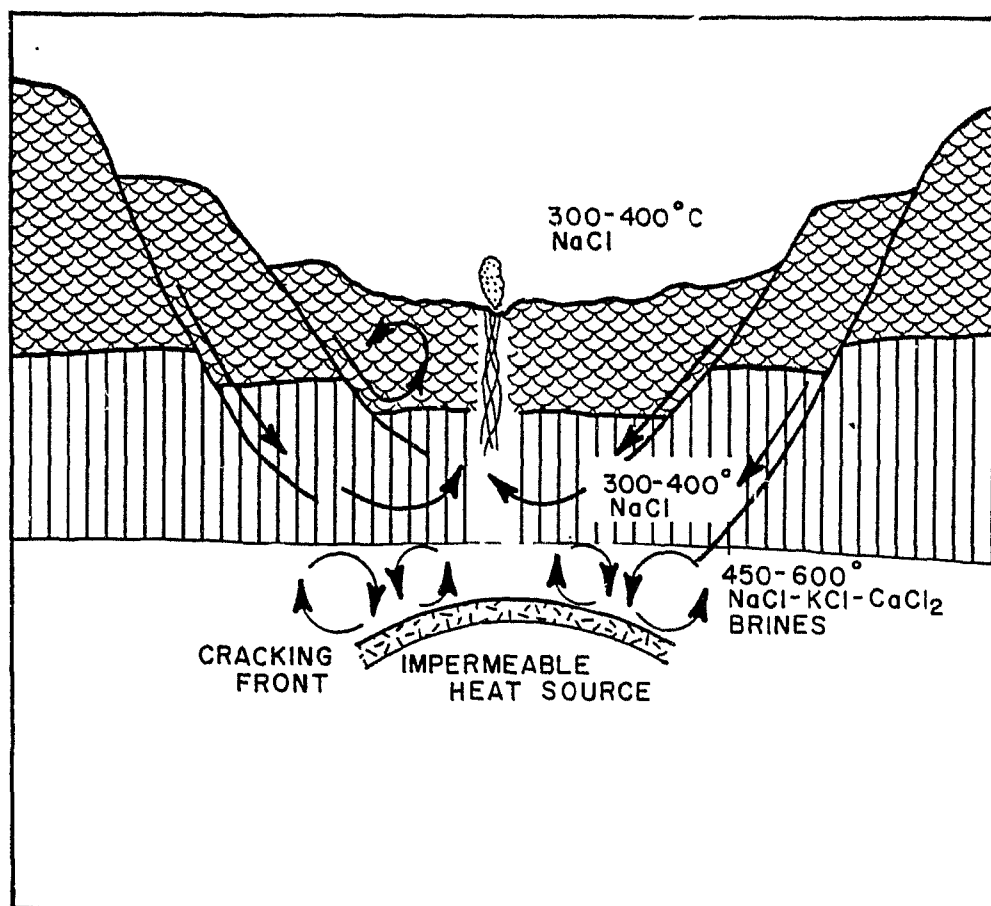


Figure 4.19 Conceptual model for fluid flow in Troodos. In the upper level intrusive sequence, deeply circulating seawater or magmatic fluids undergo two phase separation at temperatures of 450-600°C, resulting in formation of 36-56 wt% NaCl-KCl-CaCl₂ brines. Subsequent density stratification of the brine and vapor phases results in preferential entrapment of brines at depth. The highly expanded vapor phases are free migrate to shallower levels in the circulation system. During intermittent fracturing associated with magma injection, brines may be recycled as fractures are reopened, increasing salinity in the residual fluid. Transient fracturing at high temperature allows localized circulation of brines. The lower temperature fracture networks funnel 300-400°C fluids with vent-like salinities to zones of more concentrated hydrothermal upflow which feed the overlying vent system.

occurred at temperatures of 350-600°C. Hydration reactions under greenschist facies conditions, or limited mixing with phase-separated fluids, resulted in salinity variations from 70% below to 200% above seawater concentrations. Temperature and compositional relationships of the low-salinity inclusions are similar to those found in large aperture quartz veins in the sheeted dikes and to those in the overlying stockwork system hosted by the extrusive rocks (Fig 4.20). The similarities in temperatures and compositions of these inclusions suggest that the lower-temperature fracture networks in the upper level plutonic sequence may represent the feeder system for concentrated zones of hydrothermal upflow which fed the overlying hydrothermal vents.

The common occurrence of highly saline inclusions in the upper level plutonic rocks, in conjunction with the absence of brine-rich or moderately saline fluids in the overlying sheeted dike complex suggests little communication occurred between high temperature fluids circulating in the plutonic sequence and low-temperature, low-salinity fluids in the sheeted dikes. These observations provide the first strong evidence in support of previous submarine hydrothermal circulation models which suggest 1) that generation of high-temperature brines should be common in the oceanic crust (Fournier, 1987) and 2) the permeability contrast between the sheeted dikes and gabbros should result in the development of multi-tiered circulation systems (Pallister and Hopson, 1981; Bischoff, 1989).

4.6 Comparison With Other Hydrothermal Systems

The earliest models describing circulation of fluids in high temperature plutonic environments were developed to explain the alteration and isotopic haloes commonly associated with porphyry copper deposits. The characteristic development of concentric potassic, phyllic, and propylitic alteration zones radiating away from the intrusive bodies suggested that similar physiochemical processes acted during the formation of all these deposits [Fig. 4.21, (Henley and McNabb, 1977)].

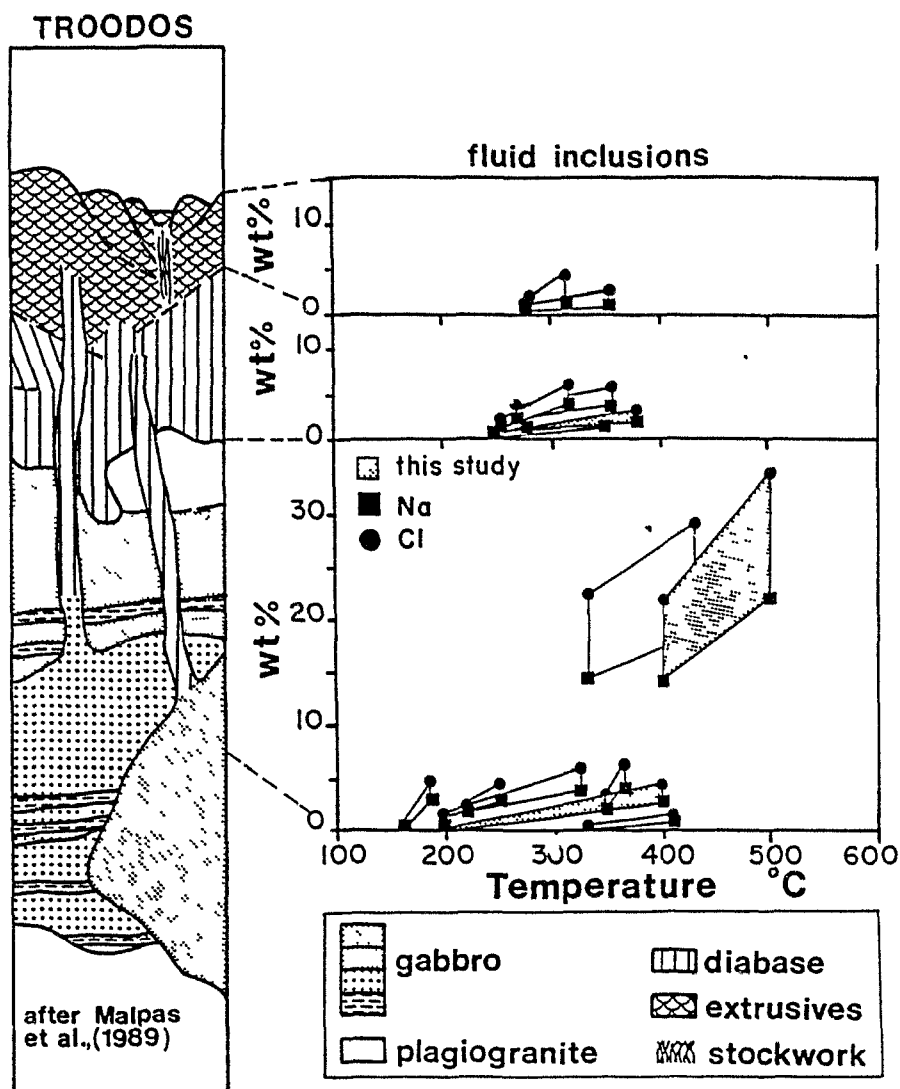


Figure 4.20 Schematic cross section of Troodos, near paleoaxis of spreading (after Malpas et al, 1989). Also shown are ranges of homogenization temperatures and corresponding Na + Cl concentrations of fluid inclusions in rocks from different crustal levels. Temperature and composition relationships of the low-salinity, low-temperature inclusions are similar throughout the crustal sequence. The low-temperature fracture networks, hosted in plagiogranite and gabbro may represent the distal feeder system for concentrated zones of hydrothermal upflow which feed the overlying vent system. High-temperature, brine inclusions are only observed in the upper intrusive sequence. Inclusion data in the extrusive section (stockwork system) are from Spooner and Bray [(1977) N=156]; data for the sheeted dikes come from Richardson et al., [(1987) N=176], Schiffman and Smith, [(1988) N=74, and Vibetti et al., (1989) N=48]; data obtained for rocks in the plutonic section are from Cowan and Cann, [(1988) N=38, and Vibetti et al, (1989) N=77]. Shaded areas indicate fluid inclusion results from this study (N=589).

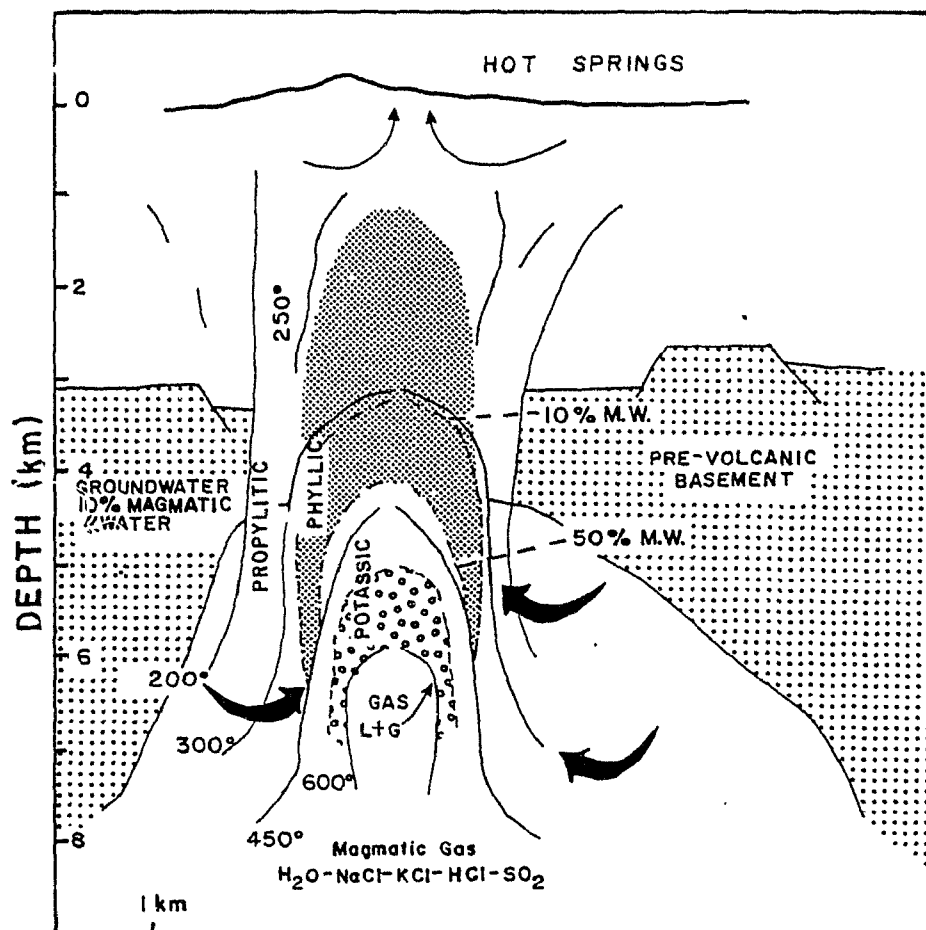


Figure 4.21 Fluid dynamic and alteration model for high temperature circulation systems associated with porphyry copper deposits (after Henley and McNabb, 1977). Phase separation of magmatic fluids and subsequent density stratification results in development of a widely dispersed vapor-rich plume. Draining back of the brines into the core of the circulation system results in potassic alteration in the central portion of the alteration envelope. At shallow depths progressive entrainment of meteoric water damps out any chemical signature of magmatically-derived fluids. At the periphery of the dispersed plume, mixing of meteoric water with higher temperature plume fluids results in increased sulfide precipitation in the outer alteration shell.

Field and laboratory studies indicate a bipartite thermal and compositional fluid evolution in these systems. Crosscutting vein relationships, in conjunction with fluid inclusion and isotopic analyses, indicate that highly saline, endogenous brines at near-magmatic temperatures are the earliest fluids to circulate through these rocks [Table VIII, Fig. 4.22A (Reynolds and Beane, 1985)]. Extreme potassic alteration occurs in the cores of these systems as the hypersaline, metal-rich fluids (30-70 wt% total dissolved salts) interact with the silicic host rocks (Fig. 4.21 & Fig. 4.22A). Phyllic and propylitic alteration envelopes form with introduction of meteoric water into the circulation system at temperatures of 200-400°C (Reynolds and Beane, 1985).

Fluid evolution and alteration patterns in porphyry systems have been interpreted in terms of interaction of a low-salinity buoyant vapor plume, generated at depth, and a shallow-level convecting system dominated by meteoric water [Fig. 4.21, (Henley and McNabb, 1977)]. In this model, two-phase separation of metal-rich magmatic fluids in the core of the circulation system, followed by density stratification of the vapors and brines, results in development of a vapor-rich dispersion plume. The magmatic component of the plume becomes progressively diluted as circulating groundwater is entrained in the system. Mixing of the groundwater into the plume may counteract plume dispersion (Cathles, 1983) and promote mineral precipitation in the periphery of the plume.

Fluid inclusion and isotopic analyses, in conjunction with alteration mineral assemblages, indicate the evolution of a hydrothermal system in a spreading ridge environment is broadly similar to that in a porphyry system (Table VIII, Fig. 4.22B). The generally lower water contents of rocks in spreading ridge environments, coupled with the superposition of several alteration events imposed on the rocks as they move away from the spreading axis, however, make identifying an unambiguous magmatic fluid signature much more difficult than for porphyry copper systems.

TABLE VIII
HYDROTHERMAL CIRCULATION MODELS

Author	Area	Rock Type	# of Events	Determination	Mineral Assemblage	T°C	D cm ²	Model
Henley & McNabb (1977)	Porphyry Copper (General)	Calc-Alkaline	2-3	Alt, F.I., Isotopes	Phyllic, Propylitic Potassic	350 350-700	10 ⁻¹⁵	Multi-tiered, phase separation of magmatic fluids in potassic core, density stratification resulting in vapor-rich dispersion plume.
Reynolds & Beane (1985)	Santa Rita, N.M.	Granodiorite Porphyry Copper	3	Veins, F.I., Isotopes	potassic alteration hypogene mineraliz. Phyllic alteration	750-950 260-500 220-360	---	Two-phase separation of fluids at >750°C, resulted in generation of brines and vapors, which resulted in potassic alteration in the core of the system, subsequent fracturing at 220-360°C allowed penetration by meteoric fluids.
Fournier (1988)	Spreading Centers	Basalt-Gabbro	--	Alt, F.I., Vent Chem.	----	600-700 500-650 400-500	---	Multi-tiered convection cells, possibly separated by double diffusive interface, lower cell consists of high density brines generated by condensation of seawater-derived fluids upper vapor-rich plume may mix with sea- and meteoric water.
Nehlig & Juteau (1988)	Semail Ophiolite	Basalt-Gabbro	5	Veins, F.I.	amph zo-ep ep qtz pre	400-530 >370 >370 >370 ---	10 ⁻⁷ - 10 ⁻⁹	Amphibole veins represent fossilized trace of cracking front, crosscutting vein system represents off axis fracturing events (zo-ep), and zone of mixing between seawater and upflowing high temperature fluids.
Bischoff & Rosenbauer (1989)	Spreading Centers	Basalt-Gabbro	--	Alt, F.I., Vent Chem.	----	700 350	---	Multi-tiered convection cells, lower cell hosted in gabbros and lower sheeted dikes is dominated by recycled brines originally formed by two-phase separation of seawater at >700°C. A diffusive interface separates the lower cell from a lower temperature upper cell (360°C).
Kelley (1990)	Troodos	Gabbro- Plagiogranite	2-3	F.I.	----	450-600 200-400	10 ⁻¹⁰	Density stratification and segregation of phase-separated brines results in preferential entrapment of 450-600°C brines at depth. Subsequent fracturing (200-400°C) events allow penetration of seawater.

qtz = quartz, amph = amphibole, ep = epidote, pre = prehnite, zo = zoisite

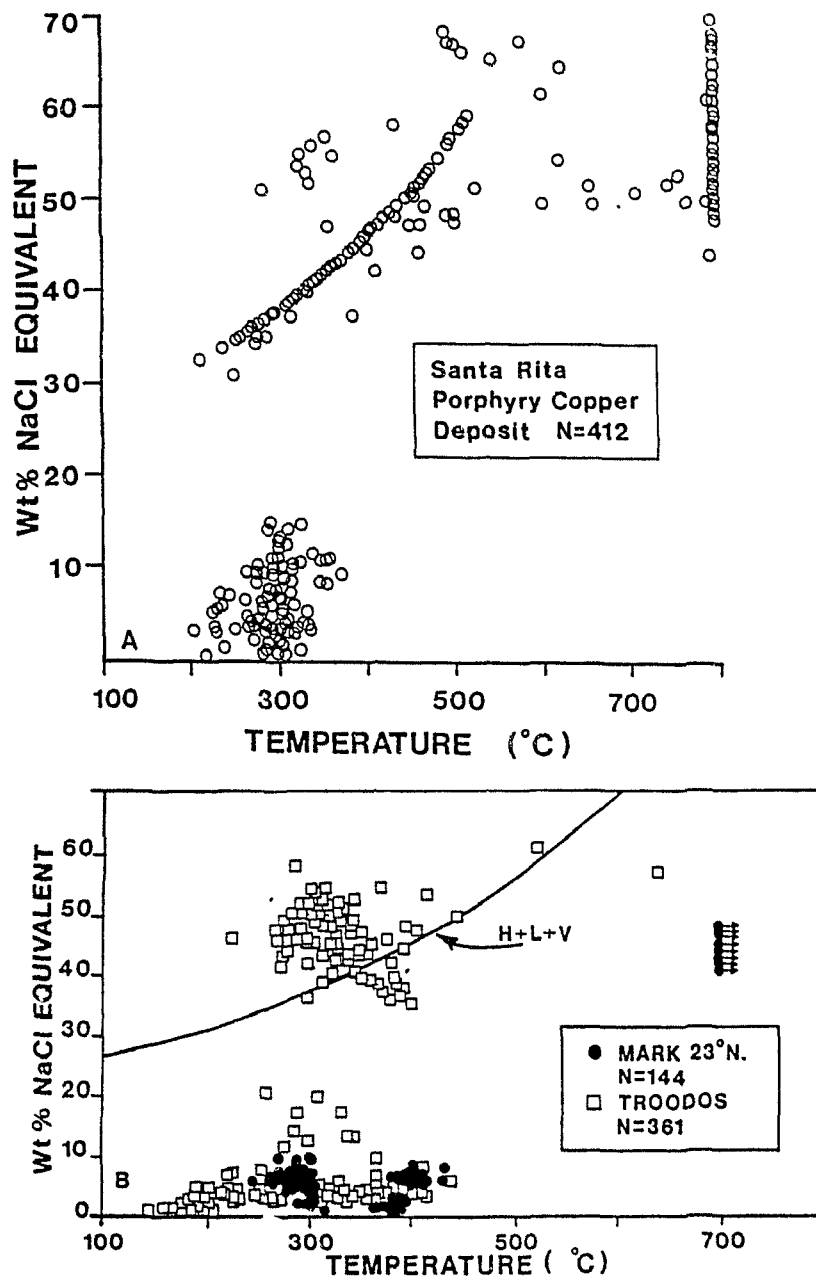


Figure 4.22 (A) Corresponding homogenization temperatures and equivalent salinities from quartz-hosted fluid inclusions in the Santa Rita porphyry copper deposit (after Reynolds and Beane, 1985). Phase separation of magmatic fluids at temperatures $>750^{\circ}\text{C}$ resulted in generation of brines (30-70 equiv. wt% NaCl+KCl). Subsequent fracturing events at $220\text{-}360^{\circ}\text{C}$ allowed circulation of lower salinity fluids (<15 wt% NaCl) which resulted in phyllic alteration of the rocks. (B) Corresponding temperatures of vapor-bubble disappearance temperatures and equivalent fluid salinities for plutonic rocks from Troodos and the Kane Fracture Zone (MARK). Fluid inclusion results indicate thermal and compositional evolution of fluids in porphyry and spreading center environments are very similar.

Isotope and fluid inclusion results from submarine rocks, in conjunction with temperatures and compositions of vent fluids, require that a two-tiered circulation system, in which high temperature fluid flow in the plutonic rocks is overlain by a low-temperature, less vigorously convecting cell hosted in the sheeted dikes [Fig. 4.23 & Fig. 4.24 (Gregory and Taylor, 1981; Fournier, 1987; Bischoff and Rosenbauer, 1989)], be considered when modeling fluid flow in submarine hydrothermal systems. These two cells may be separated by a double diffusive interface which separates circulation of high-temperature, brine-rich fluids at depth from an overlying cell dominated by fluids similar to seawater [Fig. 4.24 (Bischoff and Rosenbauer, 1989)]. The brine layer is bounded at the base by an ephemeral cracking front, and at its top by the density contrast of the high-density brines and overlying low-density fluids. The thermal barrier imposed by the brine layer, in conjunction with extrema in water properties, prevents circulating shallow-level fluids, which eventually feed the vents, from achieving temperatures greater than 360°C. Periodic fluctuations of the diffusive interface during cracking may allow local mixing of the brines and low-salinity fluids. In the high-temperature cell, upflowing brines undergo boiling; the low density vapor phase migrates upwards and eventually mixes with upwelling fluids in the overlying cell. Brines in the lower cell are continually recycled, while low-salinity fluids in the upper cell undergo a single pass cycle. The long residence times of the circulating brines results in progressive alteration of the host rocks at depth. Circulation of the highly acidic fluids leaches metals from the surrounding rocks, and with progressive albitization of plagioclase in the host rocks, fluids become enriched in Ca and depleted in Na (Fournier, 1987; Bischoff and Rosenbauer, 1989).

4.6.1 Application of Flow Models To Troodos

Fluid inclusion results from Troodos and from submarine samples are remarkably similar to analyses of porphyry copper systems (Table VIII, Fig. 4.23). In general, analogous thermal and compositional evolution in the fluids is observed; the earliest

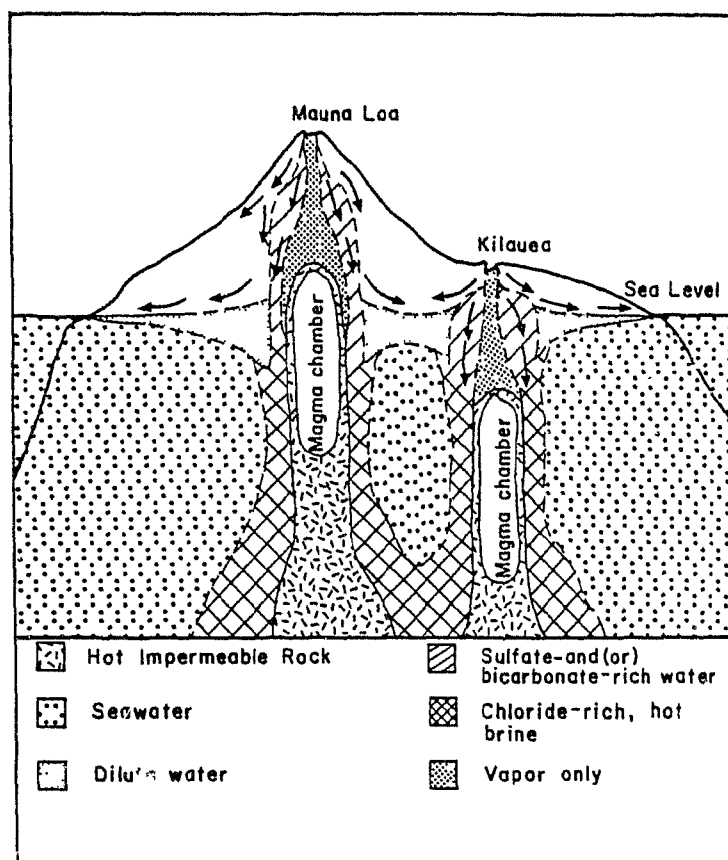


Figure 4.23 Generalized hydrothermal circulation model for fluid evolution in oceanic environments (after Fournier, 1987). In zones of multiple magma injection significant amounts of brine are generated at depth by condensation of seawater-derived fluids. Density stratification results in deep seated circulation of brines, overlain by lower salinity fluids. Where ponding of brines occurs, sulfides are likely to be deposited. At shallow crustal levels, condensation of vapor results in formation of sodium-sulfate and sodium-carbonate brines.

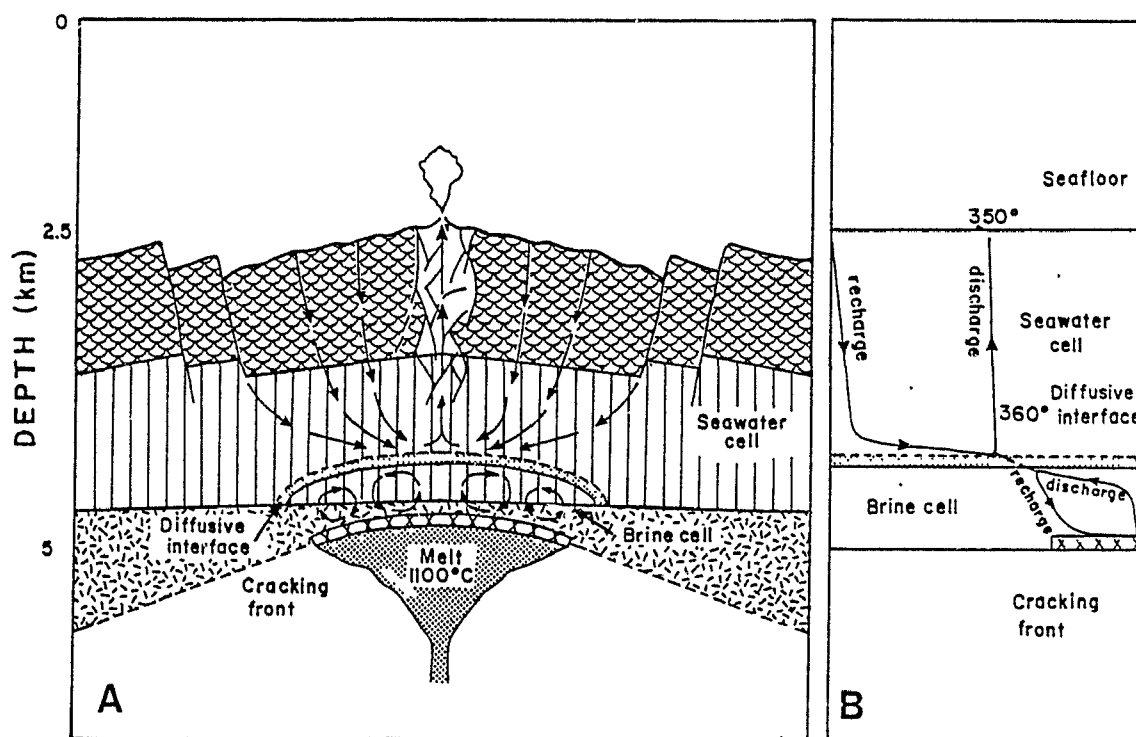


Figure 4.24 (A) Generalized model for double diffusive convection system at mid-ocean ridge spreading centers (after Bischoff and Rosenbauer, 1989). High-temperature, phase-separated brines convect near the base of the sheeted dikes. A double diffusive interface separates this high temperature cell from an overlying low temperature cell in which modified seawater circulates freely. Heat and some chemical components are diffused through this interface, resulting in varying salinities of surficial vent fluids. (B) Thermal cycle for nested cells. The diffusive interface, in conjunction with extrema in water properties, limits maximum achievable temperatures of fluids in the upper cell to 360°C. Temperatures of brine circulation in the lower cell are bounded at the base by the cracking front and at the top by fluid density constraints. During intermittent cracking and changing thermal conditions, fluctuation of the diffusive layer may result in migration of lower salinity fluids to depth.

fluids to circulate through the fractured margins of the plutonic bodies are phase-separated brine (30-70 wt% NaCl±KCl±CaCl₂) and low-salinity, vapor-rich fluids (1-10 wt% NaCl) at temperatures greater than 500-700°C. Segregation of the vapors and brines as a result of density stratification results in isolation of the brines at depth. Following collapse of the high temperature system, deeply penetrating fractures allow circulation of low-salinity fluids at temperatures of 200-400°C, which in places pervasively alter the plutonic rocks.

Results of the fluid inclusion analyses from Troodos support many aspects of these models; however, the specifics of fluid flow near the sheeted dike-gabbro interface, and the vertical relationships of vapor and brine circulation, remain to be studied. Extensive communication between fluids circulating in the sheeted dikes and underlying plutonic rocks is not indicated by results of inclusion analyses. The results may support a two-tiered circulation model; however, the data from the sheeted dikes are still preliminary. Although migration of brines was common in the upper level plutonic rocks, it is not clear from analyses of rock alteration and fluid inclusions that extensive recycling or migration of the brines occurred. For a given sample, the restricted compositions and temperatures of fracture-bound brine inclusions are not consistent with multiple, high-temperature fracturing events. Although it could be argued that each subsequent cracking episode wipes out inclusion trails recording earlier events, it is unlikely that this process is perfect and that all traces of the earlier events are removed. Fluid inclusion populations indicating such a process should exhibit multiple, but discrete, temperature-composition relationships; these are not observed in fluid inclusion data from Troodos. This study is exciting because it is the first study of submarine hydrothermal systems to provide quantitative data indicating that generation of high-temperature brines at depth in the oceanic crust is common. Additional, detailed work, however, is needed to further quantify fluid flow in these dynamic systems.

CHAPTER V

CONCLUSIONS

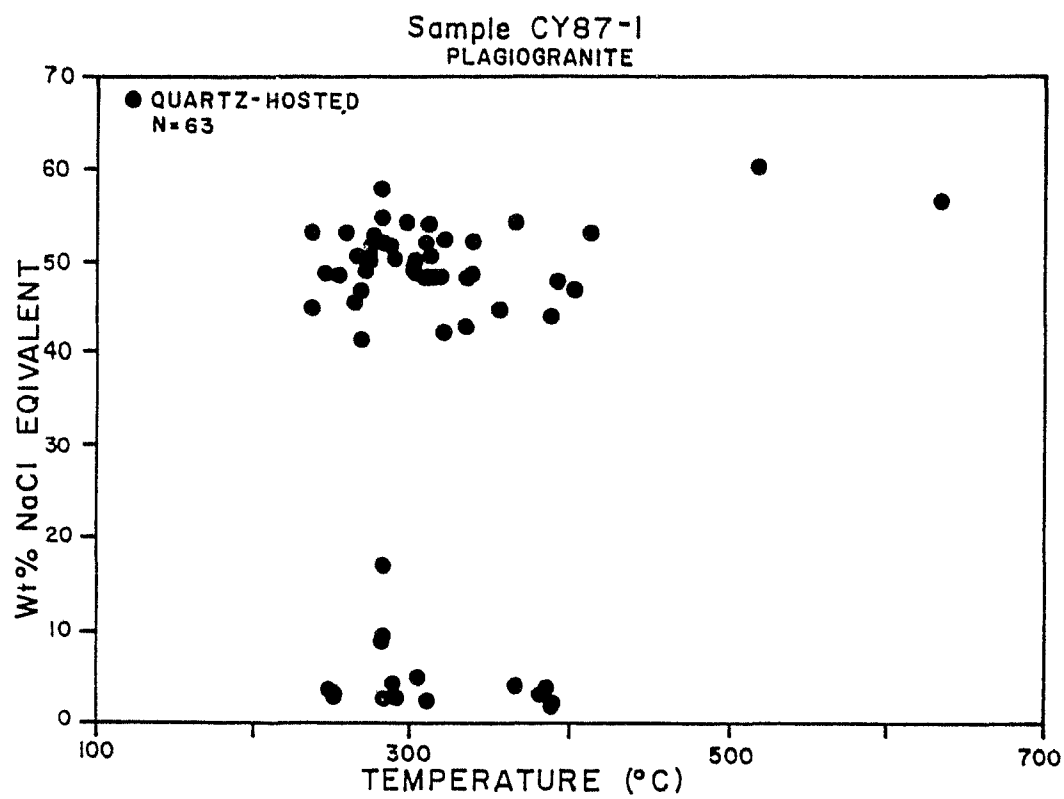
Microthermometric analyses of quartz-hosted fluid inclusions in fresh and epidotized plagiogranites and gabbros from the Troodos ophiolite, Cyprus provide the first documentation that generation of high temperature, Fe-rich brines may be common at depth in the oceanic crust. Complex networks of fluid inclusion arrays in rocks of the upper intrusive sequence record episodic fracturing events. The earliest event, at temperatures greater than 400-500°C, resulted in pervasive entrapment of brine-rich aqueous fluids, the compositions of which vary spatially throughout the complex by as much as 23 wt% NaCl (33-56 wt% NaCl equivalent). Homogenization of the high-temperature, Fe-rich inclusions by halite dissolution at 400-500°C indicates the fluids were trapped in the absence of a vapor phase.

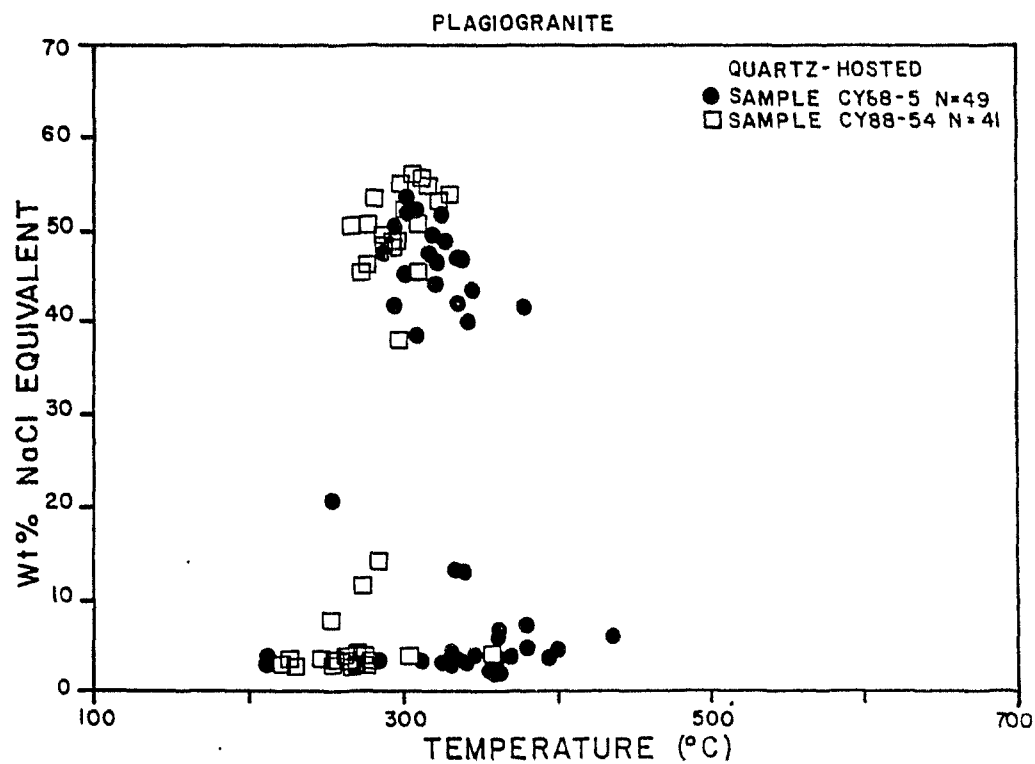
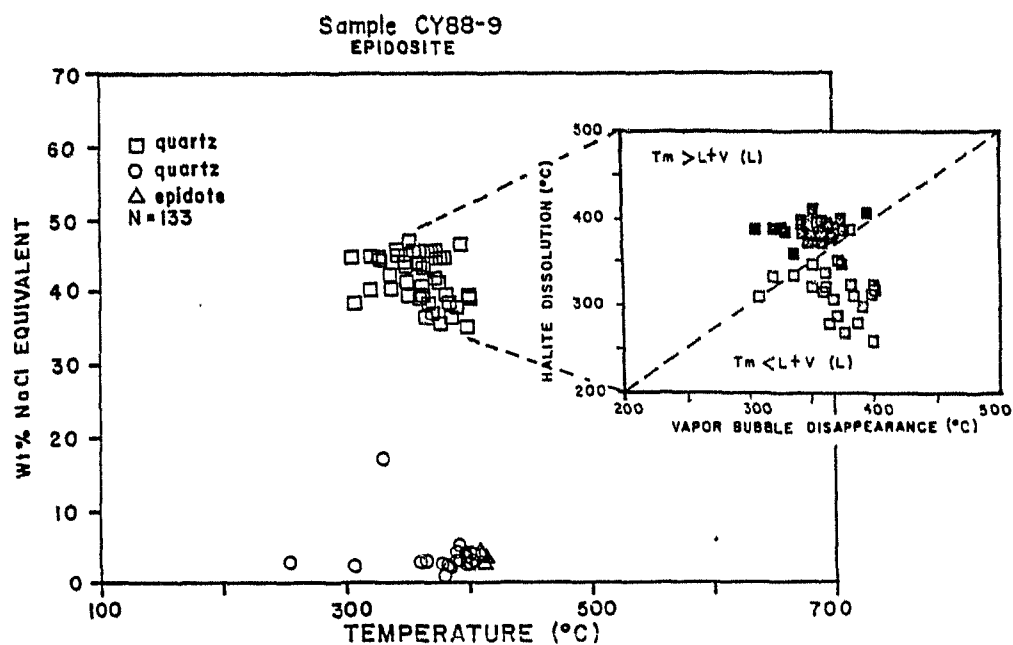
The quartz-hosted, high-salinity fluids are interpreted to have formed by two-phase separation of either hydrothermal seawater, or a magmatic aqueous phase at uncorrected temperatures of 400-500°C. Migration and segregation of brine and vapor phases along anastomosing fractures near the margins of the crystallizing plagiogranite and gabbroic bodies resulted in preferential entrapment of the brines in the deep-seated, high-temperature portions of the hydrothermal system. The temperature-composition relations of the fracture-bound fluids do not support a single-pass model for circulation of hydrothermal fluids in Troodos, but are consistent with the development of multi-tiered circulation cells in the plutonic and sheeted dike complex. Lack of brine enrichment in fluid inclusions hosted in rocks of the sheeted dike complex indicates that little communication of circulating fluids occurred between the two cells.

Subsequent fracturing of the upper level plutonic rocks at minimum temperatures of 200-400°C allowed penetration by seawater and resulted in localized intense alteration of the plagiogranites and upper level gabbros. Hydration reactions under

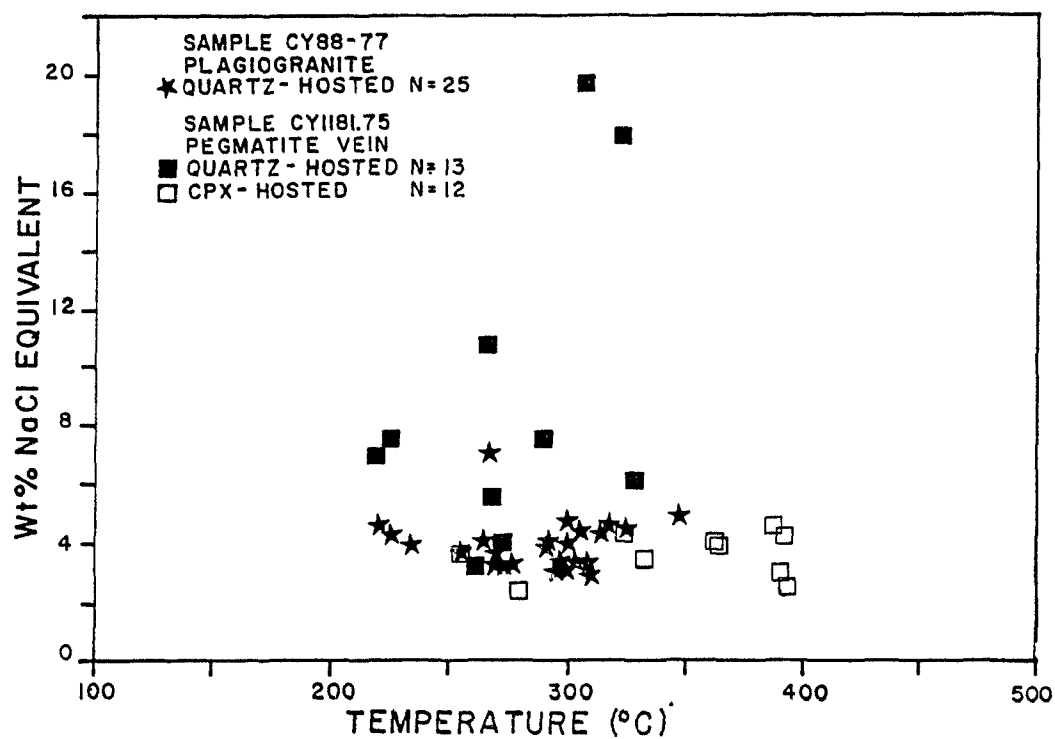
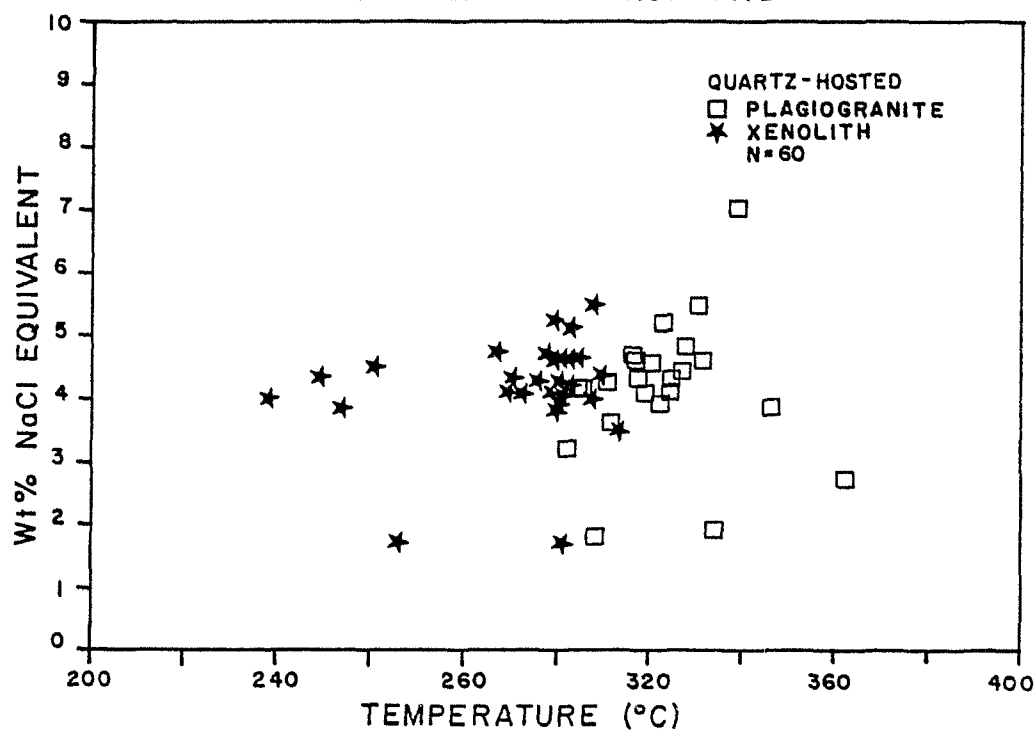
greenschist facies conditions, or limited fluid mixing with phase-separated fluids, resulted in salinity variations from 70% below to 200% above seawater concentrations. Salinities of the low-temperature inclusions (1-7 wt% NaCl equivalent) are similar to those of fluids exiting active submarine hydrothermal vents at mid-ocean ridge spreading centers. The low-temperature fracture networks may represent an extensive deep-seated feeder system for zones of more concentrated hydrothermal upflow.

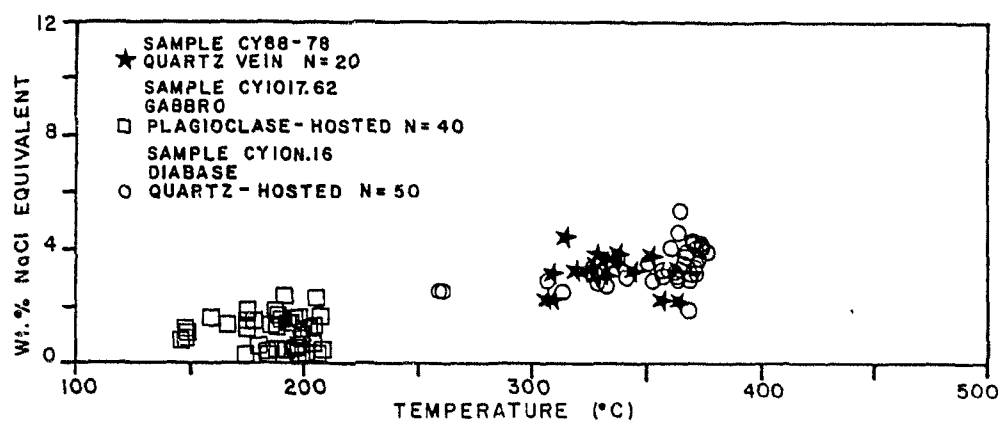
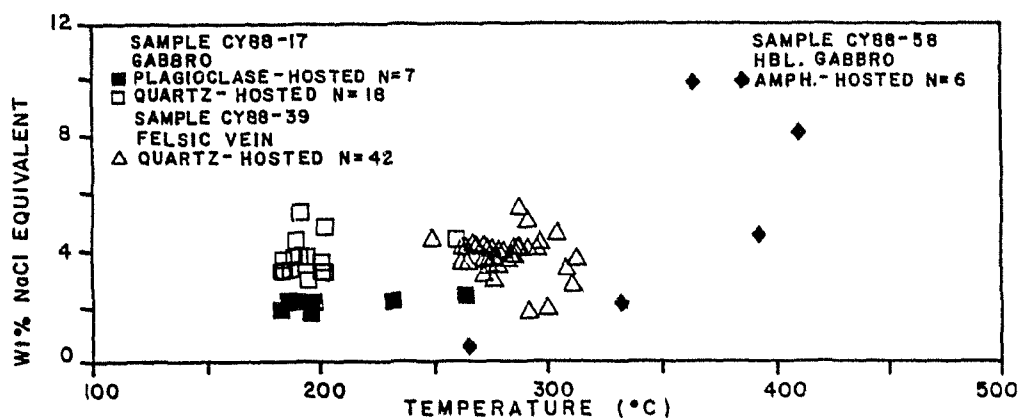
APPENDIX A.
FLUID INCLUSION ANALYSES





Sample CY88-36
DIABASE XENOLITH IN PLAGIOGRANITE





APPENDIX B. CRACKING FRONT MODEL

Convective circulation of fluids in the plutonic sequence of Troodos was studied by applying the cracking front model of Lister (1974, 1983, 1984), in which small, fluid-filled cracks propagate downward into a cooling magma body. Fluid temperatures obtained from inclusion analyses were used, in conjunction with calculations characterizing high temperature fluid flow in a porous medium, to derive initial cracking temperatures, cracking front velocities, and crack widths and spacings in the plagiogranite and gabbroic rocks (Table IX). It is important to note that the inter-related processes which govern flow of fluids in submarine hydrothermal systems are poorly understood, and models attempting to characterize these systems are still preliminary in nature. The model of Lister is intended only to provide order-of-magnitude results and illustrate general relationships with respect to permeabilities, temperatures of convecting fluids, and fracture geometry. The model and calculations used in this study are discussed below.

The theory of water penetration into hot rocks was developed to characterize convective heat transport at the base of submarine hydrothermal systems. Fracture propagation is treated one-dimensionally and is a function of the temperatures of the boundary layer (T_B), water reservoir (T_o), and heat source (T_1) (Fig. B.1). The initial assumption for which this model is based is that the convective boundary layer will control the crack spacing;

$$(1) \qquad y = \frac{h}{2N} \qquad \text{(Lister, pers comm., 1983)}$$

where y equals the crack spacing, h equals the depth of the convective slab, and N equals the Nusselt number. The Nusselt number is a non-dimensional number which

TABLE IX
RESULTS OF CRACKING FRONT MODEL

To °C	Tw °C	Tk °C	U m/yr	q w/m ²	Zo m	N	D 10 ⁻¹⁰ cm ²	A 10 ⁷	y m	d mm	t days
1250	240	350	7.4	977	4.23	2230	1.66	0.80	0.56	0.93	27.5
	275	400	10.8	1363	2.91	2718	1.64	1.18	0.46	0.86	15.6
	350	500	20.5	2370	1.53	3729	1.51	2.22	0.33	0.75	6.0
	430	600	35.4	3703	0.87	4773	1.34	3.65	0.26	0.67	2.7
	510	700	57.7	5398	0.54	5890	1.23	5.56	0.21	0.60	1.3
	600	800	91.1	7394	0.35	6902	1.04	7.6	0.18	0.54	0.7
800	245	350	13.7	971	2.30	2184	1.51	0.76	0.57	0.90	15.3
	285	400	20.6	1347	1.53	2616	1.38	1.10	0.48	0.82	8.5
	370	500	42.8	2304	0.73	3480	1.13	1.94	0.36	0.70	3.1
	470	600	85.0	3441	0.37	4149	0.79	2.76	0.30	0.59	1.3
	590	700	176.7	4423	0.18	4323	0.44	2.99	0.29	0.48	0.6

To=Initial temperature of heat source, *Tw*=temperature of circulating fluids, *Tk*=cracking temperature
U=velocity of cracking front, *q*=thermal flux, *Zo*=boundary layer thickness
N=Nusselt number, *D*=permeability, *A*=Rayleigh number, *y*=crack spacing, *d*=crack width
t=fluid residence time

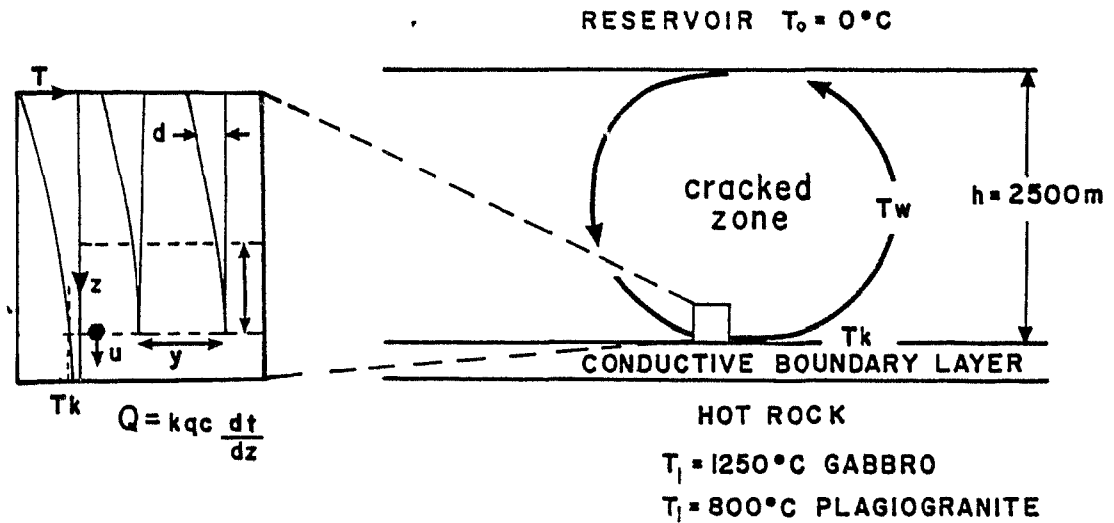


Figure B.1 Cracking front model of Lister (1974, 1983) in which water penetration into host rock occurs by advancement of a cracking front moving downward (z) at velocity (u). Thermal shrinkage at temperatures below the cracking temperature (T_k) allows fractures of width d to form at crack spacing y . The initial boundary conditions were set at 0°C for the reservoir (seawater), and temperatures of 800 and 1200°C for the heat source. The water temperature in the convecting plume (T_w) was obtained from fluid inclusion analyses. The heat flux out of the system (Q) is equal to the product of the thermal conductivity of the rock and the change in temperature with depth.

expresses the ratio of heat transported by convection to heat transported by conduction and is thought to be governed by the relationship

$$(2) \quad N = cA^b \quad (\text{Lister, 1983})$$

where c and b are constants and A equals the Rayleigh number; a measure of the instability of the system. Experimental studies indicate that the onset of convection in a porous slab with impermeable conductive boundaries occurs at $A = 40$. The relationship of the Nusselt number to the Rayleigh number is not well known. Early experiments indicated that $N = A/40$, however, more recent experimental studies indicate a breakover occurs at high Rayleigh numbers and that the relationship may more closely follow $N = cA^{1/3}$ (Fig. B.2). The $1/3$ power law is thought to be a lower limit, therefore, for this study a breakover of the curve at $A=1000$ was chosen together with an arbitrary power law of $1/2$, giving the relationship

$$(3) \quad N = 0.79A^{1/2}$$

The Rayleigh number is expressed as

$$(4) \quad A = \frac{\alpha_w g h \Delta T D}{\gamma_w k} \quad (\text{Lister, 1984})$$

where $\frac{\alpha_w}{\gamma_w}$ equals the coefficient of thermal expansion of water over the kinematic viscosity of water at the temperature of interest [$\frac{\alpha_w}{\gamma_w} = 0.127(T_w)^2$], g = acceleration of gravity, $\Delta T = T_B - T_o$, D = the permeability, and k = the thermal diffusivity of rock ($= 10^{-6} \text{ m}^2/\text{s}$).

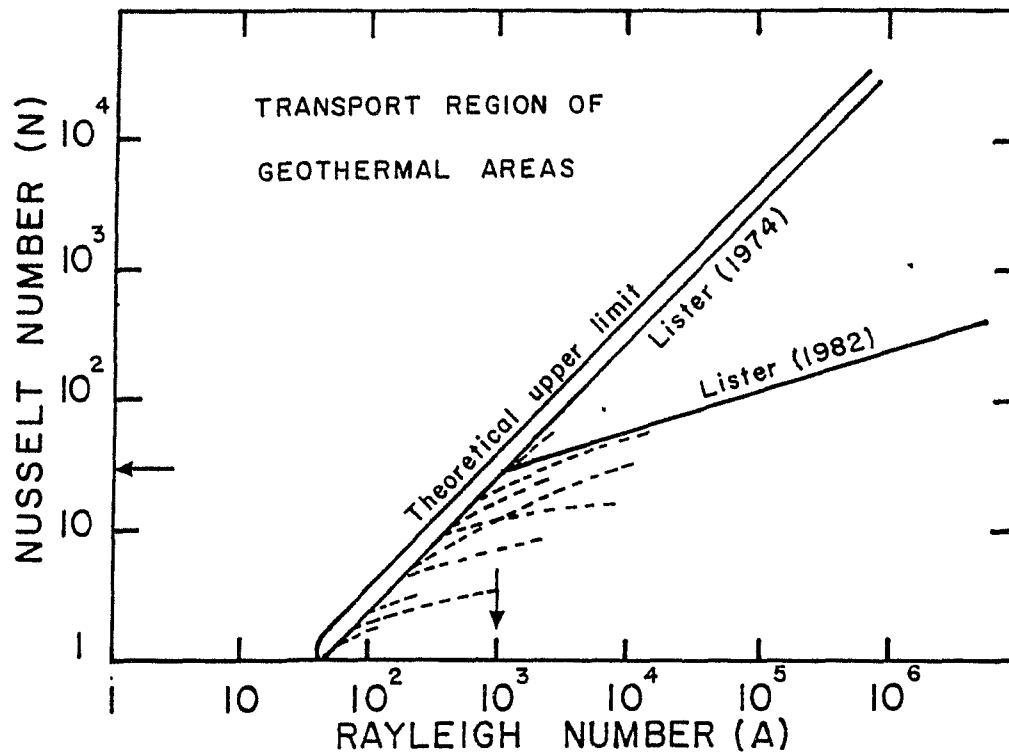


Figure B.2 Logarithmic plot of heat transport number (N) against Rayleigh number (A) for porous medium convection (after Lister, 1983). Solid lines indicate theoretical upper limit and relations used by Lister in previous theoretical water penetration models. Dashed lines indicate experimental results of other workers (see Lister, 1983). Arrows indicate the relationship used in this study for a breakover point at $A = 1000$, and a power law of $1/2$ for N .

The permeability is equal to

$$(5) \quad D = \frac{\sqrt{2}}{12} \alpha^3 y^2 (T_k - T_w)^3 \quad (\text{Lister, 1984})$$

where α is equal to the coefficient of the linear expansion of rock ($=1.5 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$), y is equal to the mean crack spacing (m), T_k is equal to the cracking temperature ($^\circ\text{C}$), and T_w is equal to the water temperature in the upwelling convective plume ($^\circ\text{C}$). Substituting equations 4 and 5 into equation 3 yields the expression for the Nusselt number

$$(6) \quad N = 0.79^{1/2} \left[\frac{h}{2N} \right]^{1/2} \left[\frac{\alpha w g h \Delta T \sqrt{2} \alpha^3 (T_k - T_w)^3}{\gamma \omega k 12} \right]^{1/4}$$

The heat transported away from the hot boundary by the convective system (q) is given by

$$(7) \quad q = u p_c (T_1 - T_B) = \frac{N k \Delta T}{h} \quad (\text{Lister, 1982})$$

where u is equal to the cracking front velocity (m/s) and p_c is equal to the density of water (1.0 gm/cm^3). Substituting K (the thermal diffusivity of the matrix for porous convection, where $K=k/p_c$) for k/p_c , and $T_B = 1/5(T_k + 4T_w)$ (Lister, 1983) into equation 7 yields the expression for the front velocity

$$(8) \quad u = \left[\frac{0.79}{2} \right]^{1/2} \left(\frac{1}{5} \right)^{3/4} \frac{k^{3/4}}{h^{1/4}} \left[\frac{1.27 \sqrt{2} \alpha^3}{12} \right]^{1/4} \underbrace{\frac{T_w^{1/2} (T_k - T_w)^{3/4} (T_k + 4T_w)^{5/4}}{5T_1 - T_k - 4T_w}}_F$$

Maximizing the polynomial expression (F) yields the temperature of fluids in the upwelling plume (T_w). This effectively results in maximizing the heat transfer in the system by maximizing the mobility of the hot water in the matrix. For this study, fluid

inclusion temperatures were assumed to be equal to T_w and F was solved iteratively to obtain cracking temperatures. The results of the calculations are presented in Table IX.

The initial boundary conditions for the reservoir temperature (seawater) were set at 0°C , the temperature for the heat source (T_1) was set at 1250°C for the gabbros and 800°C for the plagiogranites, and the thickness of the convecting plume was set at 2500 m. The model was successful in producing reasonable permeabilities, cracking temperatures, and at low temperatures producing reasonable residence times of fluids in the upwelling plumes. It was less successful in correctly predicting crack spacing and width. This may be due to the problem with accurately defining the Nusselt number because the heat transported by convection influences the advance of the cracking front directly by removing the heat of the cooling rock, and affects the crack spacing through the thickness of the convective boundary layer (Lister, 1983).

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