To Bernard
Thank you very much for

all the help & encouragement.

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Investigations on the Role of Fluid During Granulite Facies Metamorphism, Kigluaik Mountains, Seward Peninsula, Alaska

by

Clifford Scott Todd

A thesis submitted in partial fulfillment of the requirements for the degree of

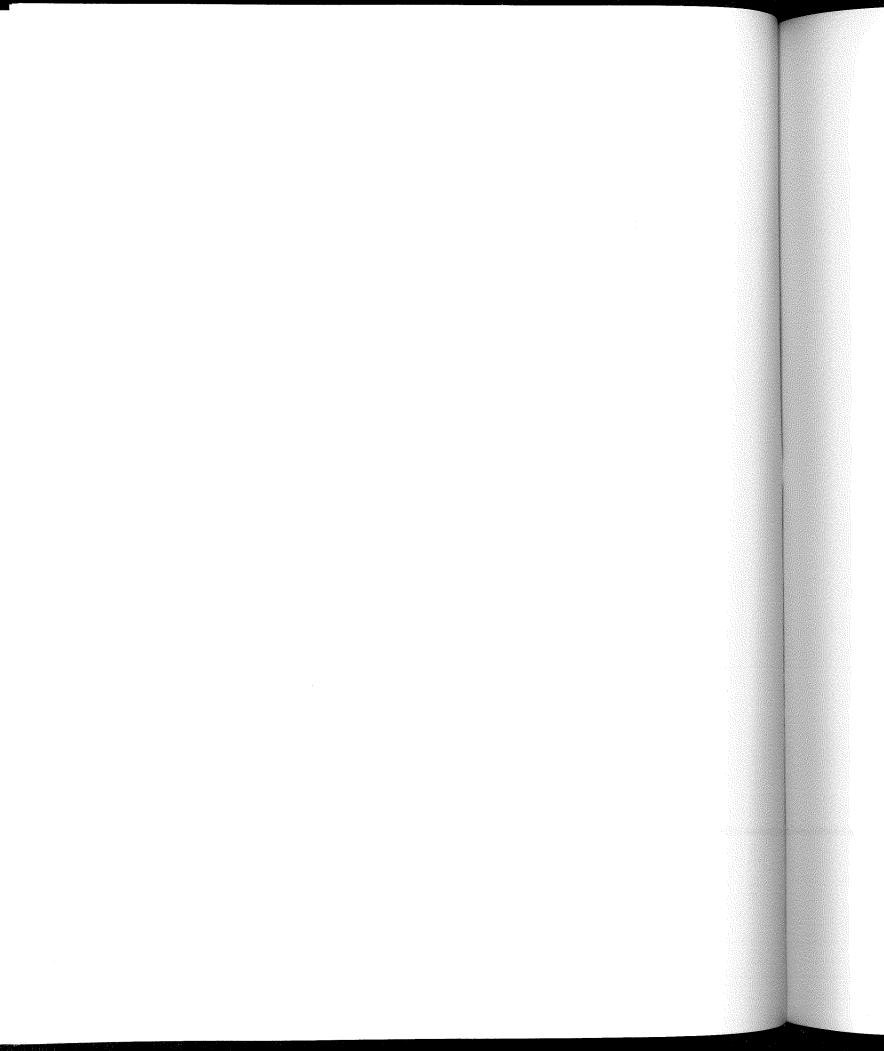
Doctor of Philosophy

University of Washington

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Abstract

Investigations on the Role of Fluid During Granulite Facies Metamorphism, Kigluaik Mountains, Seward Peninsula, Alaska

by Clifford Scott Todd

Chairperson of the Supervisory Committee: Professor Bernard W. Evans
Department of Geological Sciences

Flat-lying thick marble units acted as impermeable barriers to upward fluid flow in amphibolite to granulite grade rocks of the Kigluaik Mountains, Seward Peninsula, Alaska. The degree of impermeability can be related to the composition of the marble. The margin of a thick pure dolomite marble chemically reacted with underlying metasyenite to form a 2 cm thick border of calcite + forsterite. No fluid penetrated past this reaction front. The high temperatures at which this process occurred (nearly 800°C) allowed C and O isotopic interaction for an additional 2 cm by diffusion through the solid dolomite. A second marble with a higher silica content underwent more decarbonation, which enhanced porosity and lead to a greater extent of isotopic interaction. An estimate of fluid flux across the bottom of this marble layer based on the shape of the isotope profile is 1 cm³/cm² directed down, out of the marble. At two other marble-gneiss contacts, steep isotopic gradients exist, coincident with the lithologic contacts, indicating very little cross-lithology fluid flux.

Fluid composition during metamorphism was locally controlled by lithology. At a contact where an homogeneous Hbl-bearing gneiss lies above a marble, Hbl in the gneiss reacted to form fine-grained granular Opx, Cpx, Pl and Kfs within 60 cm of the marble. The Hbl-bearing and Hbl-free gneiss assemblages are related by Bt and Hbl

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dehydration reactions. These reactions were driven by a reduction in H_2O -activity due to dilution with CO_2 from the marble. Water-activity calculations based on biotite dehydration equilibria in the Hbl-free gneiss indicate a trend from 0.14 to 0.08 toward the marble. Mineral assemblages confirm that the marble was a source of high XCO_2 fluids. This example provides an indication of the limited role (60 cm) played by fluid movement in controlling mineral parageneses in this terrane.

It is concluded that there was no pervasive infiltration of C-O-H fluid across the thick, continuous, marble units of the amphibolite to granulite grade Kigluaik Group during peak metamorphism. Movement of volatile species and isotopic interaction between rocks during peak metamorphism was dominated by diffusive processes. No evidence for channelized fluid pathways through the marble units during peak metamorphism has been found. Therefore, heating of the terrane occurred by conduction, not advection via a fluid.

In granulite grade rocks of the Kigluaik Mountains, no peak metamorphic fluids survived as fluid inclusions. Retrograde CO₂-rich fluids were trapped late in the metamorphic cycle and have variable density around 0.5 g/cm³. In amphibolite grade rocks, aqueous fluid inclusions may represent samples of near-peak metamorphic fluids. Density of these inclusions varies from 0.9 to 0.8 g/cm³ with salinities less than 4 wt% NaCl equivalent.

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Chapter 1: Introduction and background

Definition of Problem

This paper is presented as a contribution to the ongoing debate concerning the role of fluid infiltration in deep-crustal granulite facies environments. In contrast to greenschist and amphibolite grade regional metamorphic environments where numerous recent phase equilibrium, reaction progress, and stable-isotope studies have demonstrated major involvement of fluid advection (e.g., Rumble et al. 1982, Tracy et al. 1983, Ferry 1984, 1986, Wickham and Taylor 1985, 1987, Hoisch 1991; Chamberlain and Rumble 1988, 1989), conclusions regarding fluid composition and fluxes during granulite-grade metamorphism appear to be in conflict (see Newton 1986). In lower crustal environments, it seems necessary to document the specific circumstances for each terrane (Peacock 1991); certainly, more case studies need to be presented in order to establish generalized models for the lower crust.

In any crustal environment, fluids play potentially major roles in the transfer of thermal energy (Brady 1988), as a catalyst (Rubie 1986), a medium of mass transfer (Fyfe et al. 1978), and an important factor in rheology (Etheridge et al. 1984). At deeper crustal levels, there are additional complexities related to the development and possible migration of partial melts, to the release of fluids from crystallizing magmas, and to the possible introduction of fluids from the upper mantle. While there is general agreement that granulite facies rocks were mostly hotter and drier than those with high-amphibolite facies parageneses, the role of the fluid phase during granulite grade metamorphism remains the subject of continued discussion. The present work concentrates on identifying and quantifying the composition, abundance and transport characteristics of fluid in a well-exposed, amphibolite to granulite grade metamorphic

terrane on the Seward Peninsula of Alaska. This is accomplished through the investigation of mineral assemblages and mineral chemistry, stable isotope geochemistry, and fluid inclusions.

Geologic Setting

Location

The Seward Peninsula is located in the western part of Alaska (figure 1.1), with the Bering Sea to the north, Norton Sound to the South and the Bering Straights to the west. The Peninsula is composed mostly of rolling hills covered by treeless tundra. Mountain ranges are present in the inland portions of the peninsula which expose more rugged terrain. The Kigluaik Mountains are one such range. Geologic exploration was initiated on the Peninsula when placer gold deposits were discovered on the beach at the town of Nome in 1897.

Previous Work

A good historical review of the geologic work done on the Seward Peninsula was presented by Till (1980) and Till and Dumoulin (1992), and is briefly summarized here. Following the discovery of gold, the U.S. Geological Survey conducted several reconnaissance surveys on the Seward Peninsula (Brooks et al. 1901, Collier 1902, Collier et al. 1908, Smith 1908 1910, Moffit 1913). This lead to more focussed studies on the occurrence of economic mineral deposits (Harrington 1919a b, Cathcart 1922, Steidtmann and Cathcart 1922), continued mapping (Hummel 1962a b, Sainsbury et al. 1969 1972a b c d e f, Sainsbury 1969 1972, Miller et al. 1972, Hudson 1977, Robinson and Stevens 1984) and geophysical surveys (Cady 1977, Barnes and Hudson 1977). More recent work concerning metamorphic petrogenesis on the peninsula has

been initiated by groups from the University of Washington and the University of Alaska (Till 1980, Pollock 1982, Sturnick 1984, Forbes et al. 1984, Thurston 1985, Armstrong et al. 1986, Evans and Patrick 1987, Patrick 1987 1988, Lieberman 1988, Patrick and Lieberman 1988, Patrick and Evans 1989, Buxton 1990, Evans et al. 1992, Lieberman and Petrakakis 1992), with work also being conducted from Stanford University (Miller et al. 1992a, Calvert 1992).

Current Understanding

Rocks of the Seward Peninsula of Alaska can be divided into four groups based on their metamorphic grade (Pollock 1982): 1) low grade metasediments of the York Mountains, 2) blueschist/greenschist facies metasediments and meta-igneous rocks of the Nome Group, 3) amphibolite to granulite facies rocks (Kigluaik Group) of the Kigluaik, Bendeleben and Darby Mountains, 4) unmetamorphosed Cretaceous or younger sedimentary and igneous rocks (figure 1.1). The Nome Group is of Cretaceous metamorphic age (Armstrong et al. 1986). The schists are believed to be related to the high P/T rocks of the schist belt along the southern margin of the Brooks Range (Hitzman et al. 1986; Patrick 1988; Gottschalk 1990). The protoliths of the Nome Group were continental margin related carbonates, pelites, volcanics and calcareous sediments of preCambrian (?) to Devonian age (Till et al. 1986, Buxton 1990). Together with later intrusive bodies, this package underwent subduction beneath oceanic and island arc crust (Box 1985).

In three mountain ranges on the Seward Peninsula (Kigluaik, Darby and Bendeleben), uplifts or structural arches expose Barrovian-style metamorphic complexes formed by dynamo-thermal overprint on Nome Group schists (figure 1.1). The high grade rocks of the Kigluaik Mountains, which are stratigraphically and structurally continuous with the overlying Nome Group schists (figures 1.2, 1.3 and 1.4; also see

Patrick and Lieberman 1988), grade downward through biotite, staurolite, sillimanite, and sillimanite + K-feldspar zones into orthopyroxene-bearing gneisses in the most deeply exposed parts (Till 1980). The Kigluaik Group metasediments probably include rocks at least as old as late Proterozoic (Armstrong et al. 1986). Timing of the peak of high grade metamorphism is currently under investigation, but probably occurred around 109-103 Ma (Armstrong et al. 1986, Lieberman and Van der Heyden personal communication, J. Wright personal communication), with rapid cooling of the area occurring around 85 Ma (Turner et al. 1979, Miller et al. 1992a b, Amato et al. 1992).

In the most deeply exposed portion of the Kigluaik Mountains, maximum metamorphic conditions of approximately 800° C and 8 kbar (Lieberman 1988; Lieberman and Petrakakis 1992) were followed by decompression, as indicated by mineral replacements and petrogenetic grid considerations (Ky \rightarrow Sil; Rt \rightarrow Ilm; Bt + Sil \rightarrow Crd; Grt \rightarrow Opx + Pl; abbreviations in table 1.1). P-T conditions in the isograd region are as follows (Lieberman 1988): Sta 550°C 4 kbar, Sil 660°C 4.5 kbar, Sil+Kfs 725°C 5.5 kbar.

Description of Lithologic Units

An explanation of lithologies found in the Kigluaik Mountains is presented here (figure 1.4). Additional information can be found in Till (1980), Pollock (1982), Sturnick (1984), Lieberman (1988) and Calvert (1992).

Pelite above the Thompson Creek Orthogneiss (4th pelite)

A series of isograds occur within this unit (figures 1.2, 1.3 and 1.4). By increasing grade they are: Bt, Sta, Sil and Sil+Kfs. All isograds are parallel to lithologic layering. The first occurrence of biotite and staurolite is probably controlled by the bulk composition of the rock. The Bt isograd typically is at the boundary between a graphitic

quartzite and a biotite schist. The Sta isograd occupies the boundary between the biotite schist (which contains no Al-rich minerals) and a pelitic schist. In contrast, the Sil isograd is controlled by mineral reactions in which the outer portions of garnets reacted to form fine grained mats of sillimanite (Lieberman 1988). The Sil+Kfs isograd is controlled by the reaction:

$$Ms + Qtz \rightarrow Sil + Kfs + H_2O$$
 (1)

and occurs at the base of the unit, near the Thompson Creek orthogneiss (Till 1980). In the staurolite zone, peak metamorphic mineral assemblages include: Grt + Bt + Sta + Ms + Qtz, Bt + Sta + Ky + Ms + Qtz, and Bt + Ky + Crd + Ms + Qtz (figure 1.5).

Upgrade of the Sil isograd the assemblage may be: Bt + Sta + Sil + Ms + Qtz or Grt + Bt + Sil + Qtz + Ms. Plagioclase and graphite are commonly present in all assemblages.

Calculated water activities are around unity (Lieberman 1988). A compilation of mineral assemblage information from Kigluaik pelites can be found in Appendix I.

Pelites below the Thompson Creek Orthogneiss (1st, 2nd and 3rd pelites)

The typical peak metamorphic mineral assemblage in a pelitic schist is: $Grt + Bt + Sil + Pl + Kfs + Qtz + Ilm \pm Graph$. In rare cases, graphite constitutes 80% of the rock. Calculated activities of H_2O are about 0.5 (Lieberman 1988). Figure 1.6 shows the effect of increasing grade on mineral compositions in the AFM assemblage Grt + Bt + Sil. The shift toward more Mg-rich compositions is driven by the continuous reaction:

$$Sil + Bt + Qtz \rightarrow Grt + Kfs + H_2O.$$
 (2)

In many samples from the 1st pelite, kyanite occurs as inclusions in garnet whereas sillimanite occurs in the matrix of the rock. Also, rutile commonly occurs as inclusions within garnet, but not in the matrix, where ilmenite is usually present. Both

of these relationships indicate a history of higher pressures prior to peak metamorphism via the respective reactions:

$$Ky \rightarrow Sil,$$
 (3)

and:

$$Grt + Rt \rightarrow Sil + Qtz + Ilm.$$
 (4)

In Kigluaik pelites it is not uncommon for small amounts of cordierite to occur along the biotite and sillimanite foliation, indicating retrograde decompression manifested by the continuous reaction:

Bt + Sil + Qtz
$$\rightarrow$$
 Crd + Kfs + H₂O \pm melt. (5)

This reaction can be local in extent and garnet may not have participated in the reaction leading to some of the spuriously high temperatures obtained by the Grt-Bt Fe-Mg exchange thermometer obtained in the Kigluaik mountains by Lieberman (1988).

Staurolite is found as inclusions within garnet in pelites from all stratigraphic levels, although it is not found as a matrix mineral beyond the Sil+Kfs isograd. Some of these staurolites are accompanied by hercynite, a breakdown product of staurolite in the absence of quartz. These staurolites were stabilized to higher temperatures both by being separated from other reactants ($Qtz \pm Ms$) by a mantle of garnet, and by a higher Zn content (up to 7% Zn end member). The spinel found with staurolite inclusions also has an elevated Zn content (~10% Zn end member).

Marbles

Pure dolomitic marbles are very coarse grained (up to 0.5 cm) and may be bluish-gray in color. Calcitic marbles tend to be whiter and finer grained (around 0.1 cm). Marbles are generally granoblastic with weak foliation defined by oriented micas, when present. Since there are very few marble layers in the isograd area, most marbles sampled are from approximately the same grade. By 800°C the buffer capacity of

marbles is nearly exhausted (figure 1.7). The peak metamorphic mineral assemblage is determined by the bulk composition of the rock. Most marble mineral assemblages can be described by the bold compatibility triangle in figure 1.7. Fluid compositions associated with marbles are discussed in chapter 3.

Metaperidotite

A metaperidotite unit occurs low in the stratigraphy (figure 1.4). This unit is distinctive in the field because of its orange color when weathered. It varies from about 3 m to 50 m thick. In places the metaperidotite unit is massive, and the foliation, defined by flattened discs of Opx, is concordant with the layering in nearby lithologies. In other places the metaperidotite unit is boudinaged with pegmatite or, rarely, marble filling the interstices of the jumbled, rounded blocks of metaperidotite. These blocks are typically several centimeters to one meter in diameter. The mineral assemblage in the metaperidotite is $Fo + Opx + Cpx + Spl \pm Phl \pm Prg \pm Grt$ remnants. A thorough investigation of the metaperidotite unit was done by Lieberman (1988). Associated with the metaperidotite, though not universally present, is a mafic gneiss. The assemblage is: Opx + Cpx + Pl + Ilm + Hbl + Bt + Grt.

Below the Peridotite (0th pelite)

The lowest part of the exposed stratigraphy in the Kigluaik Mountains is dominated by fine-grained felsic, intermediate and calcareous gneiss, with minor marble. These rocks are compositionally layered on a scale as small as centimeters. A common assemblage in calcareous gneiss is: $Cpx + Pl + Qtz \pm Tnt$. In the few marbles sampled, the assemblage is: $Cal + Fo \pm Dol \pm Spl \pm Phl$. The assemblage observed in felsic compositions is: Cal + Calcare + Cal

assemblage from the 1st pelite on an AFM projection. Since tie lines do not cross, the difference in assemblage may be due to a difference in bulk composition rather than in temperature.

Post-metamorphic Igneous rocks

Crosscutting pegmatite dikes are common. Where these are in contact with marble layers, skarn assemblages (including wollastonite, grossular and vesuvianite) may occur. In several localities at the base of the main marble, graphite deposits have developed in vugs within the pegmatites and along joints. This graphite occurrence may be related to mixing of reduced vein fluids with oxidized marble fluids (Rumble and Hoering 1986). Mafic dikes occur, but are less common. Unfoliated Cretaceous plutonic bodies are found throughout the Kigluaiks.

Table 1.1: Abbreviations used in text. Following the convention in Kretz (1983) mineral names are capitalized, whereas mineral component names are not.

Mineral name a	abbreviations
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Miller at 11	I liame appreviations	
Aln	allanite	Ca ₂ FeAl ₂ Si ₃ O ₁₂ OH with rare earth elements added
And	andalusite	Al ₂ SiO ₅
Ap	apatite	Ca ₅ (PO ₄) ₃ OH
Bt	biotite	K(Mg,Fe) ₃ AlSi ₃ O ₁₀ (OH) ₂
Cal	calcite	CaCO ₃
Chu	clinohumite	Mg ₉ Si ₄ (OH) ₂
Cpx	clinopyroxene	Ca(Mg,Fe)Si ₂ O ₆
Crd	cordierite	$(Mg,Fe)_2Al_4Si_5O_{18} \cdot nH_2O,CO_2$
Di	diopside	CaMgSi ₂ O ₆
Do	dolomite	CaMg(CO ₃) ₂
Fo	forsterite	Mg ₂ SiO ₄
Graph	graphite	C
Grt	garnet	(Ca,Mg,Fe,Mn) ₃ Al ₂ Si ₃ O1 ₂
Hbl	hornblende	$(Na,K)_{0-1}Ca_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$
Ilm	ilmenite	FeTiO ₃
Kfs	K-feldspar	KAlSi ₃ O ₈
Ky	kyanite	Al ₂ SiO ₅
Ms	muscovite	KAl ₂ AlSi ₃ O ₁₀ (OH) ₂
Opx	orthopyroxene	(Mg,Fe)SiO ₃
Phl	phlogopite	KMg ₃ AlSi ₃ O ₁₀ (OH) ₂
Pl	plagioclase	CaAl ₂ Si ₂ O ₈ - NaAlSi ₃ O ₈
Prg	pargasite	NaCa ₂ (Mg,Fe) ₅ AlSi ₇ O ₂₂ (OH) ₂
Qtz	quartz	SiO ₂
Rt	rutile	TiO ₂
Sil	sillimanite	Al ₂ SiO ₅
Spl	spinel	MgAl ₂ O ₄
Sta	staurolite	Fe ₄ Al ₁₈ Si _{7.5} O ₄₄ (OH) ₄
Tnt	titanite	CaTiSiO ₅
Tr	tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
Zm	zircon	ZrSiO ₄

Table 1.1 continued

Mineral component abbreviations

biotite	ann	annite	KFe ₃ AlSi ₃ O ₁₀ (OH) ₂
	phl	phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$
feldspar	ab	albite	NaAlSi ₃ O ₈
	An	anorthite	CaAl ₂ Si ₂ O ₈
	kfs	K-feldspar	KAlSi ₃ O ₈
garnet	alm	almandine	Fe ₃ Al ₂ Si ₃ O ₁₂
	grs	grossular	Ca ₃ Al ₂ Si ₃ O ₁₂
	prp	pyrope	Mg ₃ Al ₂ Si ₃ O ₁₂
pyroxene	di	diopside	CaMgSi ₂ O ₆
	en	enstatite	MgSiO ₃
	fs	ferrosilite	FeSiO ₃
	hd	hedenbergite	CaFeSi ₂ O ₆

Fluid species

 C_{o}

 $C_{\mathbf{f}}$

1	
H_2O	water, or the supercritical equivalent
CO_2	carbon dioxide, or the supercritical equivalent
CH_4	methane, or the supercritical equivalent
N_2	nitrogen gas, or the supercritical equivalent
H_2	hydrogen gas, or the supercritical equivalent
$T_{\mathbf{m}}$	temperature of final melting of solid
T_h	temperature of homogenization to one phase
σ	error associated with stable isotope measurement
φ	porosity
D	effective diffusion coefficient
D _{fluid}	diffusion coefficient of element in fluid
$\rho_{\mathbf{f}}$	density of fluid
ρ_s	density of solid
K_d	wt% element in solid/wt% element in fluid

isotopic composition at edge of marble isotopic composition of unaltered marble

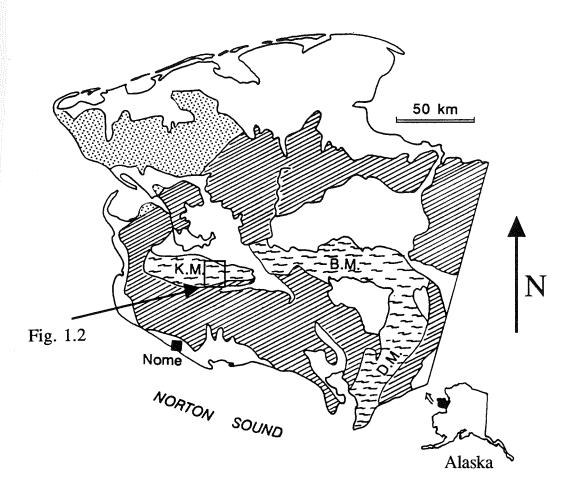
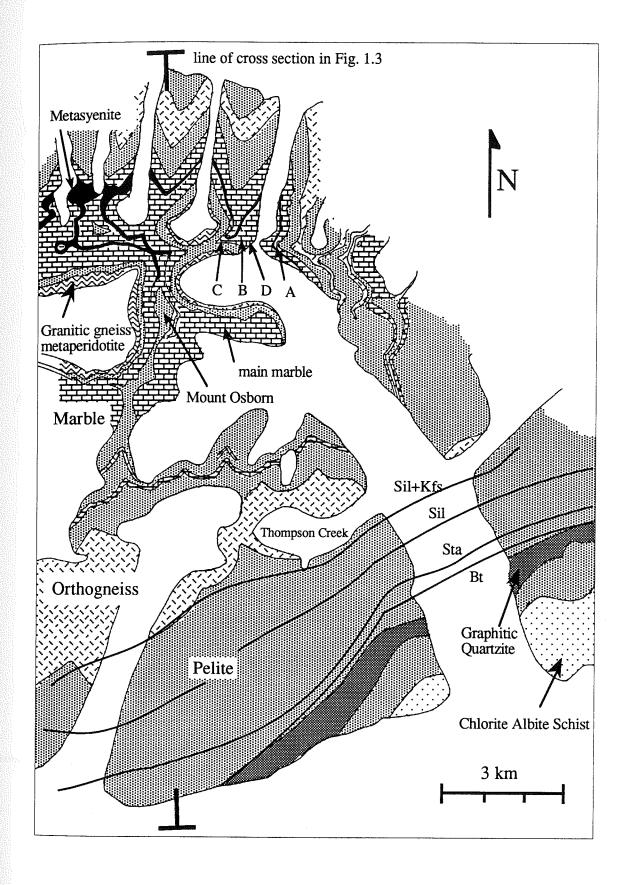


Figure 1.1: Location map Seward Peninsula, Alaska. K.M. Kigluaik Mtns., B.M. Bendeleben Mtns., D.M. Darby Mtns. Diagonal rule is Nome group blueschist/greenschist; wavy pattern is high grade gneiss complexes and Cretaceous plutons; stipple is York Mtns, unmetamorphosed sediments; unpatterned is Quaternary deposits. Modified from Patrick (1987).

Figure 1.2 Lithologic map, Grand Central Valley area, Kigluaik Mtns.

Location of outcrops discussed in chapters 2 and 3: A, AB89-41; B, AB89-61; C, AB90-13; D, AB90-27. Lithologic contacts south of Thompson Creek from Lieberman (personal communication).



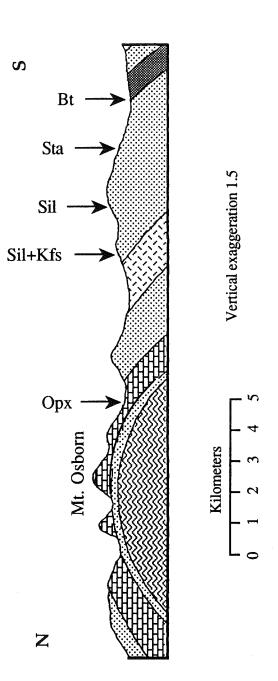
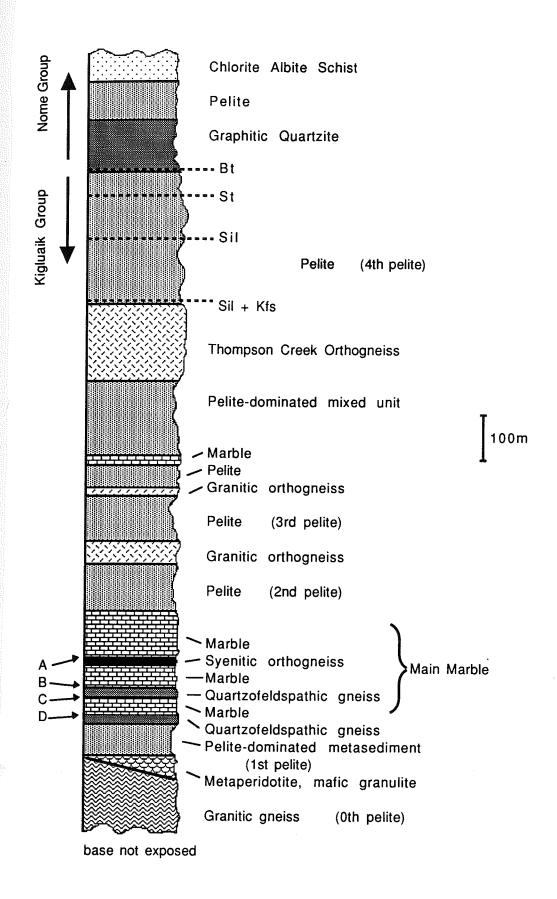


Figure 1.3 N-S cross section through Kigluaik mountain range, showing isograd locations. Modified from Lieberman (1988).

Figure 1.4: Stratigraphic section, Grand Central Valley area. A, B, C and D as in Figure 1.2.



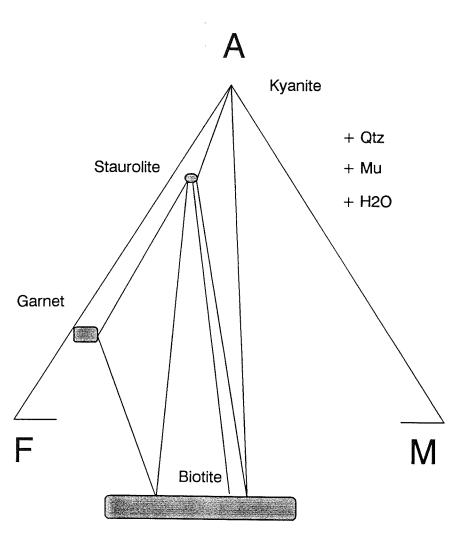


Figure 1.5 AFM projection, staurolite zonepelites. Grt-bearing AB87-220.1; two-phase AB87-218; Ky-bearing SL81-425.1. Shaded mineral compositions are schematic.

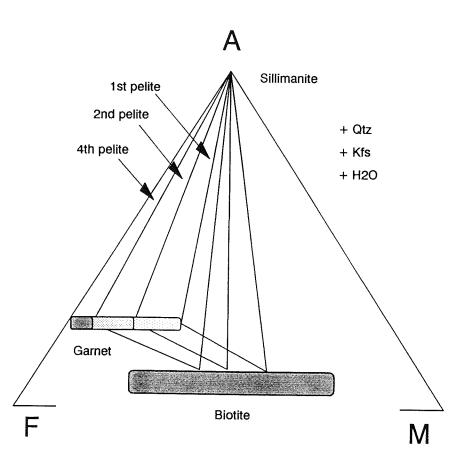


Figure 1.6 AFM projection, Sil+Kfs zone pelites. 1st pelite OS-56; 2nd pelite OS-43; 4th pelite OS-91. Mineral compositions taken from Lieberman (1988). Shaded mineral compositions are schematic.

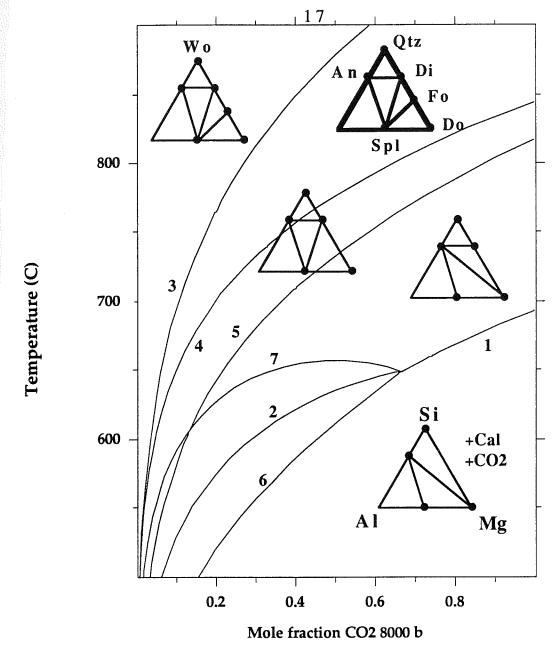


Figure 1.7 T-XCO₂ diagram, Kigluaik marbles. Calculated for the system Ca-Mg-Al-Si-C-O-H projected from calcite. Most peak metamorphic mineral assemblages sampled can be characterized by the bold compatibility triangle. Reaction stoichiometries are as follows:

- $\begin{array}{l} \text{Di} + 2 \text{ CO}_2 = 2 \text{ Qtz} + \text{Dol} \\ \text{H}_2\text{O} + 3 \text{ CO}_2 + 5 \text{ Di} = 3 \text{ Cal} + 2 \text{ Qtz} + \text{Tr} \\ \text{CO}_2 + \text{Wo} = \text{Cal} + \text{Qtz} \\ 4 \text{ Cal} + 2 \text{ Fo} + 2 \text{ CO}_2 = 3 \text{ Dol} + \text{Di} \\ 2 \text{ CO}_2 + \text{Spl} + \text{Di} + 2 \text{ Cal} = \text{An} + 2 \text{ Dol} \\ 7 \text{ CO}_2 + \text{Tr} + 3 \text{ Cal} = 5 \text{ Dol} + 8 \text{ Qtz} + \text{H}_2\text{O} \\ \text{H}_2\text{O} + \text{CO}_2 + \text{Dol} + 4 \text{ Di} = 3 \text{ Cal} + \text{Tr} \end{array}$ (A) (B) (C) (D) (E) (F) (G)

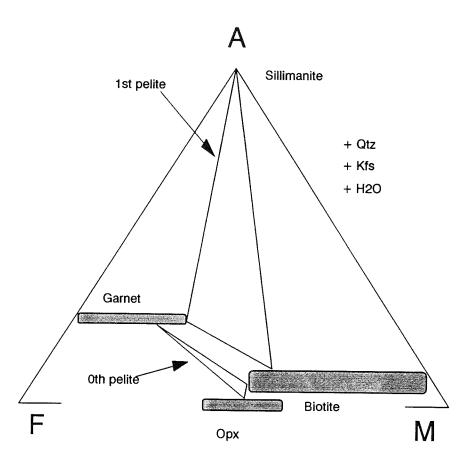


Figure 1.8 AFM projection, granulite grade pelites. Opx-bearing AB90-19.5; Silbearing OS-56. Shaded mineral compositions are schematic.

Chapter 2: Fluid-rock interaction at marble-gneiss contacts

Introduction

Stable isotopes have been used to constrain the fluid histories of metamorphic rocks (see review in Valley 1986). For the last several decades this has been limited to "box model" fluid-rock interaction and effects due to devolatilization. Recent work has applied the mathematical framework of fluid flow through porous media to constrain the flux of fluid through lithologic layers employing stable isotopes as tracers (Baumgartner and Rumble 1988, Bickle and McKenzie 1987, Bickle and Baker 1990a b, Blattner and Lassey 1989). The present work concentrates on using these techniques to quantify and identify the mode of cross-lithology transport of fluid in a well-exposed, amphibolite to granulite grade metamorphic terrane on the Seward Peninsula of Alaska. Here, thick, regionally extensive, flat-lying marble horizons, alternating with metasedimentary and meta-igneous rock types, provide an opportunity to investigate the role of lithology in determining the regional scale of fluid migration.

Analytical procedures

Microprobe analyses of minerals were carried out on a JEOL 733 Superprobe at the University of Washington, Department of Geological Sciences. Stable isotope analyses were carried out on a Finnigan Mat Delta E spectrometer at Department of Geosciences, New Mexico Tech, Socorro, NM. Methods used in collecting and normalizing the data, along with the data, are listed in appendices 2 and 3, respectively.

All thermodynamic calculations were carried out using Ge0calc software (Berman et al. 1987, Lieberman, pers. com.) using the data base of Berman (1988). Provisional data on annite and hedenbergite were also used (Berman, pers. com.) along with data on clinohumite (Rice 1980). Activities of end member mineral components

were calculated by Ge0calc software using the following models: garnet, Berman (1990); feldspars, Fuhrman and Lindsley (1988); biotite, McMullin et al. (1992); calcite in equilibrium with dolomite (Skippen 1974); and ideal multi-site activity models for spinel, forsterite, pyroxenes and clinohumite.

Descriptive and Analytical Data

Closely-spaced samples were collected on five traverses across contacts between the main marble and gneiss units. Sampling was perpendicular to layering, as much as possible. The samples were studied petrographically and subsequently analyzed for oxygen and carbon isotopes. These profiles yielded isotopic gradients sufficiently straight-forward to allow interpretations of fluid transport to be drawn, and have sample numbers AB89-41, AB89-61, AB90-13, AB89-62 and AB90-27 (Appendix 3).

AB89-41

At this contact (A in figures 1.2 and 1.4), a ~100 m thick, dolomitic marble subhorizontally overlies a ~15 m thick metasyenite/metamonzonite unit. The mineral assemblage in the metasyenite is: Hbl + Bt + Cpx + Pl + Kfs \pm Ilm \pm Grt with abundant and large accessory Ap, Zrn and Aln; Qtz is not present. The metasyenite is granoblastic, coarse-grained and moderately well foliated; it displays minor lithologic layering on the scale of meters. Whole-rock chemical analyses of three metasyenite samples are listed in table 2.1. Except at the contact (see below), the marble above the contact is homogeneous on the scale of cm; it is very coarse-grained (~0.5 cm) and composed of more than 90% Dol with minor Cal + Fo + Phl + Graph + Spl \pm Chu \pm Cpx. However, the lowermost 1.9 cm of the marble unit consists of more than 90% calcite + forsterite, with minor Dol + Spl + Phl + Graph (table 2.2). Calcite displays exsolution plates and rods of dolomite. Calcite-dolomite thermometry on a reintegrated Cal yields T ~650°C indicating that some whole-grain exsolution of Dol out of the Cal

occurred during retrogressive cooling, a common process in high grade marbles (Essene 1982). Mineral compositions are listed in Appendix 2.

The δ^{18} O composition of feldspar in the metasyenite ranges from 9.9 to 14.9‰. The marble far from the metasyenite retains sedimentary values of 23.0‰ δ^{18} O and -0.5‰ δ^{13} C. The calcite-forsterite zone is characterized by O and C isotopic values of 13.0‰ and -2.0‰, respectively. The transition in isotopic composition occurs within the dolomite marble over a distance of little more than 2 cm from the Cal+Fo zone (figures 2.1 and 2.2).

AB89-61

This is another flat-lying contact with marble overlying gneiss (B in figures 1.2 and 1.4). In this case the gneiss is a quartzofeldspathic rock consisting of equal amounts of Bt + Qtz + Pl with lesser amounts of Grt \pm Cpx \pm Kfs with accessory Ap and Tnt. The marble is compositionally variable on the scale of cm. Most samples consist of Cal, Dol, Cpx and Phl and, in addition, variable combinations of Fo, Spl, Pl and (late) Tr. There is generally much more Cal than Dol; silicates constitute 15-40% of the rock. Calcite displays exsolution lamellae and rods of dolomite.

Quartz δ^{18} O values are around 16‰, comparable to the composition of quartz near the base of this stratigraphic unit (figure 2.3). δ^{18} O of Cal varies in a regular fashion from 24.3‰ at about 7 m from the gneiss to 16.2‰ at 2 cm from the contact.

AB90-13

At this locality (C in figures 1.2 and 1.4), a flat-lying calcitic marble is overlain by a thick unit of relatively homogeneous Hbl-bearing quartzofeldspathic gneiss. The gneiss is coarse-grained and displays a moderate foliation defined by oriented mafic minerals. Except within 60 cm of the underlying marble, the assemblage in the gneiss is Hbl + Qtz + Pl + Bt with accessory $Ap + Zrn + Aln \pm Ilm$. Within 60 cm of the marble

Hbl is no longer present; instead, the assemblage is: $Cpx + Opx + Kfs \pm Grt$. Both pyroxenes are fine grained (0.1 mm diameter) and granular. Garnet is embayed and in places surrounded by Pl + Opx symplectite. In the two-pyroxene zone, large plagioclase crystals are antiperthitic. In a narrow transition zone Hbl, Cpx and Opx coexist. Details regarding the mineralogical relationships at this outcrop are covered in chapter 3. The marble is coarse-grained and granoblastic and contains varying amounts of Phl, Cpx, Scp or Pl, Kfs and late Tr.

Figure 2.4 shows δ^{18} O analyses of calcite in the marble and quartz, hornblende and biotite in the gneiss. Calcite away from the gneiss retains sedimentary values of δ^{18} O and δ^{13} C. Within 50 cm of the gneiss, δ^{18} O values of Cal are slightly lowered. In the hornblende zone quartz, hornblende and biotite display constant δ^{18} O values of 15, 12 and 8‰ respectively. In the two-pyroxene zone quartz values increase slightly to 16.0‰; biotite has a variable isotope composition increasing from 7.0 to 12.0‰ towards the contact with marble, which may be attributed to late alteration due to the ease with which biotite resets (Schwarcz et al. 1970).

AB89-62 and AB90-27

Both of these outcrops are at the base of the Main Marble unit (D in figures 1.2 and 1.4) within 0.5 km of each other. At this horizon, calcitic marble overlies mixed metasedimentary rocks. The metasedimentary rocks consist of graphitic pelite (Qtz + Bt + Pl + Sil + Graph + Grt \pm Kfs), biotite schist (Qtz + Bt + Pl \pm Graph \pm Kfs), and calcilicate (Cal + Cpx + Ttn + Pl + Qtz \pm Scp \pm Graph) alternating in layers ranging in thicknesses from a few cm to m. The assemblage in the marble is Cal + Dol + Fo + Phl \pm Graph; there is some variability in relative proportions of the minerals. Figure 2.5 compiles data from both outcrops and shows the δ^{18} O composition of Cal in marble and Qtz in schist as a function of perpendicular distance from the base of the marble (note

that the quartz values represented in the figure have been lowered by 0.33% so as to represent calcite which would have been in equilibrium with the quartz at 800° C (Clayton et al. 1989)). The interior of the marble unit retains sedimentary values of 22.6% and is isotopically quite homogeneous. Within about 5 m of the contact, δ^{18} O is lowered more than 3.5%. The isotopic composition of the quartzofeldspathic rocks is somewhat variable, with δ^{18} O ranging from 19.0 to 20.2%.

Interpretation of Data

Baumgartner and Rumble (1988) showed that a change in isotopic composition of a rock caused by diffusive and infiltrative processes results, as time progresses, in distinctive patterns on plots of $\delta^{13}C$ vs $\delta^{18}O$. Diffusion-dominated processes produce a relatively straight-line diagonal trend on plots of $\delta^{13}C$ vs $\delta^{18}O$, relatively independent of the XCO₂ of the fluid. Processes involving advection of material via an H₂O-CO₂ fluid show curved or box-like patterns on plots of $\delta^{13}C$ vs $\delta^{18}O$. Additional complexities can arise if local equilibrium is not maintained (Blattner and Lassey 1989), but, during the time-scale of regional metamorphism, local equilibrium may be assumed. The interior parts of main marble layers in all outcrops show $\delta^{18}\mathrm{O}$ in the mid to low 21.4 to 24.3 and $\delta^{13} C$ approximately zero (figure 2.6), appropriate for unaltered high grade marbles (Valley 1986). The convergence of stable isotope ratios from all marble horizons to these values lends support to the conclusion that the interior of marble layers have not been changed since their formation. Both carbon and oxygen isotope compositions are low near contacts with other lithologies. The oxygen isotope composition of fluid in equilibrium with the adjoining lithologies can be presumed to have been somewhere between ~9% (igneous) and ~17% (pelitic). The marbles show varying amounts of oxygen isotope exchange with such a fluid. Unfortunately, the carbon isotope composition of the interacting fluid is less constrained. The linear variation of $\delta^{18} O$ and

 δ^{13} C suggests principally diffusive interaction rather than combined diffusive-advective interaction between the main marble units and their adjoining lithologies. The oxygen isotope composition toward which marble margins trend is controlled by the composition of the adjacent lithology. In the cases where the adjacent lithology is clearly sedimentary (AB89-62, AB90-27), δ^{18} O is lowered less than in the case where the adjacent lithology is clearly igneous (AB89-41). Infiltration of an external pervasive fluid would have homogenized isotopic compositions in gneissic units. But gneisses retain the protolith signature of oxygen isotopic composition indicating that a pervasive fluid did not homogenize the isotopic composition of the rocks.

AB89-41

The uniform, SiO_2 -poor mineralogic composition of the marble beyond the thin Cal+Fo zone at this contact suggests that the Cal+Fo zone was formed by chemical interaction between the metadolomite and the metasyenite. By influx of silica, calcite and forsterite can be produced from dolomite by the reaction:

$$2 \text{ Dol} + \text{SiO}_2 \text{ (dissolved)} \rightarrow 2 \text{ Cal} + \text{Fo} + 2 \text{ CO}_2.$$
 (1)

The growth of the Cal+Fo zone through the introduction of SiO₂ is strongly supported by the results of modal analyses; calcite and forsterite are present almost exactly in the required molar ratio 2:1 (table 2.2). In reaction (1), SiO₂ is added to the metadolomite via a fluid and the activity of silica is necessarily less than 1 (quartz standard state). Depending on silica activity, reaction (1) is not stable under all fluid compositions (figure 2.7). The reaction from dolomite to calcite + forsterite *could* have been driven by an increase in silica activity and/or a decrease in CO₂ activity, presumably by dilution with H₂O (or CH₄?). Reaction (1) is univariant at constant P and T and puts limits on either aSiO₂ or aCO₂. Since about 15 wt% silica was added to the metadolomite to form forsterite and because aSiO₂ in the syenite was much greater than aSiO₂ in the

metadolomite (see below), it is reasonable to infer that the reaction was not only accompanied by SiO₂ influx, but actually driven by an increase in aSiO₂. The proposed path followed by fluid in the Cal+Fo zone is indicated on the diagram. The metadolomite started at a low value of aSiO₂, in equilibrium with Fo, Cal and Chu. With an increase in silica activity, CO₂ was produced, increasing the activity of CO₂. The fluid was buffered along the reaction curve until the fluid was pure CO₂. The system remained at these conditions until all the Dol was exhausted by reaction with silica. Then aSiO₂ could increase into the Cal+Fo field. The activity of SiO₂ never reached the diopside-forming reaction (except in one late cross-cutting vein).

Although the metasyenite was undersaturated in silica (no quartz is present in the gneiss), the phases present in the rock define a silica activity. As long as the silica activity was higher in the metasyenite than in the metadolomite, silica would move down its chemical potential gradient from the gneiss into the marble. The silica activity in the metasyenite can be defined by the reaction:

$$3 \text{ an} + 3 \text{ di} = \text{prp} + 2 \text{ grs} + 3 \text{ SiO}_2$$
 (2)

and the equivalent Fe end member reaction:

$$3 \text{ an} + 3 \text{ hd} = \text{alm} + 2 \text{ grs} + 3 \text{ SiO}_2.$$
 (3)

These reactions are shown in P-T space in figure 2.8, adjusted for the mineral compositions in a sample 33 cm from the contact. The intersection of reactions (2) and (3) defines a Grt-Cpx Fe-Mg exchange equilibration temperature, 825°C, which agrees satisfactorily with previous estimates from this area (Lieberman 1988; Lieberman and Petrakakis 1992). For pressures of 7.5 to 8 kbar, the silica activity is about 0.8; this is higher than in any Dol-bearing assemblage (see figure 2.7). Therefore silica would move from the gneiss into the marble. Even though all the silica in reaction (1) was added to the system via a fluid, there was still an 8% volume decrease of solids, due to a

density increase and loss of CO₂. Therefore, the reaction was not inhibited by volume constraints.

The data indicate extensive stable isotope interaction between the Cal+Fo zone and the metasyenite. Rayleigh distillation during decarbonation according to reaction (1) can account for the carbon isotope depletion, and some, but not all, of the observed oxygen isotope depletion (figure 2.9). The remaining oxygen isotope depletion can be attributed to interaction with the gneiss. The vehicle of such interaction can be ascribed to a fluid. The composition of this fluid can be examined using mineral equilibria. The H₂O activity in the syenite as defined by biotite dehydration reactions was about 0.2 (figure 2.10). At these high temperatures, fluids mix almost ideally, so, if a fluid was present, $XH_2O = 0.2$. The other constituents of the fluid would presumably have been either CO₂ or CH₄. However, the carbon isotopic composition of the Cal+Fo zone was not changed beyond that attributed to Rayleigh distillation. Therefore, it is unlikely that any upward infiltrating fluid was carbon-bearing, except in the unlikely case that the δ^{13} C composition of the fluid was in exact equilibrium with the calcite of the Cal+Fo zone. A more reasonable interpretation is that the pore spaces of the metasyenite were unsaturated in fluid and that isotopic interaction between the metasyenite and the Cal+Fo zone occurred through the CO2 that was forced downwards, away from the Cal+Fo reaction front. In a similar manner, silica was transported from the metasyenite to the Cal+Fo reaction front by diffusion against the flow of CO₂ evolving from the reaction. Unfortunately, little is known about the diffusion rate of silica in C-O-H fluids of any composition. Silica has a very low solubility in CO₂ fluid (Walther and Orville 1983). This may have been the cause of the very limited (2 cm) extent of silica influx into the metadolomite. A flux of less than 1 g SiO₂/cm² from the gneiss into the marble occurred during the course of the entire metamorphic cycle.

The metadolomite at 2-4 cm from the syenite contact contains 99% carbonate + graphite (table 2.2). Therefore, the depletion of $\delta^{18}O$ and $\delta^{13}C$ in this zone could not be the result of devolatilization. The isotopic change most likely occurred by advectivediffusive transport. Since the Cal+Fo zone shows, within error, no gradient in $\delta^{18}O$ or δ^{13} C, it is assumed that interaction with the metasyenite kept the isotopic composition of calcite in the Cal+Fo zone at 13% and -2.2%, respectively. The equations developed by Bickle and McKenzie (1987) for one-dimensional, combined advective-diffusive transport can be employed to quantitatively estimate the extent of fluid advection up into (or away from) the metadolomite. A moving reference frame is adopted here, where the origin is set at the interface between the Dol zone and the Cal+Fo zone; the positive direction is up. In this convention, as the Cal+Fo reaction progresses into the metadolomite the rock body is moving down with respect to the coordinate system, and hence has a negative velocity. The fits to the $\delta^{18}O$ and $\delta^{13}C$ data (figure 2.2) were determined by minimizing the quantity $\sum ((p-x)/\sigma)^2$ (Bickle and Baker 1990a); p is the predicted value of isotope composition, \boldsymbol{x} is the measured value and $\boldsymbol{\sigma}$ is the error of the measurement. For this data set, the best fit is obtained when downward directed velocity is used. The isotopic composition of Cal was adjusted to represent Dol in equilibrium with the measured Cal at 800°C; 0.2 was added to $\delta^{18}\text{O}$ values of Cal (Sheppard and Schwarcz 1970; Northrop and Clayton 1966), and 0.33 was added to δ^{13} C values of Cal (Sheppard and Schwarcz 1970).

Equation (26) from Bickle and McKenzie (1987) calculates the change in isotopic composition in terms of the Peclet number, non-dimensional time, composition at the boundary (C_f), and the original composition of the lithology (C_o). The Peclet number is defined as w ϕ L/D, and is a measure of the relative importance of advection vs. diffusion in transporting the material; w is the vertical velocity of the fluid, L is a

characteristic length scale, D is the effective diffusion coefficient of the isotope, and ϕ is porosity. For transport by a fluid in a porous medium D is taken as ϕD_{fluid} . D_{fluid} is assumed to be 10^{-8} m²s⁻¹, independent of temperature (Rubie 1986; Bickle and McKenzie 1987). Non-dimensional time is approximately $(Dt/L^2)(\rho_f/\rho_s K_d)$; t is time, ρ_f is the density of the fluid (~1 g/cm³ at 800°C, 8 kbar), ρ_s is the density of the solid (~2.8 g/cm³), and K_d is the solid-fluid partition coefficient (0.55, Cartwright and Valley 1991). For this outcrop, C_0 =-1.9, C_f =-0.3 for $\delta^{13}C$; C_0 =13.2, C_f =23.2 for $\delta^{18}O$; L=1 m.

The fits to the data are listed in table 2.3. The fact that a downward directed velocity best fits the data indicates that the Cal+Fo reaction encroached into the metadolomite faster than O and C advected into the metadolomite. The fit for nondimensional time can be rearranged to yield an estimate of porosity (Bickle and Baker 1990a). For time scales >1 Ma the derived porosities are around 10⁻¹⁰ or less, questionably low to have sustained transport of stable isotopes over millions of years. A more likely possibility is that no fluid was present in the dolomite zone and that isotope transport occurred by lattice diffusion through the Dol crystals. In this case the $(\rho_f/\rho_s K_d)$ term of non-dimensional time is unity. For the same time scale as above, the derived diffusion coefficients for oxygen and carbon isotopes in Dol must be < 3 X $10^{-18} \,\mathrm{m^2 s^{-1}}$ and $< 1 \,\mathrm{X} \,10^{-18} \,\mathrm{m^2 s^{-1}}$, respectively. These estimates agree very well with those measured on Dol by Anderson (1972) under dry conditions at 800°C. The presence of fluid is known to enhance crystalline diffusion rates (Sharp 1991). Measurements of oxygen diffusion rates in calcite increase 2 to 3 orders of magnitude under vapor saturated compared to dry conditions (Anderson 1969; Kronenberg et al. 1984). The fact that diffusion rates in the dolomite zone were no more than $10^{-18} \text{ m}^2\text{s}^{-1}$ further supports the conclusion that there was no fluid present in the dolomite zone.

Similar arguments were used by Baker (1990) to imply the absence of grain-boundary fluids for extended time periods during the metamorphism of lower crustal rock in the Ivrea Zone, Italy.

Bickle and Baker (1990a) showed that an estimate of time-integrated flux can be calculated from the derived values of Peclet number and non-dimensional time. For this outcrop, where no fluid is present, flux represents the downward movement of the metadolomite towards the Cal+Fo reaction boundary, or can be thought of as the amount of dolomite that reacted to form Cal+Fo. The measured thickness of the Cal+Fo zone is 1.9 cm. Accounting for the 8% volume loss of the reaction, 2.0 cm of metadolomite have been converted to Cal+Fo. The flux calculations derived from oxygen and carbon isotope data are 0.0065 and 0.0026 m³/m², respectively, or 0.65 and 0.26 cm of metadolomite consumed; these estimates are consistent within an order of magnitude of the observed 2.0 cm metadolomite consumed.

AB89-61

At outcrop AB89-61 the zone of isotopic lowering in the marble is more than two orders of magnitude wider than at AB89-41 (compare figures 2.2 and 2.3). Since pressure, temperature and time of metamorphism were the same for both outcrops, clearly there must have been a significant difference in fluid conditions between the two. In order to fit an infiltration model to the data as previously described, 0.33 was subtracted from the measured quartz values of δ^{18} O to represent calcite that would have been in equilibrium with the quartz at 800°C (Clayton et al. 1989). For this outcrop the pinned boundary equation of Bickle and Baker (1990a) is used, with the boundary fixed at the marble-gneiss contact. For this outcrop, L=1000 m, C₀=15.8, C_f=24.1. The results of the fit are given in table 2.3 and shown in figure 2.3. As with AB89-41, the best fit is obtained when a downward directed velocity is used. The boundary at this

outcrop is not moving relative to the rock body, therefore the parameter fits indicate downward movement of fluid. The quantity of fluid calculated as the time integrated flux is $-.0085 \, \text{m}^3/\text{m}^2$, i.e. about 1 cm of fluid per cm² was forced out the bottom of the marble. The porosity estimate for a time scale >1 Ma is < $5.4 \, \text{X} \, 10^{-6}$. If the interior part of a thick marble layer is essentially impermeable, then it is not unreasonable to conclude that any fluid generated internally near the bottom of the marble would be forced down, out of the marble.

AB90-13

At this outcrop there are indications of interaction on both sides of the lithologic contact. Analysis by singular value decomposition (Fisher 1989) indicates that the two pyroxene zone was formed by dehydration of the amphibole-bearing gneiss (more details in chapter 3). Since no significant pressure or temperature gradients could have existed during this process, the reaction must have been driven by a change in fluid composition to lower aH₂O, presumably by dilution with CO₂ from the underlying marble. The length-scale of this fluid interaction into the gneiss is 60 cm. The inflection point in the steep stable isotope gradient between gneiss and marble occurs at the lithologic contact. This observation indicates that transport was dominated by diffusion, otherwise this inflection point would have been moved into the downstream rock by the advecting fluid (Ganor et al. 1989). The oxygen isotope length-scale of interaction in the marble is about 50 cm. Since length-scales of interaction are almost identical on both sides of the boundary, transport dominated by diffusion, not advection, is indicated (Bickle and McKenzie 1987).

AB89-62 and AB90-27

The lithologic variation at this stratigraphic level (base of the main marble) is more extensive in the vicinity of the marble contact than at other outcrops described

here, making modeling of isotopic variation more complex. However, the interior of the marble unit retains sedimentary $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ compositions, indicating little interaction with external fluids. As at AB90-13, a steep isotopic gradient exists at the lithologic boundary, indicating a diffusion-dominated transport process at the lower contact of the marble. The extent of isotopic depletion in the marble is similar to that at AB89-61.

Conclusions

The steep isotopic gradients found at all lithologic contacts described in this chapter preclude the infiltration of large quantities of fluid across the main marble, otherwise the isotopic step in composition would have been propagated into the downstream lithology (Ganor et al. 1989). The main marble acted as an effective aquitard to cross lithology fluid flow, as has been found for marbles in other terranes (Rye et al. 1976, Nabelek et al. 1984, Ferry 1989). The gradient is so steep at AB89-41 that a pervasive, interconnected fluid must never have been present. The isotopic interaction between lithologic layers is dominated by diffusive processes. The amount of this diffusive interaction is related to the bulk composition of the marble. Pure carbonate marbles underwent little devolatilization, and therefore developed no porosity through which interaction could have occurred. Impure marbles underwent devolatilization reactions during the development of silicate minerals such as diopside and forsterite. This lead to the development of interconnected porosity, allowing isotopic interaction via a fluid. The implications of this study are that fluid was only present in marbles during transient devolatilization events. In addition, the lack of isotopic homogeneity between different gneissic units indicates that large amounts of fluid have not interacted with these layers.

3 2
Whole-rock composition of metasyenites

v.	AB90-3.1	AB90-40.2	AB90-40.3
SiO ₂	53.75	56.66	55.94
TiO ₂	0.89	0.40	0.26
Al ₂ O ₃	18.88	18.56	17.08
Cr ₂ O ₃	0.02	0.03	0.02
Fe ₂ O ₃	7.65	7.60	9.27
MnO	0.11	0.24	0.50
MgO	2.00	1.01	1.00
CaO	4.44	3.31	3.56
BaO	0.17	0.04	0.03
SrO	0.09	0.03	0.03
Na ₂ O	3.40	3.51	1.94
K ₂ O	6.83	7.51	8.42
P_2O_5	1	1	1
LOI	0.29	0,32	0.22
Sum	99.52	100.22	99.27

Table 2.1

Table 2.2 Modal analyses of marbles

	Cal	Dol	_ Fo	Chu	Spl	Phl	Graph	Di	points
AB89-41	Mo	ole%			_				
Cal+Fo	65.1	5.9	28.8	0.0	0.2	0.0	0.0	0.0	3193
Dol	5.8	90.4	0.0	0.1	0.5	0.3	2.9	0.0	3340
AB89-61	Ap	proxima	ate Area	$\mathfrak{l}\%$					
<u>cm</u>									
2.5	75							2 5	
9	75					5		25	
11	5 5	10	3 5						
15	65	5				10		20	
33	5	90				5			
41	5 5	20	20			5			
53	80							20	
7 1	60					5		3 5	
94	65	10	20			5			
102	50	10	30			10			
107	60	10	5			10		1 5	
135	100								
366	50	3 5	5			5		5	
671	85	5						10	

Table 2.3 Fit parameters for stable isotope gradients

	C_{0}	$C_{\mathbf{f}}$	Pec	t'	L(m)
AB89-41 ¹⁸ O	13.2	23.2	66	9.9 X 10 ⁻⁵	1
AB89-41 ¹³ C	-1.9	-0.3	62	4.2 X 10 ⁻⁵	1
AB89-61 ¹⁸ O	15.8	24.1	5	1.1 X 10 ⁻⁶	1000

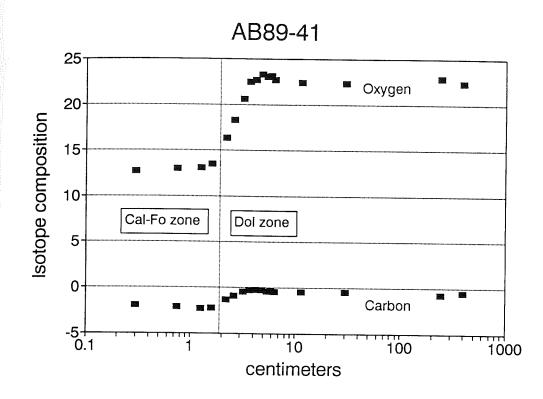
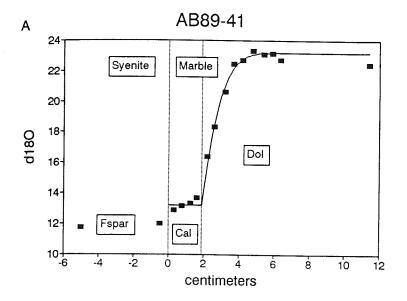


Figure 2.1 Stable isotope composition, AB89-41 marble. Metasyenite contact is at 0.0 cm; note logarithmic scale for horizontal axis.



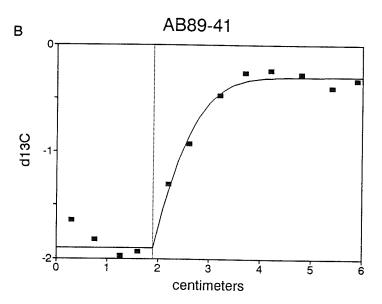


Figure 2.2 Fit through stable isotope data, AB89-41. Calcite and feldspar compositions have been adjusted to represent the composition dolomite would have in equilibrium with the measured value at 800°C.

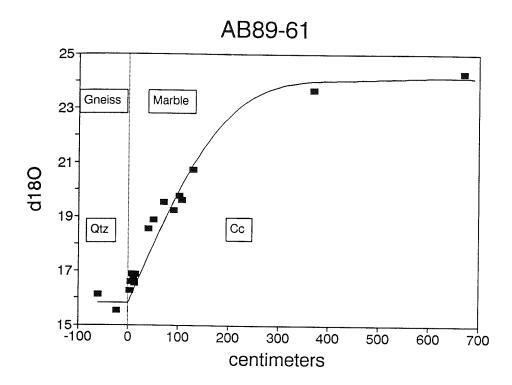


Figure 2.3 Fit through oxygen isotope data, AB89-61. Qtz values have been adjusted to represent Cal in equilibrium with the measured Qtz values at 800°C.

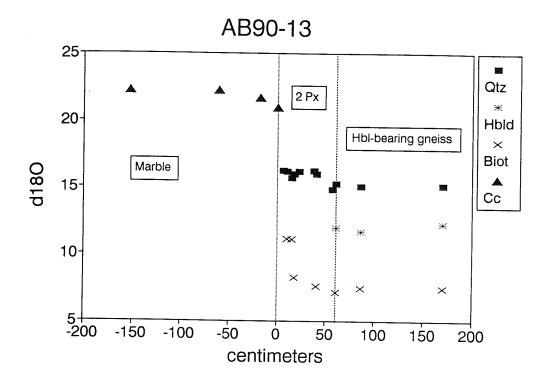


Figure 2.4 Stable isotope data, AB90-13.

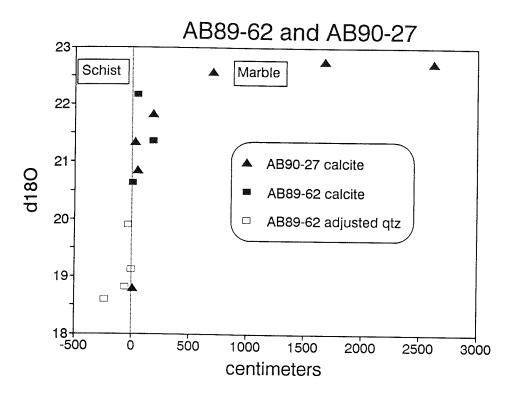


Figure 2.5 Stable isotope data, AB89-62 and AB90-27. Qtz values have been adjusted to represent Cal in equilibrium with the measured Qtz values at 800°C.

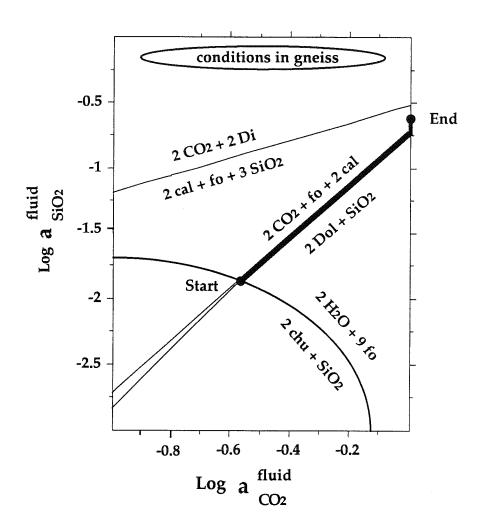


Figure 2.7 Log aSiO₂ vs. log aCO₂, AB89-41 marble. Thick line shows proposed buffering path followed by fluid in Cal+Fo zone. See text for details.

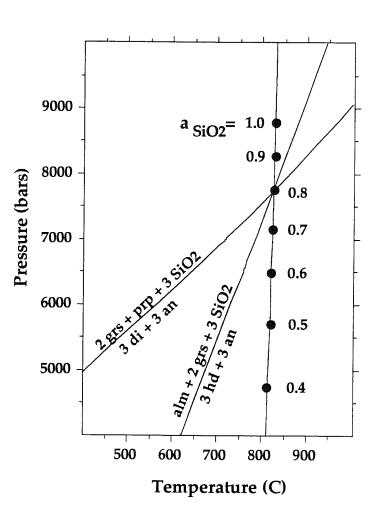


Figure 2.8 Activity of SiO₂, AB89-41 metasyenite. Equilibria involving Grt, Cpx, Pl for a sample 33 cm below the marble. The vertical line represents the reaction: alm + 3 di = prp + 3 hd. The intersection near 8000 bars is obtained when aSiO₂ is set to 0.8. The large dots show the location of the intersection at other values of silica activity.

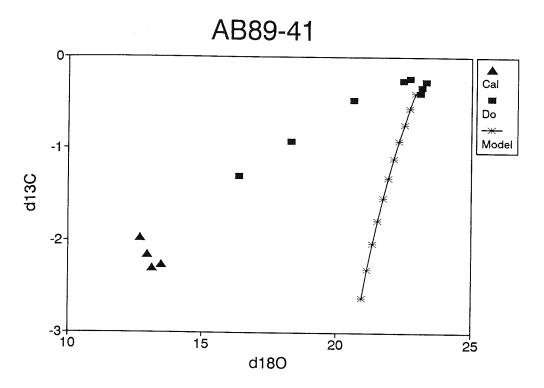


Figure 2.9 δ^{13} C vs. δ^{18} O, AB89-41. Thick line shows the path followed by calcite during the reaction 2Dol + SiO₂ = 2Cal + Fo + 2CO₂ following the method of Rumble (1982). For calculation, Dol starts at -0.2% δ^{13} C and 23% δ^{18} O, SiO₂ is 12% δ^{18} O. Fractionation factors taken from Sheppard and Schwarcz (1970) and Northrop and Clayton (1966). Tick marks indicate 10% reaction toward completion.

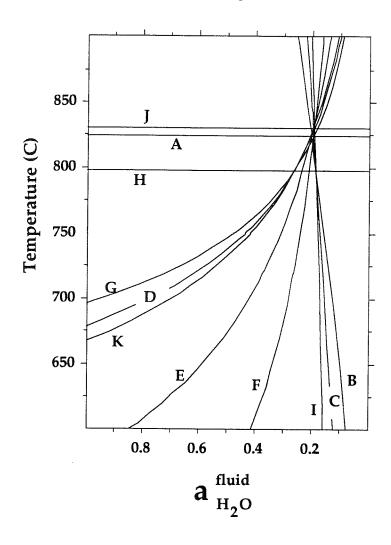


Figure 2.10 T-aH₂O, AB89-41 metasyenite. Diagram calculated at 8 kbar for equilibria involving Grt, Cpx, Bt, Pl and Kfs indicating H₂O activity ~0.2. Qtz is not involved in any reaction. It can be noted that reactions D, E, F, G and K are prograde hydration reactions.

- (A)
- (B)
- (C)
- (D)
- (E)(F)
- prp + 3 hd = alm + 3 di 2 H₂O + 3 prp + 2 kfs + 6 hd + 3 grs = 2 ann + 6 an + 9 di 2 H₂O + 3 prp + 2 kfs + 3 grs = 6 an + 3 di + 2 phl 2 ann + 6 an + 3 hd = 2 H₂O + 2 kfs + 3 grs + 3 alm 2 ann + 6 an + 3 di = 2 H₂O + prp + 2 kfs + 3 grs + 2 alm 6 an + 3 hd + 2 phl = 2 H₂O + 2 prp + 2 kfs + 3 grs + alm 6 an + 9 hd + 2 phl = 2 H₂O + 2 kfs + 3 grs + 6 di + 3 alm phl + 3 hd = ann + 3 di 2 H₂O + 3 prp + 2 kfs + 3 grs + ann = 6 an + 3 hd + 3 phl prp + ann = alm + phl 3 ann + 6 an + 3 di = 2 H₂O + 2 kfs + phl + 3 grs + 3 alm (G)
- (H)
- (I)
- (J)
- (K)

Chapter 3: Localized fluid-controlled granulite grade assemblage Introduction

One of the characteristic changes in mineral paragenesis from amphibolite to granulite grade metamorphic rocks is the disappearance or decline of hornblende coincident with the appearance of orthopyroxene alongside clinopyroxene in mafic rocks. Where this occurs, it has in many cases been ascribed to a reduction in H₂O activity due to dilution with CO₂ (Touret 1985, Hansen 1984, Bradshaw 1989, Harris and Bickle 1989, Santosh et al. 1990, Pattison 1991). Among possible sources of CO₂ is one that has received little attention, namely CO₂ evolved from carbonate metasediments (Glassley 1983, Glassley et al. 1989). This is because many granulite terranes contain little carbonate material. In this chapter I present a field example which clearly shows the association of a CO₂-evolving marble and localized progress of amphibolite to granulite dehydration reactions. It is a local phenomenon superimposed on the temperature rise which is responsible for the regional granulite facies assemblages found in the Kigluaik Mountains.

Outcrop Description

The lowermost member of the main marble unit consists mostly of a calcite and forsterite dominated marble, but has some variability, especially towards the top, where it is a calcite-diopside marble. It is overlain by a 100 m thick unit of relatively homogeneous Hbl-bearing quartzofeldspathic gneiss. Detailed sampling of the marble-gneiss contact has revealed that the lowermost 60 cm of the gneiss, instead of containing homblende, contains orthopyroxene and clinopyroxene (figure 3.1). The outcrop described in this paper is located in the north wall of the east cirque of Mount Osborn (C in figure 2.1).

Diopside and phlogopite are the major silicate phases in the coarse-grained (0.5 mm) granoblastic marble near the gneiss contact; plagioclase, scapolite and orthoclase are also present in small quantities. Dolomite is rare or absent, and when present is fine grained and interstitial which suggests it may represent exsolution from calcite upon cooling. Late tremolite formed at the expense of diopside in some samples. The gneiss is coarse-grained (0.5 mm) and displays a moderate foliation defined by oriented mafic minerals. The typical gneiss is composed of 35% plagioclase, 30% hornblende, 20% quartz, 15% biotite (figure 3.1) and accessory apatite, zircon, allanite. Its homogeneity on the outcrop scale suggests that the protolith might have been an igneous rock.

Within 60 cm of the underlying marble, hornblende is no longer present.

Instead the gneiss contains 40% feldspar (mostly plagioclase), 25% quartz, 20% biotite and 15% pyroxenes, with ilmenite as an additional accessory phase. In one sample (17 cm from the marble), garnet is present and clinopyroxene is absent. Both pyroxenes are fine grained (0.1 mm diameter) and granular and do not clearly form pseudomorphs after Hbl (mineral abbreviations in table 1.1). Garnet is embayed and in some cases is surrounded by Pl + Opx symplectite. Plagioclase crystals display a range of grain sizes from 0.1 to 1.0 mm; some of the large crystals are antiperthitic. In a narrow transition zone Hbl, Cpx and Opx coexist.

Mineral Compositions

The following section describes the compositions of minerals in selected samples from the Hbl-bearing gneiss, Hbl-free gneiss, and the transition between the two.

Mineral compositions are listed in appendix 2.

Hornblende

The amphibole in the Hbl-bearing gneiss is green and pleochroic (X pale green, Y green, Z dark brown-green). Its composition falls in the range of ferroan pargasitic

hornblende, bordering on ferroan ferri-pargasitic hornblende (names from Leake, 1978); amounts of exchange components are (Thompson 1982a, Dymek 1983): X_{tk} (Mg_1Si_1 AlAl) ≈ 1.13 , X_{ed} (\square _1Si_1 NaAl) ≈ 0.54 , X_{tispl} (Al_2 MgTi) ≈ 0.17 , X_{ab} (Ca_1Al_1 NaSi) ≈ 0.10 . No compositional zoning is observed within individual grains, and there is little inter-sample variation (figure 3.2). In a sample from the transition zone, the amphibole composition is more variable and less aluminous than that of the Hbl-bearing gneiss, ranging through edenitic hornblende to magnesio-hornblende (figure 3.2); $X_{tk} = 0.77$, $X_{ed} = 0.25$, $X_{tispl} = 0.07$, $X_{ab} = 0.12$. In one sample from the Hbl-free gneiss (15 cm from the marble) a small brown amphibole grain was found. It is not an inclusion, but occurs between a quartz and feldspar grain. The composition of this amphibole overlaps with that of the Hbl-bearing gneiss when plotted on figure 3.2, but differs significantly in Ti content (see appendix 2); $X_{tk} = 1.13$, $X_{ed} = 0.55$, $X_{tispl} = 0.42$, $X_{ab} = 0.16$. The appropriate name is titanian ferroan pargasitic hornblende.

Feldspars

In the Hbl-bearing gneiss plagioclase is not zoned, but varies from An₄₂ to An₄₉ from sample to sample. The orthoclase component is always less than 3% and no antiperthite is visible microscopically. In the Hbl-free gneiss feldspar compositions are more complex, with plagioclase ranging in composition from An₄₈ to An₇₆ (figure 3.3). The gap in feldspar composition from An₅₉ to An₆₅ is an artifact of sampling. Orthoclase component remains below 3%. None of the more anorthitic feldspars are antiperthitic and they are commonly no more than 0.1 mm in diameter. They are typically found in a mass of biotite and pyroxene grains. Some large (1 mm) more albitic plagioclase grains are antiperthitic.

In the Hbl-free gneiss Kfs is present in three forms: (i) as rims separating quartz from plagioclase (figure 3.4a); (ii) as separate grains; (iii) in antiperthite (figure 3.4b, c,

d). Only large plagioclase grains, but not all of them, are antiperthitic. The host composition is usually about An₅₂, slightly more anorthitic than Pl in the Hbl-bearing gneiss. The Kfs guest composition is ~Or90-Ab9-An1. Results of two-feldspar thermometry on host and guest compositions using MTHERM3 (Fuhrman and Lindsley 1988) yield T=~600°C, indicating that the host and lamellae reequilibrated upon cooling. A microprobe linescan across several Kfs guests within a Pl host shows no consistent enrichment or depletion of plagioclase components adjacent to the Kfs blebs (figure 3.5). An increase in anorthite component approaching a Kfs bleb has been taken to indicate formation of antiperthite from a previously homogeneous feldspar (Kay, 1977). However, the spacing of Kfs lamellae in the present case (~20 µm) may be too small to manifest the build-up. The reintegrated composition of one typical antiperthite grain (25% Or, 34% Ab, 41% An; figures 3.4d and 3.6) lies well within the two-feldspar field at 800°C. This indicates that antiperthite formation was not caused by exsolution from a previously homogeneous feldspar, but must have occurred by some sort of replacement process (e.g. Griffin 1968). The geometry of some Kfs blebs within plagioclases, such as figure 3.4d, rules out Kfs growth along cracks, fractures or cleavages.

Other Mafic Minerals

Biotite Mg# varies from sample to sample from 0.53 to 0.65 in an unsystematic way. In vector component notation (Thompson, 1982a; Dymek, 1983) X_{tk} remains constant at about 0.25 as does X_{tlc} ($K_{-1}Al_{-1}$ $\square Si$) at about 0.05, but X_{tispl} and X_{dioct} (Mg-3 Al₂ \square) increase somewhat from the Hbl-bearing gneiss to the Hbl-free gneiss (0.20 to 0.41 and 0.10 to 0.25, respectively). X_{tispl} and X_{dioct} are highly positively correlated among the 6 analyses, suggesting that the Ti substitution occurring in these

biotites may be Mg₋₂ Ti . Fluorine contents are low and show no variation with distance from the marble.

Mineral analyses of pyroxenes and garnet are listed in appendix 2. The low Ca content of Opx from 18 cm is due to the fact that it does not coexist with Cpx; instead, garnet is present. The garnet composition is: $X_{alm} = 0.55$, $X_{prp} = 0.25$, $X_{sps} = 0.05$, $X_{grs} = 0.15$. For the two samples analyzed where Opx and Cpx coexist, the two-pyroxene solvus thermometer (Lindsley 1983) yields approximately 800°C, in agreement with previous estimates from the field area (Lieberman 1988, Lieberman and Petrakakis 1992).

Mineral reactions

The two mineral assemblages present in the gneiss, $Hbl + An_{50} + Qtz + Bt$ and $Opx + Cpx + (up to) An_{76} + Qtz + Kfs + Bt$, could be the result of similar environmental conditions (P, T, aH_2O) affecting slightly different bulk rock compositions, or the metamorphism of the same bulk composition under differing environmental conditions. In order to distinguish between these two possibilities (Greenwood, 1967) the mineral assemblages were analyzed by matrix methods.

The programs written by Fisher (1989) utilizing singular value decomposition were employed in order to look for possible reaction relationships between the two assemblages. The sample from 86 cm represents the Hbl-bearing assemblage, whereas the 15 cm sample represents the Hbl-free assemblage with the exception of biotite. A single composition of biotite was used in the analysis.

The data input and output for the analysis are listed in table 3.1. Ilmenite is a minor phase and has not been quantitatively analyzed; it is listed as a pure Feendmember component. Although An₇₆ is the most extreme composition found in the thin section analyzed, more anorthitic plagioclase may exist. In order to account for the

anorthitic plagioclase in the Hbl-free gneiss, end-member anorthite is listed as a phase. Orthoclase is also listed as the pure end-member phase. As recommended by Fisher, Si and H were omitted from the calculation because they can be balanced later by quartz and water. Goodness of fit as evaluated by examining the ratio {(data minus model) / error}, ideally less than one, is acceptably small in most cases. Although 11 (19%) of the residuals are greater than one, seven of them are minor components in the mineral and therefore not critical.

Two reaction relationships were found among the minerals present in the two assemblages (table 3.1). Since the most obvious feature of this outcrop is the appearance of pyroxenes, the equations were normalized to produce one mole of Opx.

Quartz and H₂O stoichiometries were calculated using the original mineral compositions.

Discussion

Reaction (B) listed in table 3.1 is consistent with modal changes at this outcrop. It consumes Bt, Hbl and Qtz and produces feldspars and both pyroxenes. In contrast, reaction (A) consumes Cpx and anorthite component and produces Hbl along with Opx! However, these reactions can be linearly combined in order to isolate a reaction that consumes Hbl and one that consumes Bt. These are:

$$Hbl + 1.96 Qtz =$$

$$1.22 Cpx + 1.47 Opx + 1.01 An63 + 0.26 Kfs + 0.26 Ilm + H2O$$

$$Bt + 2.59 Qtz + 0.18 Cpx =$$

$$1.32 Opx + 0.16 An89 + 0.93 Kfs + 0.20 Ilm + H2O.$$
(2)

For each reaction, the two plagioclases have been combined and expressed as the appropriate intermediate plagioclase. Cast in these terms the reactions are recognizable as a Hbl breakdown reaction (1) and a biotite breakdown reaction (2). These reactions are depicted graphically in figure 3.7, a form of reaction space (Thompson 1982b). The

horizontal and vertical axes represent reaction (1) and (2), respectively. The tick marks indicate progress of the reactions as written per liter of rock. For the measured modal amounts of minerals in the Hbl-bearing gneiss, eventually a reactant will be exhausted for either reaction. These limits are shown by the dashed lines and labeled with the mineral which is exhausted. The light lines represent the direction of reaction progress that neither produces nor consumes the mineral which labels the line. The plus and minus signs indicate whether the mineral is produced or consumed if the direction of reaction falls to one side or the other of the line.

Modal composition data constrain the direction of reaction progress to be dominated by reaction (1), sub-horizontal to the right in figure 3.7. Biotite is abundant in the Hbl-free gneiss. Therefore the reaction direction must reach the limit of hornblende well below the point where the limit of biotite and the limit of hornblende intersect. The lower limit of reaction direction comes from the Kfs line; Kfs component has been produced in the Hbl-free gneiss. This circumstance even allows for the possibility that the biotite reaction ran backwards, producing biotite from Kfs and Opx.

A combination of reaction (1) and (2), dominated by (1) adequately explains all the mineralogic differences between the Hbl-bearing and Hbl-free gneiss: Hbl is exhausted; Cpx, Opx, Kfs and An component are produced. The fact that these reaction relationships exist between the minerals in the two assemblages indicates that the assemblages must have equilibrated under different environmental conditions, and their differences cannot be attributed solely to variations in bulk composition (Greenwood, 1967). Since, during regional metamorphism a temperature or pressure gradient cannot be maintained over just 60 cm, the only environmental condition left is fluid composition.

Fluid Composition

Both (1) and (2) are dehydration reactions, and therefore could have been driven by a decrease in water activity. Dilution with CO₂, presumably from the underlying marble, is a mechanism capable of lowering water activities. This idea can be tested by examining fluid composition in the gneiss as a function of distance from the marble. Figure 3.8 is an isobaric T-aH₂O diagram for equilibrium among the components:

$$phl + 3 Qtz = 3 en + Kfs + H_2O$$
 (3)

for three different rocks in the Hbl-free gneiss. The three lines are labeled with distance in cm from the contact with marble. At 800°C, the calculated water activity decreases from 0.24 at 61 cm to 0.20 at 15 cm, indicating a trend toward more H₂O-poor conditions near the marble. The absolute value of the calculated aH₂O could change by choosing different solid solution models for the phases involved or different P or T conditions, but the trend toward more water-poor conditions is still valid.

The mineral assemblage in the marble indicates that it could be a source of high XCO₂ fluid. Figure 3.9 is an isobaric T-XCO₂ diagram appropriate for bulk compositions of marbles like this one, namely relatively high in K and Al. This diagram is projected from calcite and anorthite in the KCMASCH system. For bulk compositions that lie near the Di-Phl tie line, fluid composition was probably buffered along the path shown (Greenwood 1975). For a marble originally composed of Cal + Dol + Qtz + Ms at some arbitrary low value of XCO₂, the first reaction encountered upon heating was:

$$5 \text{ Dol} + 8 \text{ Qtz} + \text{H}_2\text{O} \rightarrow \text{Tr} + 3 \text{ Cal} + 7 \text{ CO}_2.$$
 (4)

As temperature rose, fluid composition buffered to invariant point (I). At this point, the net mineral reaction which proceeded (Rice and Ferry 1982) at $XCO_2 = 0.4$ was:

 $0.9 \text{ Dol} + 2.3 \text{ Ms} + 1.2 \text{ Tr} \rightarrow$

$$Cal + 5.1 Qtz + 2.3 An + 2.3 Phl + 0.8 CO2 + 1.2 H2O.$$
 (5)

Since the only tremolite in the marble was produced while buffering along reaction (4), tremolite was most likely the first reactant exhausted (Rice and Ferry 1982). Upon further heating, fluid composition buffered along:

$$Dol + Ms + 2 Qtz + H2O \rightarrow Cal + Phl + CO2$$
 (6)

until invariant point (II) was reached. With additional heat, Kfs appeared and Ms was exhausted by the net reaction at $XCO_2 = 0.55$:

$$3 \text{ Dol} + 16 \text{ Cal} + 38 \text{ Qtz} + 19 \text{ Ms} \rightarrow$$

$$19 \text{ An} + 18 \text{ Kfs} + \text{Phl} + 18 \text{ H}_2\text{O} + 22 \text{ CO}_2. \tag{7}$$

As heating continued, fluid composition buffered to invariant point (III) along:

$$3 \text{ Dol} + \text{Kfs} + \text{H}_2\text{O} \rightarrow 3 \text{ Cal} + \text{Phl} + 3 \text{ CO}_2. \tag{8}$$

At invariant point (III) the net reaction was:

$$16 \text{ Qtz} + 3 \text{ Phl} + 9 \text{ Cal} \rightarrow 8 \text{ Di} + \text{Dol} + 3 \text{ Kfs} + 3 \text{ H}_2\text{O} + 7 \text{ CO}_2.$$
 (9)

Depending on bulk composition, either quartz or phlogopite was exhausted. In the marble from this locality, quartz was exhausted, leading to continued buffering along reaction (8) as temperature rose until Dol or Kfs was exhausted. The resulting assemblage is Cal + Di + Phl + An + (Kfs or Dol).

Much of the marble unit well below this outcrop consists of Cal + Dol + Fo + Phl \pm Spl. Fluid in marbles of this bulk composition are buffered to high XCO₂ along reactions such as:

$$Dol + 2 Qtz \rightarrow Di + 2CO_2$$
 (10)

$$2 \text{ Dol} + \text{An} \rightarrow 2 \text{ Cal} + \text{Di} + \text{Spl} + 2 \text{ CO}_2$$
 (11)

$$3 \text{ Dol} + \text{Di} \rightarrow 4 \text{ Cal} + 2 \text{ Fo} + 2 \text{ CO}_2 \tag{12}$$

(reactions A, E and D, respectively, in figure 1.7). Therefore, the observed mineral assemblages indicate that this marble was a viable source of CO₂-rich fluids with which to dilute fluids in the overlying gneiss. It is interesting to note that high XCO₂ fluids from marbles were only possible if fluid composition was internally buffered. If the equilibrium pore fluid composition was dominated by an infiltrating fluid, the bulk of reaction progress would have produced the observed mineral assemblages in the presence of fluids of much lower CO₂ content.

Conclusions

The change from amphibolite to granulite facies paragenesis at this outcrop is not a manifestation of a difference in bulk composition, but a consequence of a difference in pore fluid composition during metamorphism. The difference in fluid composition was caused by CO₂ evolved from the underlying marble. Mineral assemblages in the marble are consistent with the marble being a source of CO₂-rich fluids. The decrease in H₂O activity of fluid in the gneiss drove dehydration reactions which consumed hornblende and quartz ± biotite, and produced orthopyroxene, clinopyroxene, anorthite-rich plagioclase, orthoclase (sometimes as antiperthite) and ilmenite. This reaction was restricted to within 60 cm of the marble, indicating the limited role of fluid movement in controlling mineral parageneses in this terrane. Since no graphite was precipitated during the introduction of CO2-rich fluids, oxygen fugacity during metamorphism must have been above graphite stability (Lamb and Valley 1985). Pervasive influx of H2Orich fluids into the marbles can be ruled out because this would have lead to marblederived fluids that were more H₂O-rich than the observed aH₂O=0.2 in the gneiss. Pervasive influx of CO₂-rich fluids into the gneissic units can be ruled out because the dehydrated mineral assemblage is spatially associated with the marble.

5 4 Table 3.1 Singular value decomposition								
Tac	Hbl	Pl	Bt	Ilm	Opx	Срх	An	Kfs
Si	6.465	2.544	2.789	0	1.957	1.945		3
Ti	0.183	0	0.235	1	0.003	0.006	$\bar{0}$	ŏ
Āl	2.014	1.456		0	0.035	0.069	2	i
Fe	2.197	0	1.205	1	0.900	0.341	$\overline{0}$	Ō
Mn		0	0.012	0	0.016	0.007	ŏ	ŏ
Mg		0	1.349	0	1.058	0.728	ŏ	ŏ
Ca	1.806	0.462	0.000	0	0.031	0.884	ĭ	ŏ
Na	0.386	0.511	0.009	0	0.001	0.020	Õ	ŏ
K	0.285	0.014	0.956	0	0	0	Ŏ	ĭ
H	2	0	2	0	0	Ö	ŏ	Ô
esti	mated e				V			
Ti	0.050	0.005	0.070	0.005	0.005	0.005	0.005	0.005
Al	0.100	0.080	0.070	0.005	0.010	0.010	0.005	0.005
Fe	0.100	0.005	0.070	0.005	0.100	0.050	0.005	0.005
Mn	0.010	0.005	0.010	0.005	0.010	0.010	0.005	0.005
Mg	0.100	0.005	0.070	0.005	0.100	0.070	0.005	0.005
Ca	0.100	0.080	0.010	0.005	0.008	0.050	0.005	0.005
Na	0.020	0.080	0.005	0.005	0.005	0.010	0.005	0.005
K	0.020	0.010	0.050	0.005	0.005	0.005	0.005	0.005
3.6	11							-
	del matri		0.200	1 000	0.007	0.000	0.000	
Ti	0.261	-0.004	0.208	1.000	0.007	-0.008	-0.000	0.003
Al	2.035	1.455	1.278	0.000	0.036	0.065	2.000	1.001
Fe	2.032	0.008	1.295	1.000	0.891	0.371	0.000	-0.005
Mn	0.036	0.001	0.019	0.000	0.016	0.010	0.000	-0.000
Mg	2.422	-0.007	1.276	0.000	1.065	0.703	-0.000	0.005
Ca	1.768	0.464	0.019	-0.000	0.029	0.891	1.000	-0.001
Na	0.378	0.511	0.014	-0.000	0.001	0.021	0.000	-0.000
K	0.273	0.015	0.929	-0.000	-0.001	0.002	0.000	1.000
(Dat	ta-Mode	1)/error						
Ti	-1.57	0.76	0.39	-0.02	-0.81	2.84	0.04	-0.52
Al	-0.21	0.01	0.15	-0.01	-0.11	0.37	0.04	-0.32
Fe	1.65	-1.61	-1.28	0.05	0.09	-0.60	-0.09	1.10
Mn	1.64	-0.16	-0.66	-0.00	0.03	-0.28	-0.01	0.08
	-1.40	1.36	1.04	-0.04	-0.07	0.36	0.08	-0.93
Ca	0.38	-0.02	-1.94	0.01	0.24	-0.14	-0.02	0.95
Na	0.38	-0.00	-0.98	0.00	0.24	-0.14	-0.02	0.23
K	0.58	-0.06	0.54	0.00	0.03	-0.14	-0.00	0.03
		0.00	U.J.T	0.00	0.14	0.74	-0.01	0.00

Dag	ctions
IX Ca	CHORS

Reac	tions									
	<u>Hbl</u>	Pl	Bt	Ilm	Opx	Срх	An	Kfs	Otz	Water
Α	1.47	-0.93	-2.41	0.08	1.00	-2.24	-0.15	1.85	-3.28	0.47
B	-0.26	0.19	-0.47	0.16	1.00	0.23	0.14	0.51	-1.72	0.36

Figure 3.1 Cartoon cross section of outcrop AB90-13. Shows change in modal mineralogy from the Hbl-bearing gneiss to the Hbl-free gneiss.

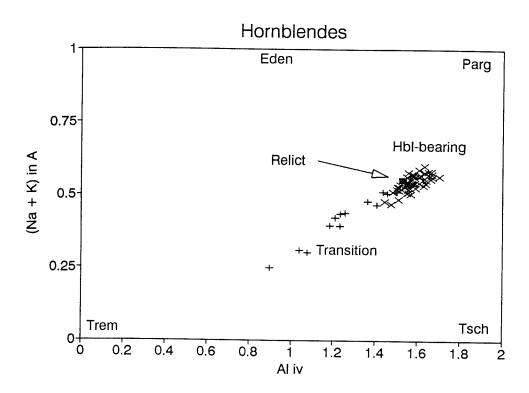


Figure 3.2 (Na+K)^A vs. Al^{iv} for Hbl. X are compositions in three different samples from the Hbl-bearing gneiss (86, 244 and 594 cm). Crosses are compositions in one thin section from the transition zone (61 cm). Filled square is the composition of the one relict amphibole grain in the Hbl-free gneiss (15 cm).

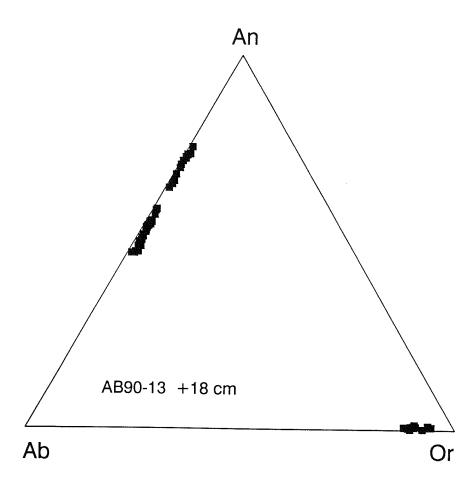


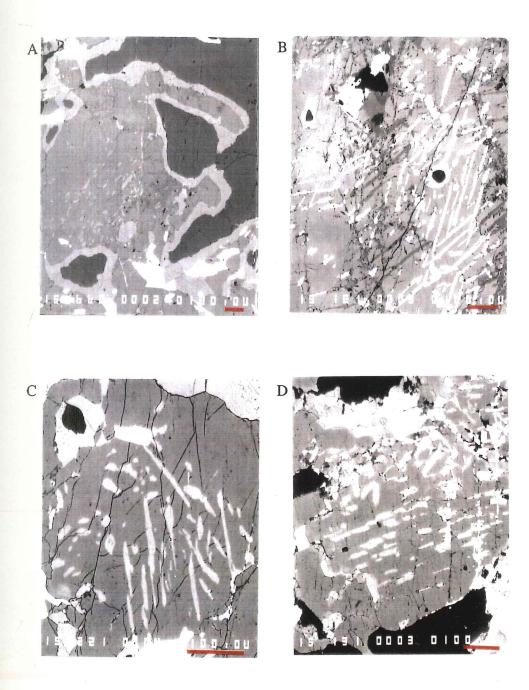
Figure 3.3 Feldspar ternary diagram, Hbl-free gneiss. Shows compositions of feldspars in one thin section from the Hbl-free gneiss (18 cm).

Figure 3.4 Backscatter photomicrographs of Kfs in Hbl-free Gneiss.

a) - Kfs (light) forming rims separating Qtz (dark) from Pl (medium).

b) - Antiperthite with up to 3 orientations of Kfs lamellae (light) in Pl host (medium); dark is sericitic alteration of Kfs. c) - Antiperthite.

d) - Antiperthite showing blocky-shaped Kfs blebs (light) in Pl host (medium). All from 18 cm. All scale bars are 100 µm.



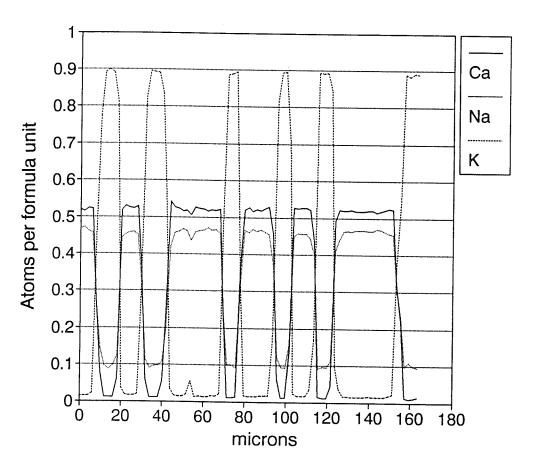


Figure 3.5 Microprobe traverse across antiperthite lamellae. Traverse taken from grain shown in figure 3.4b. Note that there is no consistent increase or decrease of plagioclase components near Kfs lamellae.

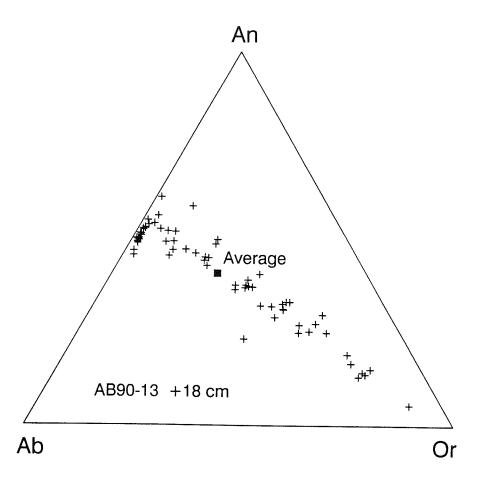
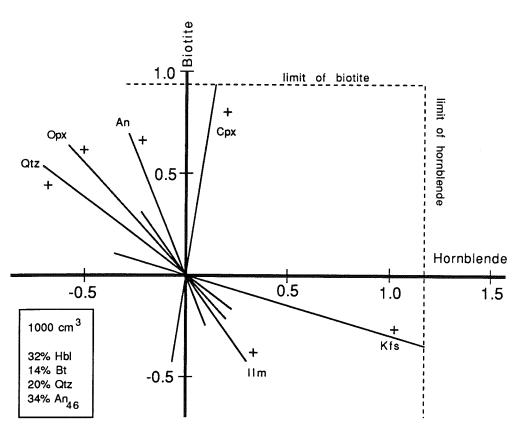


Figure 3.6 Feldspar ternary diagram of reintegrated antiperthite. Grain chosen is shown in Fig 16d. Crosses are individual 30 μ m diameter spots. Filled square is integrated average.



Hbl: Hbl + 1.96 Qtz = $1.22 \text{ Cpx} + 1.47 \text{ Opx} + 1.01 \text{ An}_{63} + .26 \text{ Kfs} + .26 \text{ Ilm}$

Bt: Bt + 2.59 Qtz + .18 Cpx = 1.32 Opx + .16 An₈₉ + .93 Kfs + .20 Ilm

Figure 3.7 Reaction space for Hbl-bearing to Hbl-free transition. See text for details.

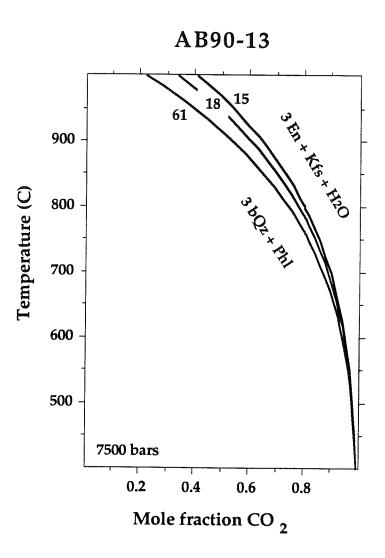


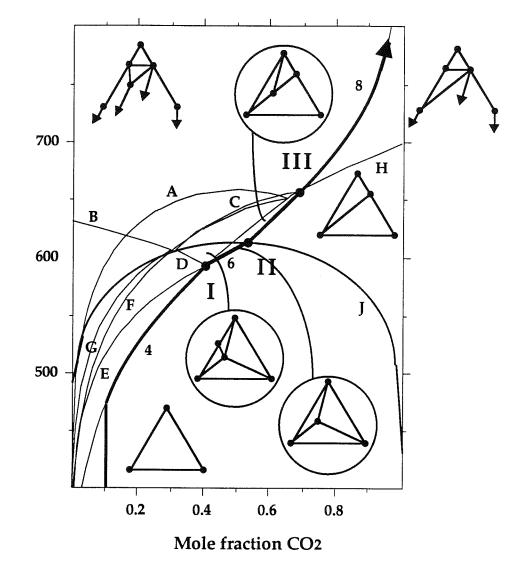
Figure 3.8 T-XCO₂ diagram, Hbl-free gneiss. Calculated for rocks from the transition zone (61) and the Hbl-free gneiss (18 and 15); lines labeled with distance (cm) from the marble. Water activities are lower near the marble.

Figure 3.9 T-XCO₂ diagram, AB90-13 marble. Calculated for 8 kbar projected from Cal and An for marbles of bulk composition similar to the marble at AB90-13 in the system KCMASCH for a binary H₂O - CO₂ fluid. Some reactions have been omitted for clarity. The numbered reactions on the figure correspond to the ones in the text. The bold line shows the buffering path described in the text.

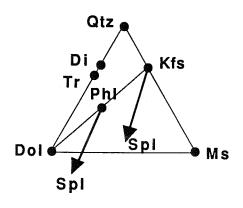
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 \begin{array}{lll} (4) & 7 \ CO_2 + Tr + 3 \ Cal = 5 \ Dol + 8 \ Qtz + H_2O \\ (6) & 4 \ CO_2 + Phl + 2 \ Cal + An = 3 \ Dol + Ms + 2 \ Qtz \\ (8) & 3 \ Cal + Phl + 3 \ CO_2 = H_2O + Kfs + 3 \ Dol \\ (A) & H_2O + CO_2 + Dol + 4 \ Di = 3 \ Cal + Tr \\ (B) & 2 \ H_2O + 2 \ Kfs + Phl + 3 \ An = 3 \ Di + 3 \ Ms \\ (C) & H_2O + 3 \ CO_2 + Kfs + 3 \ Di = 3 \ Cal + Phl + 6 \ Qtz \\ (D) & 5 \ An + Cal + 5 \ Phl + 14 \ Qtz + 3 \ H_2O = CO_2 + 3 \ Tr + 5 \ Ms \\ (E) & H_2O + 9 \ CO_2 + 4 \ Phl + 5 \ Cal + 4 \ An = 7 \ Dol + 4 \ Ms + Tr \\ (F) & 5 \ Di + 3 \ CO_2 + H_2O = Tr + 2 \ Qtz + 3 \ Cal \\ (G) & 2 \ H_2O + 4 \ CO_2 + Phl + 7 \ Di + An = 4 \ Cal + Ms + 2 \ Tr \\ (H) & Di + 2 \ CO_2 = 2 \ Qtz + Dol \\ \end{array}
```

 $H_2O + CO_2 + Kfs + An = Cal + Ms + 2 Qtz$

(J)



Temperature (C)



Chapter 4: Fluid inclusions

Introduction

The study of fluid inclusions in metamorphic rocks provides information about the composition of the fluid phase present during the metamorphism, its evolution during metamorphic mineral growth, and the pressure and temperature conditions of metamorphism. Fluid inclusions also form from fluids either generated in the rock or introduced after the peak of metamorphism, during cooling and uplift. Interpretation of the properties of the several generations of fluid inclusions commonly preserved in metamorphic minerals may give evidence on the uplift history of the metamorphic terrane or about specific recrystallization or deformational events affecting the fluid inclusion-bearing phase.

M.L. Crawford (1981, p. 157)

Fluid inclusions are small quantities of fluid encased in mineral grains. In metamorphic rocks these inclusions vary widely in size, but are frequently less than 30 µm in diameter. Fluid can be trapped in inclusions during growth of the mineral (primary) or along healed fractures in existing minerals (pseudosecondary and secondary). The fluid in inclusions is generally considered to have been trapped at or after the peak of metamorphism because most prograde P-T paths are such that the internal pressure of the inclusion would increase to the point that it would burst (decrepitate) along this path.

Concerted fluid inclusion work in high grade rocks was inspired by the discovery of a profound change in fluid inclusion composition from H₂O to CO₂ at the amphibolite to granulite facies transition in Norway (Touret 1971). Since granulite facies assemblages are characterized by a lower activity of H₂O than their amphibolite counterparts, the CO₂ in the inclusions may represent the H₂O-poor, peak metamorphic fluid (Touret 1985). This has lead to theories of granulite facies paragenesis development due to CO₂ streaming from some deeper source (Newton et al. 1980). However, the idea that CO₂-rich inclusions contain peak metamorphic fluids has been called into question by Lamb et al. (1987) on the grounds that carbonic inclusions have been found in granulite grade rocks for which mineral assemblage information indicates H₂O-rich peak metamorphic fluids.

In this chapter the results of fluid inclusion analysis across the blueschist to amphibolite and amphibolite to granulite facies transitions is examined in order to assess the composition of fluid trapped during the metamorphic cycle and the timing of entrapment.

Sample locations

Two suites of samples were analyzed for fluid inclusion composition and density. One suite consists of nine pelitic quartzofeldspathic schists from the isograds area to below the peridotite layer. The other suite consists of five quartz veins located in Nome group schists and Kigluaik group schists from the area near the isograds (figures 4.1 and 4.2). Fluid inclusions data is listed in appendix 4.

Pelite Leucosomes

62 fluid inclusions were analyzed from the pelite suite, chosen to represent the spectrum of metamorphic grades exposed. Most samples have the assemblage: Grt + Bt

+ Qtz + Pl + Graph + (Ms + Sta) or (Sil + Kfs) (table 4.1), with the exception of AB90-19, which has the assemblage: Grt + Bt + Qtz + Pl + Kfs + Opx. The inclusions measured occur within quartz, especially in quartz segregations. This inclusion population is dominated by low density CO₂. In the upper part of the stratigraphy (4th pelite) a small population of low-salinity H₂O inclusions occur.

CO₂-rich inclusions

Seven of the nine pelite samples contain CO2-rich fluid inclusions. Size and abundance vary systematically with stratigraphic location. Inclusions are very abundant and large (5-20 µm diameters) low in the stratigraphic section (0th, 1st, 2nd and 3rd pelites). In the mixed unit and 4th pelite, CO₂ fluid inclusions are rare and not as large (3-10 µm diameters). At room temperature, the inclusions are usually two phase (L + V), dominated by the vapor phase. Rarely, the inclusions are only vapor phase. In one case, a thin meniscus of a second liquid phase was seen at a necked down corner of a carbonic inclusion, indicating that a small amount of H₂O may be present in these inclusions. Because of the dark walls of CO₂ inclusions, up to 20% H₂O may be present in the carbonic inclusions and not visible under the microscope (Roedder 1972). Some inclusions homogenize to liquid, most to vapor; in two samples, critical behavior was observed. The carbonic inclusions are pseudosecondary or secondary in nature. Usually the planes of inclusions do not cross grain boundaries. In samples with abundant carbonic inclusions there are multiple orientations of the planes of inclusions. In samples with rare carbonic inclusions there is generally only one orientation of their planar arrays, perpendicular to schistocity.

H₂O-rich inclusions

Five of the nine pelitic samples contain aqueous fluid inclusions. Aqueous inclusions in schists are smaller than carbonic inclusions (2-10 µm diameters). Aqueous

inclusions are two phase (L + V) with varying proportions of bubble size at room temperature. All inclusions homogenize to liquid. Aqueous inclusions are not present in the 0th, 1st, 2nd and 3rd pelite, and are moderately rare to rare in the mixed unit and 4th pelite. The aqueous inclusions are pseudosecondary to secondary in nature. No trails were observed to cross grain boundaries. These planar arrays are generally limited to one or two orientations. There are three samples in which both CO₂- and H₂O-rich fluid inclusions occur. In these samples, there are more planes of H₂O inclusions than CO₂ inclusions, and the H₂O inclusion planes have more inclusions/mm². Due to the rarity of both sets of inclusions, no clear textural or timing relationships were interpreted concerning the two compositions of inclusions.

Qtz vein traverse

35 fluid inclusions from the quartz vein suite were examined in order to assess any variation in fluid composition across the Nome group to Kigluaik group transition. Quartz veins which do not cross cut foliation were chosen in order to examine the earliest generations of fluid inclusions. Fluid inclusions in this suite are low salinity H₂O of varying density. Read and Meinert (1986) also investigated fluid inclusions in quartz veins similar to ones investigated here within Nome Group schists (their type I veins). Along with aqueous inclusions of similar characteristics to the ones reported here, they found mixed H₂O-CO₂ and carbonic inclusions. The CO₂ within these inclusions had characteristics similar to the carbonic inclusions from the 4th pelite discussed in this chapter, namely a depressed melting point (-58.5 to -62.2°C) and homogenization temperatures generally in the teens.

H₂O-rich inclusions

All five of the Qtz vein samples investigated contained H₂O fluid inclusions. CO₂-bearing fluid inclusions were not found in any sample. The Qtz vein aqueous

inclusions are larger (3-15 μ m diameters) than their pelite counterparts. All are two phase (L + V) with varying proportions of V to L. The inclusions are very abundant. There are multiple orientations of planar arrays of inclusions in each sample. The inclusions are secondary in nature; inclusions trails cross grain boundaries.

Fluid Inclusion thermobarochemistry

Carbonic inclusions

 T_m (temperature at which the solid melts) of CO_2 is slightly depressed below the pure melting temperature of -56.6°C (figure 4.3). The positive correlation between T_m and T_h (temperature at which the inclusion homogenizes to either vapor or liquid) in carbonic inclusions (figure 4.4) indicates that the lowering of T_m is caused by dilution of CO_2 with a small amount of fluid other than H_2O (Thomas et al. 1990), commonly CH_4 or N_2 (Swanenberg 1980, Kreulen and Schuiling 1982, Rudnick et al. 1984, Schreurs 1984, Althaus and Istrate 1990, Samson and Williams-Jones 1991, Winslow et al. 1991). This small amount of lowering (down to -59°C) could be caused by ~20% CH_4 or N_2 (Burruss 1981, Hall and Bodnar 1990, Kerkhof 1990).

Th for carbonic inclusions that homogenize to liquid ranges from 31 to 12° C with most inclusions above 25° C (figure 4.5), indicating a density of around 0.55 g/cm³. However, the vast majority of inclusions homogenize to vapor, indicating a density less than 0.47 g/cm³, similar to low density carbonic inclusions described in forsterite from lower crustal xenoliths by Roedder (1965). In addition, since the inclusions with the lowest homogenization temperature also indicate the highest level of dilution with extra component (figure 4.4), the actual density of inclusions with T_m <- 56.6 is less than that calculated if pure CO_2 is assumed (Touret 1981, Touret and Kerkhof 1986). For example, a pure CO_2 inclusion with $T_h(liq)$ =15°C has a density of 0.82 g/cm³ (Angus et al. 1976), whereas an inclusion that is 80% CO_2 and 20% CH_4

with a $T_h(liq)=15$ °C has a density of 0.45 g/cm³ (Burruss 1981, Holloway 1981). Therefore, I conclude that carbonic fluid inclusions in pelite leucosomes have a density near that of the critical point, 0.47 g/cm³. There is a systematic trend toward more pure CO_2 deeper in the stratigraphic section.

21% N₂ was found in one Kigluaik inclusion by laser Raman spectroscopy (Touret written communication 1989), the remainder being 71% CO₂ and 2.4% CH₄. The other inclusions analyzed were 100% CO₂.

Pelite aqueous inclusions

The final melting temperature of this small population of aqueous fluid inclusions is only lowered to about -0.5°C (figure 4.6). This indicates a salinity of about 0.9 wt% NaCl equivalent (Potter and Brown 1977). T_h ranges from ~175° to 250°C with most around 175°C, and all homogenize to liquid (figure 4.7). This corresponds to a density of ~0.90 g/cm³. Two additional groups of aqueous inclusions were measured in 4th pelite leucosomes (figure 4.8). One has T_m and T_h of -4 and 175°C, found in a pelite from the mixed unit, another has temperatures of -8° and 350°C, found in a 4th pelite from the 2nd Sil isograd ("normal" pelite aqueous inclusions also occur in this sample). These data indicate salinities of 6.4 and 11.7 wt% NaCl equivalent, and corresponding densities of 0.94 and 0.77 g/cm³, respectively.

Qtz vein aqueous inclusions

These inclusions overlap in composition and density with those of the pelite leucosomes, but have a greater degree of variability in density (figures 4.6, 4.7 and 4.8). T_m in Kigluaik group 4th pelite Qtz veins ranges from -0.2 to -2.2°C (figure 4.6), corresponding to salinities less than 3.7 wt% NaCl equivalent. These fluid inclusions have a range of T_h from ~200° to 325°C, most at about 280°C (figure 4.7), corresponding to a density of 0.78 g/cm³. Aqueous inclusions in Nome group Qtz

veins cluster more tightly at $T_m = -1.9$ and $T_h = 225$ °C (figure 4.8). This corresponds to a salinity of 3.2 wt% NaCl equivalent and a density of 0.86 g/cm³. These findings are in agreement with measurements on aqueous fluid inclusions in quartz veins from Nome Group schists investigated by Read and Meinert (1986).

The similarity in composition and density of aqueous inclusions between pelite matrix, pelite quartz vein and Nome Group quartz vein leads to the interpretation that all these inclusions are cogenerational.

Discussion

Calculation of isochores (Nicholls and Crawford 1985) for the carbonic and aqueous inclusions (figure 4.9) leads to some straight-forward conclusions. Isochores for aqueous inclusions from the Sta and Sil+Kfs isograds pass through the estimated P-T conditions of peak metamorphism of their enclosing rocks and may therefore represent peak metamorphic fluids. Isochores for Nome group aqueous inclusions and those for Kigluaik group carbonic inclusions fall well below their respective estimated peak P-T conditions and therefore cannot represent unmodified peak metamorphic fluids.

Petrogenetic grid constraints indicate that the P-T path followed by Kigluaik group rocks is clockwise in nature (Ky to Sil, Bt + Sil to Crd, Rt to Ilm, Grt to Opx + Pl). Such a path crosses all the isochores determined in this study, allowing the interpretation that the fluid in inclusions is late and has not been modified since trapping. It is also possible that fluids were trapped at the peak of metamorphism and have since been modified. Modifications could include change in inclusion volume, diffusion of fluid species in/out of or leakage of material out of the inclusion (Roedder 1984). These possibilities are explored in the following sections.

Changes in shape and composition

Changes in volume which would decrease the density of trapped peak fluids include precipitation of daughter minerals, partial decrepitation, and stretching of the inclusions. Since daughter minerals are denser than the fluid from which they precipitate, the remaining fluid must become less dense; however, no daughter minerals were observed. Partial decrepitation of fluid inclusions has been identified in other granulite grade rocks by the distinctive texture of a large central inclusion with a planar cluster of smaller inclusions around it (Touret 1977, Swanenberg 1980). None of these "decrepitation clusters" or "exploded inclusions" were identified in Kigluaik carbonic inclusions. However, this does not preclude the possibility that such features have since annealed into more regular-looking arrays of inclusions. Given a retrograde path of mostly isothermal decompression, fluids trapped at peak conditions would be expected to decrepitate upon a pressure differential of one or two kbar, for the size of inclusions measured in this study (Roedder 1981, Bodnar et al. 1989). This size dependence of decrepitation potential would be manifested in a systematic variation in density with inclusions size, smaller inclusions being more dense. No such systematic variation was observed in Kigluaik carbonic inclusions. Hence, most inclusions have not decrepitated. Stretching via plastic deformation in a host mineral is viable in softer minerals such as halite and fluorite (Roedder 1981, Bodnar and Bethke 1984), and has recently been experimentally established in quartz (Sterner and Bodnar 1989) at temperatures of 600° to 700°C on the time scale of days to weeks. Therefore it must be concluded that Kigluaik carbonic inclusions could have undergone a change in volume due to stretching after trapping.

The two most likely candidates for diffusion or leakage out of inclusions are H_2 and H_2O . Diffusion of H_2 into fluid inclusions has experimentally been shown to occur

(Hall et al. 1989, Morgan et al. 1991). Addition of H₂ to CO₂-bearing fluid inclusions would drive the reaction: $CO_2 + 4H_2 = CH_4 + 2H_2O$. Hydrogen is a minor component in most metamorphic fluids, and especially in CO2 dominated fluids (French 1966, Ohmoto and Kerrick 1977, Frost 1979, Rice and Ferry 1982). However, variation in the fugacities of fluid species along fO2 buffers on the retrograde path in the matrix pore fluid can lead to significant overpressures of fH2 in the matrix with respect to the inclusion depending on the specific external conditions (Hall and Bodnar 1990). For a retrograde path that is convex to the temperature axis (clockwise), as is the path for Kigluaik rocks, the overpressure in fH₂ calculated by Hall and Bodnar is 30 bars or less for fO₂ conditions one log unit below FMQ, and only a few bars for more oxidizing conditions (one log unit above FMQ). Such a fugacity gradient in H₂ would have promoted diffusive addition of H2 to Kigluaik inclusion, but the quantity of mass influx at these very low gradients is probably quite small, suggesting that H2 did not enter the inclusions. Pasteris and Wanamaker (1988) showed experimentally that matrix oxygen fugacity communicated with pure CO2 inclusions in forsterite by movement of crystal defects, not molecular O2. The fugacity gradients experimentally imposed were quite large (4-5 log units) and therefore compositional change to Seward Peninsula inclusions due to fO₂ communication with the matrix is unlikely.

Experimental evidence shows that the density of H₂O inclusions can change in response to a pressures gradient between inclusion and confining pressure (Pecher and Boullier 1984, Sterner and Bodnar 1989, Sterner et al. 1988) and may be attributable to diffusive movement of H₂O through the confining quartz. Sterner and Bodnar (1989) concluded that at 600°C diffusion of H₂O through quartz did not occur or was below the detection limits of ~0.5 wt% H₂O loss. However, Sterner et al. (1988) indicate that at higher temperatures (~825°C), H₂O diffusion through quartz may be a viable

mechanism. Hollister (1988, 1989) proposed that H_2O from a homogeneous H_2O - CO_2 mixture can preferentially leave the inclusion and diffuse away, leaving CO_2 behind, aided by plastic deformation in the quartz. This process is controversial and has not been experimentally verified.

Figure 4.10 illustrates the magnitude of diffusive loss of H₂O and volume change necessary to convert fluid trapped at 8 kbar and 800°C to pure CO₂ with a density of 0.45 g/cm³. Ideal mixing of H₂O and CO₂ is assumed, with densities of 0.825 and 1.15 g/cm³, respectively. The density after diffusive loss of H₂O depends on the amount of H₂O originally in the inclusion. In the Kigluaiks, peak metamorphic XCO₂ is probably in the range 0.5 to 0.8 (Lieberman 1988, this dissertation chapter 3), leading to CO₂ densities of 0.7 to 1.0 g/cm³ after H₂O loss. The increase in size of the inclusion due to stretching necessary to bring the density to 0.45 g/cm³ is a 20 to 30% increase in radius, assuming spherical geometry. If the peak fluid was 80% CO₂ and the fluid inclusions hide the 20% H₂O so no diffusive loss of H₂O is needed, then a 37% increase in radius is necessary to bring about the change in density to 0.45 g/cm³. These calculations indicate that a combination of H₂O loss and stretching could turn mixed volatile inclusions into pure CO₂ with the appropriate density, and that stretching is always necessary to accomplish this.

Timing of inclusion entrapment

Although stretching of fluid inclusions in quartz may occur at temperatures over 800°C, there is no experimental evidence that stretching occurs at temperatures reached in the isograd area (550° to 700°C). If stretching is called upon to explain the low densities of the high-grade carbonic inclusions, then the carbonic inclusions in the isograds should not have stretched, and should display higher densities. This is not the case. If it is argued that on geologic time scales, stretching could occur at the lower

temperatures of the isograds, then H₂O inclusions should have stretched also. However, many aqueous inclusions have higher densities, compatible with peak isograd conditions. The data is reconcilable if the isograd aqueous inclusions were trapped earlier and have not all undergone a substantial amount of stretching, and the carbonic inclusions were simply trapped later at very low pressures. Since peak fluid compositions in the isograds were water-rich (Lieberman 1988) these aqueous inclusions could contain peak Kigluaik isograd fluids.

The array of isochores is interpreted to represent trapping along a clockwise P-T retrograde path. Aqueous inclusions were trapped in rocks of the isograd area near the peak of metamorphism. Additional aqueous fluids were trapped there during decompression, or some peak inclusions were modified (stretched?) along this path. Carbonic inclusions were trapped very late along this retrograde path and do not represent trapped peak metamorphic granulite facies fluids. Carbonic fluid inclusions in the Adirondack granulites are also thought to have been trapped after the peak of metamorphism (Lamb et al. 1987, Morrison and Valley 1988).

Source of aqueous fluids

The ranges of aqueous fluid inclusion salinities and densities overlap among Kigluaik pelites, Kigluaik quartz veins, and Nome group quartz veins. This allows the interpretation that they all have the same source, indicating that the inclusions are late at least with respect to metamorphism in the Nome group. The source of aqueous fluids could be connate, magmatic or metamorphic. Connate waters from continental shelf sediments would likely be more saline than these fluid inclusions (Roedder 1984).

Igneous fluids likewise have high salinities (Roedder 1984). Metamorphic fluids have the appropriate low salinity. Substantial dehydration has occurred in Kigluaik group pelites; dehydration-derived fluids would have driven off connate fluids. Therefore I

conclude that aqueous fluid inclusions in the isograd area are metamorphic in origin, rising from local dehydrating sediments.

Source of carbonic fluids

The source of carbonic fluids is more problematic. There are three possible sources of N_2 in fluid inclusions: atmospheric N_2 , ammonia released from silicate minerals during dehydration reactions such as: $2(NH_4)Al_3Si_3O_{10}(OH)_2 + \frac{3}{2}O_2 = N_2 + 6H_2O + 3Al_2SiO_5 + 3SiO_2$ (O_2 is supplied by the buffer capacity of the rock, such as $2Fe_2O_3 = 4FeO + O_2$, where iron oxides are components in biotite or iron oxides), and nitrogen compounds released from organic matter during maturation to graphite (Samson and Williams-Jones 1991). None of these sources are completely satisfactory to explain late CO_2 - N_2 . The possibility that any atmospheric gas could survive an entire granulite grade metamorphic cycle is remote. Ammonia from dehydration and nitrogen from organic maturation are given off during prograde metamorphism, not during the waning stages of uplift. The dehydration scenario is especially difficult to justify because it requires that N_2 is trapped, but not the H_2O given off by the same reaction.

Conclusions

Two generations of fluid inclusions have been identified in Kigluaik Group and Nome Group lithologies. The earlier generation consists of low salinity aqueous inclusions with a density of ~0.9 g/cm³. These were trapped at and following the time of peak metamorphism in the isograd area of the Kigluaiks. The other generation of fluid inclusions consists of nearly pure CO₂ with low densities (around the critical density of 0.47 g/cm³). These carbonic inclusions were trapped late in the metamorphic cycle, as was concluded for Adirondack carbonic inclusions (Lamb 1987, Morrison and Valley 1988, Lamb et al. 1991). This contrasts with other granulite grade terranes where (higher density) carbonic inclusions are taken to represent samples of peak fluids

(Newton et al. 1980, Hansen et al. 1984, Touret 1985, Santosh et al. 1991). In the granulite grade rocks of the Kigluaik mountains, no peak metamorphic fluids survived as fluid inclusions.

77 Fluid inclusion host rock assemblages. Arranged stratigraphically Table 4.1 Sample# Pelites AB87-218 Unit Isograd Grt Bt Qtz Pl Kfs Ms Sta Sil Gr Op
 IV
 Sta
 X
 X

 IV
 Sta
 X
 X
 X

 IV
 Sta
 X
 X
 X
 X

 IV
 Sil+Kfs
 X
 X
 X
 X
 X

 IV
 Sil+Kfs
 X
 X
 X
 X
 X
 X

 III
 Sil+Kfs
 X
 X
 X
 X
 X
 X

 I
 Sil+Kfs
 X
 X
 X
 X
 X
 X

 0
 Opx
 X
 X
 X
 X
 X
 X
 X
 X X X X X X X X X i AB87-220 IV AB87-290 IV AB87-254.2 IV AB85-208.1 IV X X X X X X X X X X X X AB89-33.2 mi: AB89-1.1 III OS-18 I AB90-19.1 0 Quartz veins Nome qtz vein lineated subparallel to foliation Nome strong pencil structure qtz rods IV veined and brechiated qtzite AB87-201 AB87-208 AB87-212 AB87-217 AB87-257 large quartz pod (1 X 2 m) IV IV qtz vein

Figure 4.1 Fluid inclusion sample location map. See figure 1.2 for explanation of map patterns.

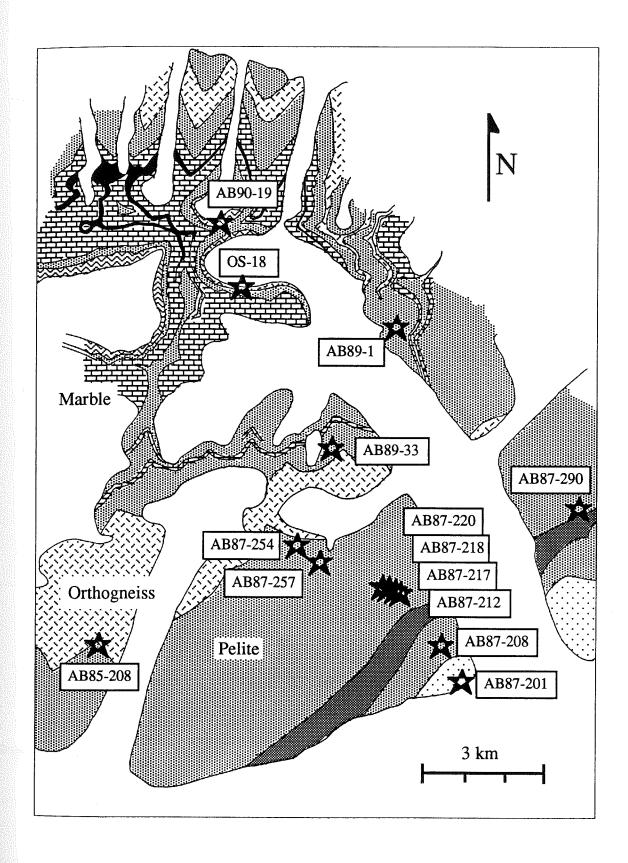
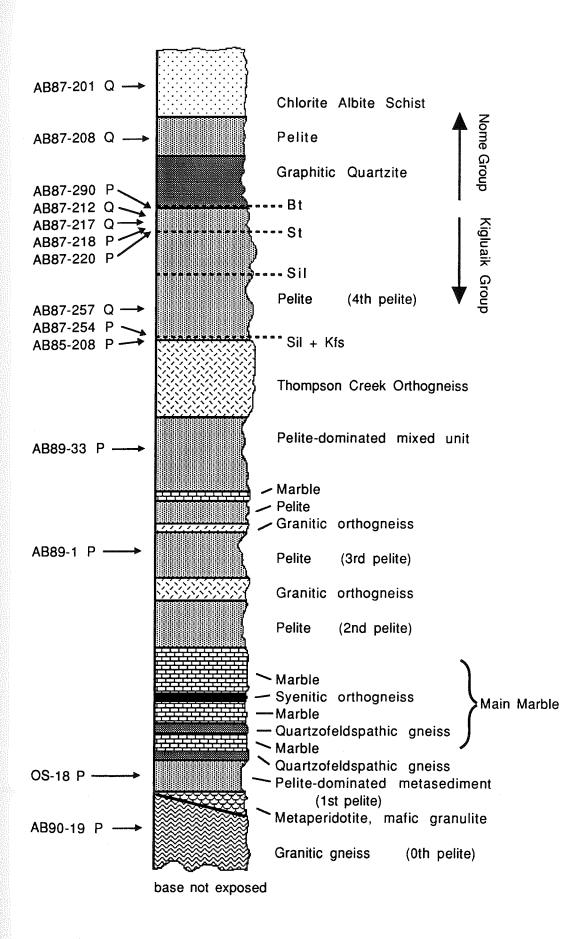


Figure 4.2 Stratigraphic location of fluid inclusion samples. Q = quartz vein sample; P = pelite sample. Vertical scale as in figure 1.4.



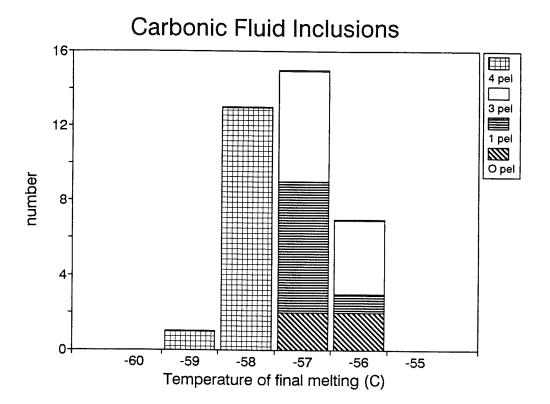


Figure 4.3 T_m carbonic inclusion histogram.

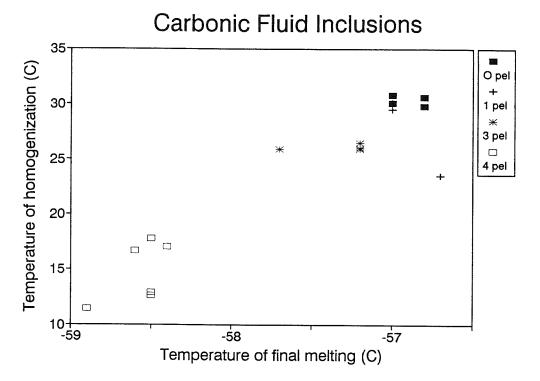


Figure 4.4 T_m vs. T_h for carbonic inclusions. The positive correlation indicates dilution with up to 20% CH₄ or N₂.

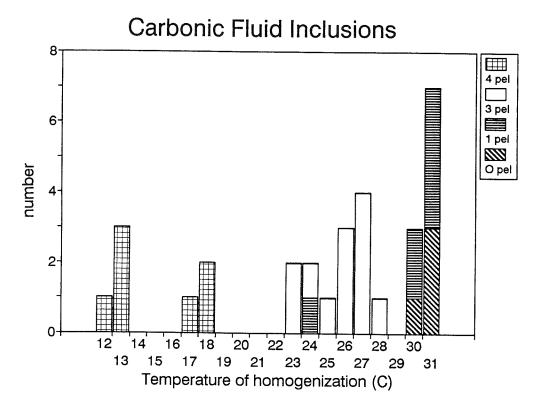


Figure 4.5 T_h carbonic inclusion histogram.

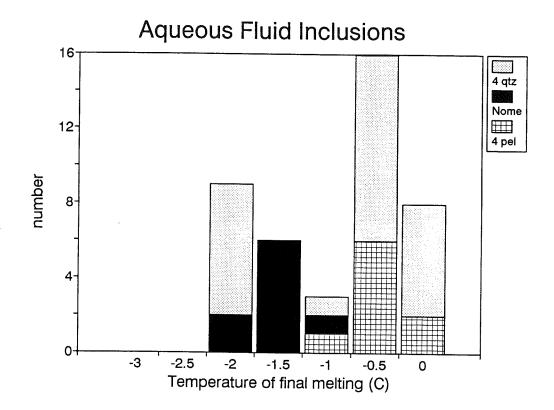


Figure 4.6 T_m aqueous inclusion histogram.

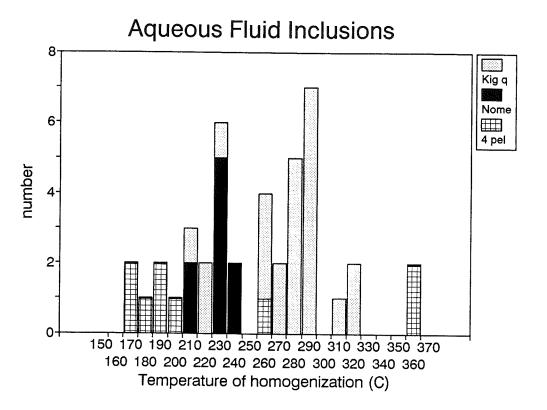


Figure 4.7 T_h aqueous inclusion histogram.

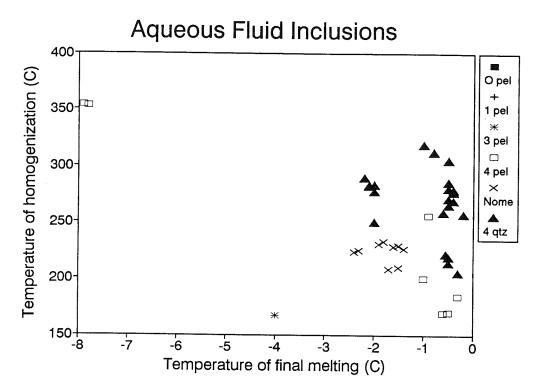


Figure 4.8 T_m vs. T_h for aqueous inclusions. The high degree of overlap in T_m and T_h of quartz vein and pelite samples suggest that the fluids are cogenerational.

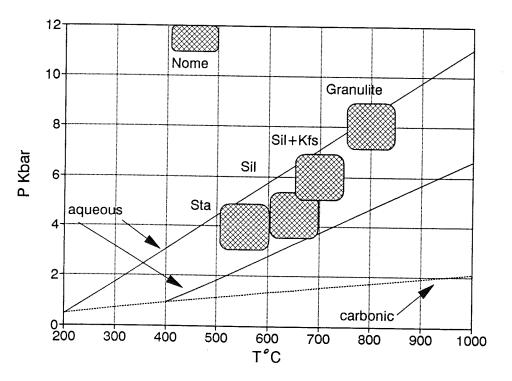


Figure 4.9 P-T diagram showing isochores for fluid inclusions. The solid lines span the range in aqueous densities measured from 0.9 g/cm³ (upper) to 0.7 g/cm³ (lower). The dashed line shows the isochore for carbonic fluids of 0.45 g/cm³ density. The hatchured boxes represent peak metamorphic conditions attained (Lieberman 1988, Patrick and Evans 1989). See chapter 1 for explanation of isograd zones.

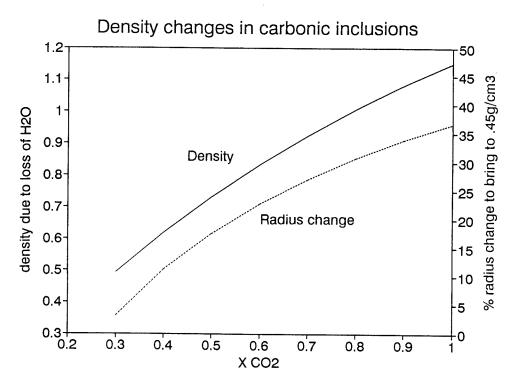


Figure 4.10 Fluid inclusion density change due to change in shape or composition. See text for details.

Chapter 5: Summary and Conclusions

Stable isotope profiles across lithological boundaries only provide information on the component of transport parallel to the profile. In the main marble unit of the Kigluaik Mountains (transitional amphibolite-granulite facies), steep oxygen and carbon isotope profiles attest to extremely small amount to no time integrated fluid flux across lithological boundaries (see also Baker 1990, Cartwright and Valley 1991 1992). Pervasive upward fluid flow is ruled out. Both marble and gneissic units retain oxygen isotope signatures characteristic of their protolith, indicating that an external fluid did not homogenize rock compositions. The small amount of fluid that did advect across lithologic boundaries is inferred to have been CO₂-rich and derived from marble, moving downwards in two cases out of three. The H₂O evolved during prograde metamorphism of the underlying pelite-bearing layer left no measurable isotopic imprint on the main marble above. This H₂O, and the H₂O released from crystallizing partial melt in the pelites, presumably departed along mainly horizontal channels external to the main marble. The main marble was an effective aquitard. Cross-cutting veins in marble, composed of monomineralic diopside, are extremely rare. Only during the waning stages of metamorphism did the injection of pegmatite dikes permit fluids, in this case H₂O-rich, to penetrate the main marble and, at pegmatite-marble contacts, precipitate garnet, clinopyroxene, epidote, wollastonite, and fluorite. In addition, small amounts of late, channelized H2O-rich fluid locally converted forsterite to serpentine and diopside to tremolite.

The isotopic profiles are interpreted to be dominated by diffusive processes.

The extent of isotopic interaction is related more to lithological type (compare marble at AB89-41 with that at AB89-61) than to stratigraphic horizon (compare AB89-62 + AB90-27 at the base of the main marble with AB89-61 in the interior). Outcrop AB89-

41 involves a relatively pure dolomitic marble whereas marble at AB89-61 has a varied composition with a much higher proportion of silicate phases (table 2.2). AB89-61 would have undergone much more devolatilization during prograde metamorphism than AB89-41. Devolatilization reactions enhance porosity, leading to more extensive interaction with fluid (Rumble and Spear 1983). Other workers have found thick pure carbonate marbles to be very effective barriers to infiltrating fluid (Gerdes et al. 1991; Frueh-Green et al. 1991). The estimate of porosity for AB89-61 based on a 1 Ma timescale is nevertheless very low and it is questionable that transport of material could have occurred under these circumstances. If fluid was present only during transient devolatilization events (Thompson 1983, Hoernes and Hoffer 1985) in the marble, the corresponding time scale would be much less than 1Ma and calculated porosity increased to levels more appropriate for fluid interconnectivity regardless of solid-fluid dihedral angle (Brenan 1991). Ductile thinning of this section (factor of two?) may have occurred (Miller et al. 1992a), but this amount of thinning would not significantly effect the conclusions presented here.

The estimates of time integrated fluid flux calculated here (0 and 0.01 m³/m²) are four to six orders of magnitude less than those calculated for metasedimentary rocks in low to medium grade regional metamorphic terranes (Ferry and Dipple 1991). The method used by Ferry and Dipple is based on reaction progress, whereas the calculations presented here are based on advective-diffusive displacements of stable isotope discontinuities (Bickle and McKenzie 1987). Many stable isotope studies are consistent with estimates of fluid advection monitored by reaction progress (Ferry 1986). The difference in estimated flux may be reconcilable in that the present calculations are for cross-lithology transport and those of Ferry and Dipple represent layer-parallel flux. A difference in crustal level could affect the extent of fluid movement

possible (Baker 1990), but since the *time integrated* fluid flux is small, practically no fluid advected across the main marble units at *any time* during metamorphism. The present flux parameters are one to two orders of magnitude smaller than those calculated by Bickle and Baker (1990a) for outcrops in an amphibolite grade terrane in the Cyclades of Greece using the same methods of calculation.

Granulite facies metamorphic parageneses are usually characterized by a reduced activity of H₂O (e.g. Newton 1986), and this field location is no exception (Lieberman 1988 and figure 2.10 here). The present results render unlikely the possibility that this was caused by an influx of pervasive externally derived H₂O-poor fluid, such as CO₂ streaming from the mantle (Janardhan et al. 1982) or from mantle-derived mafic magma (Frost and Frost 1987). The main marble extends across the entire mountain range (figure 1.3) and formed an impermeable barrier to upward pervasive flow of fluid, CO₂ or otherwise, during metamorphism. Passage of H₂O-undersaturated symmetamorphic plutons (Frost and Frost 1987) can be ruled out because the layering in the Kigluaik Mountains has only been disrupted by *late* plutons and pegmatites. Because orthogneiss units comprise only a small part of the lithologic sequence, heating of previously dry rocks (e.g. Valley and O'Neil 1984) can also be ruled out. There are two internal methods left of altering pore fluid composition: (1) extract H₂O by partial melting (e.g. Crawford and Hollister 1986) and (2) add CO₂ by local decarbonation of graphite or carbonate minerals (Glassley et al. 1989). Both may occur. In the vicinity of marble contacts, it was argued in chapter 3 that (2) operated on a decimeter scale. Fluid movement played a limited role in controlling mineral parageneses in the Kigluaiks.

The retrograde path followed by rocks in the Kigluaik Mountains was dominated by decompression. This is supported by mineral replacements, petrogenetic grid

considerations and fluid inclusion microthermometry. In the lower part of the stratigraphy, no peak metamorphic fluids were trapped. In the isograd area, however, aqueous inclusions may represent fluids trapped at the peak of metamorphism. Rocks at all levels of the Kigluaik Group contain low density CO₂-rich inclusions trapped late along the retrograde path. This is in contrast to other terranes, where carbonic inclusions have been used in support of theories of CO₂ from mantle sources (Newton et al. 1980, Touret 1985).

In view of the above, I conclude that heat was transported into the section by conduction alone. Most likely, the source of heat was syn-metamorphic intrusions below the present level of exposure, or perhaps exposed to the west of this field area (Amato et al. 1992). The data presented here demonstrate the large effect that can be played by lithologic layering during metamorphism. Differing lithologies can control fluid movement deep in the crust just as they do in the near-surface environment.

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Appendix 1: Mineral assemblages in Kigluaik group pelites

This appendix is organized into two parts; one where the information is arranged by sample number, the other where the information is organized by stratigraphic horizon. Mineral identifications were made petrographically or by electron microprobe. Samples were collected by Alison Till (XXX KT78), Steve Pollack (SL81-XXX), Josh Leiberman (OS-XX, AB85-XXX, AB86-XXX, AB87-XXX), Brian Patrick (AB84-XXX) and Clifford Todd (AB89-XX, AB90-XX). Unit refers to the stratigraphic horizon from which the sample came (see figure 1.4): 0th, 1st, 2nd, 3rd, and 4th refer to pelite units; TGOC refers to the Thompson Creek Orthogneiss; mixed refers to the mixed metasedimentary unit between the TGOC and the 3rd pelite; syen refers to the metasyenite unit within the main marble. The Isograd column denotes the isograd zone from which the sample was taken (see chapter 1 for explanation of isograd zones). Mineral abbreviations are listed in table 1.1, with the exception of "Tourm" tourmoline, and "Op", which stands for opaque, usually ilmenite. "X" signifies that the mineral is present. "inc" signifies that the mineral is present only as an inclusion within another mineral, usually garnet. "It" signifies that the mineral is texturally late. "tr" signifies a trace amount of the mineral. An exclamation point means that the mineral is very abundant. "fib" refers to fibrolite, the fine grained fibrous form of sillimanite. "A" in the Ky column stands for andalusite, instead of kyanite. "Lithol" describes the lithology of the sample: gqtzite = graphitic quartzite, btgneiss = biotite gneiss.

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Sample# AB87-281 AB87-282	AB87-283.2 AB87-285	AB87-286	AB87-287	AB87-289	AB87-290	AB89-01.1	AB89-01.2	AB89-01.3	AB89-02	AB89-07	AB89-10.1	AB89-10.3	AB89-10.4	AB89-10.5	AB89-11.1	AB89-11.2	AB89-13	AB89-15	AB89-16	AB89-20	AB89-21.1	AB89-21.2	AB89-23.3	AB89-29	AB89-33.1	AB89-33.2	AB89-35	AB89-37.1	AB89-40.03	AB89-40.07	AB89-40.08	AB89-40.09	AB89-40.10	AB89-40.11

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Sample# AB89-48.3	AB89-57.2	AB89-58	AB89-60.3	AB89-64.2	AB89-64.3	AB89-64.5	AB89-65.2	AB89-65.6	AB89-65.8	AB89-67.1	AB89-67.2	AB89-71	AB89-77.1	AB89-78.1	AB89-78.2	AB89-82.2	A BOO OUT	A 100 04.1	ABS0-04.2	AB90-07	AB90-17	AB90-18.3B	AB90-19.1	AB90-19.5	AB90-19.6	AB90-19.7	AB90-19.9	AB90-23.2	AB90-23.7	AB90-26.06	AB90-26.12	AB90-35.5	AB90-39.1	AB90-39.2	AB90-40.1	AB90-44	AB90- 6 1.1

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Sample#	AB30-61.2	AB90-65A	AB90-65B	AB90-67	AB90-70.3	AB90-78.2	AB90-79	AB90-80	AB90-81

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Sample# AB85-005	155 KT78	AB84-149	AB84-152	AB85-021	AB85-022.1	AB85-023	AB85-026	AB85-033	AB85-034.1	AB85-034.2	AB85-036	AB85-036.2	AB85-037.1	AB85-041	AB85-049.2	AB85-065	AB85-067.1	AB85-067.2	AB85-067.3	AB85-069	AB85-070	AB85-071	AB85-072	AB85-073	AB85-076	AB85-077.2	AB85-222.2	AB85-249	AB86-006	AB86-007.2	AB87-213.1	AB87-218	AB87-220.1	AB87-220.3	AB87-221.2	AB87-222	AB87-244.1

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Sample#	AB87-252.2	AB87-256	AB87-257	AB87-257.2	AB87-257.3	AB87-274	AB87-275	AB87-285	AB87-286	AB87-287	AB90-78.2	AB90-79	AB90-80	AB90-81	SL81-504.1	SL81-504.2	SL81-506.1	SL81-512.1	038 KT78	039 KT78	042 KT78	043 KT78	AB85-208.1	AB85-208.2	AB85-215.1	AB85-217	AB85-228.1	AB85-229	AB87-253.1	AB87-253.2	AB87-253.3	AB87-254.1	AB87-254.2	AB87-255	AB87-277	AB87-278	AB87-281

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Sample#	AB87-282	AB87-283.2	OS 91	055 KT78	066 KT78	068 KT78	063 KT78	076 KT78	082 KT78	085 KT78	AB89-29	AB89-33.1	AB89-33.2	AB89-67.1	AB89-67.2	AB89-71	096 KT78	098 KT78	099 KT78	100 KT78	101 KT78	156 KT78	AB89-01.1	AB89-01.2	AB89-01.3	AB89-02	AB89-07	AB89-20	AB89-21.1	AB89-21.2	AB89-35	AB89-37.1	AB89-40.03	AB89-40.07	AB89-40.08	AB89-40.09	AB89-40.10	AB89-40.11

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Isograd Sil+Kfs Sil+Kfs Sil+Kfs Sil+Kfs Sil+Kfs Sil+Kfs	Si + 45° Si = 45° Si	Sil + Kfs Sil + Kfs Sil + Kfs Sil + Kfs Sil + Kfs	SII + Kfs
Unit		<u> </u>	1 float 1 float 1 float 1 float 1 float 1 float 0 fth 0 fth
Sample# AB86-105.2 AB86-118.2 AB86-123 AB89-10.1 AB89-10.3	AB89-10.5 AB89-11.1 AB89-11.2 AB89-23.3 AB89-60.3 AB90-04.1 AB90-07 AB90-17 AB90-17 AB90-67 OS 06	0S 52.1 0S 52.1 0S 56 0S 70 0SW 2	AB89-64.2 AB89-64.3 AB89-65.2 AB89-65.8 AB90-19.1 AB90-19.5 AB90-19.5 AB90-19.7 AB90-35.5 AB90-65A AB90-65B

Appendix 2: Major element mineral compositions

Microprobe analyses of minerals were carried out on a JEOL Superprobe 733 at the University of Washington, Department of Geological Sciences. The accelerating voltage was 15 kvolts and sample current 15 namps for biotite, feldspar and carbonate and 25 namps for all other phases. Natural minerals and synthetic glasses were used as standards. Data were reduced using the method of Bence and Albee (1968).

Biotites were normalized to 11 oxygens assuming all Fe measured is Fe²⁺, so that the solution model of McMullin et al. (1992) could be used for thermodynamic calculations. (OH) was determined by the formula (OH) = 2 - F - Cl, and a wt% H₂O calculated accordingly. Definition of exchange vectors (Thompson 1982, Dymek 1983) and formulas used to caclulate them are defined as follows: $X_{tlc} = K_{-1}Al_{-1}\Box Si = 1 - K - Na - Ca$; $X_{an} = K_{-1}Si_{-1}CaAl = Ca$; $X_{tispl} = Al_{-2}TiMg = Ti$; $X_{dioct} = Mg_{-3}\Box Al_2 = 3 - Mg - Fe - Mn - Al^{vi} - Ti$; $X_{tk} = Mg_{-1}Si_{-1}Al_2 = 3 - Si - X_{an} - X_{tlc}$.

Feldspars were normalized to Ca + Na + K = 1.

Garnets were normalized to 8 cations. Fe³⁺ was calculated so as to bring the number of oxygens to 12.

Hornblende stoichiometry calculated from microprobe data is dependent on the normalization scheme used (Robinson et al. 1982). I have chosen to normalize to the average of 15 (excluding K and Na) and 13 (excluding K, Na and Ca) cations (Hollocher 1991). Niether F nor Cl were measured; (OH) was assumed to be 2. Wt% H_2O was calculated based on this stoichiometry. Definition of exchange vectors (Thompson 1982) and formulas used to caclulate them are defined as follows: $X_{ed} = \Box_{-1}Si_{-1}(Na,K)Al = (Na + K)^A; X_{tspl} = Al_2TiMg = Ti; X_{ab} = Ca_{-1}Al_{-1}NaSi = Na^{M4}; X_{tk} = Mg_{-1}Si_{-1}Al_2 = 8 - Si_{-1}Al_{-1} + X_{ab}$. "xsO" is the oxygen wt% correction for Fe^{2+} to Fe^{3+} conversion.

Olivine was normalized to 3 cations, clinohumite to 13 cations and chondrodite to 7 cations, assuming all Fe measured is Fe²⁺. The (OH) content of clinohumite and chondrodite was determined by the formula (OH) = 2 - F - 2Ti, and a wt% H₂O calculated accordingly.

Pyroxenes were normalized to 4 cations. Fe³⁺ was calculated so as to bring oxygens to 6. "xsO" is the oxygen wt% correction for Fe²⁺ to Fe³⁺ conversion.

Spinels were normalized to 3 cations. Fe³⁺ was calculated so as to bring oxygens to 4. "xsO" is the oxygen wt% correction for Fe²⁺ to Fe³⁺ conversion.

Staurolites were normalized to Si + Al = 25.53 (Holdaway et al. 1986). Fe³⁺ is assumed to be 0.25; lithium is assumed to be 0.2; hydrogen is assumed to be 3.06 (Holdaway et al. 1986). Wt% Li₂O and H₂O was calculated accordingly.

																	1	2	2																
ត	+594 cm	38.09	3.58	14.41	15.93	0.01	14.11	0.01	0.0	9.78	0.45	0.05	-0.20	3.80	100.08	2.836	1.164	0.101	0.200	0.992	0.001	1.566	0.001	0.009	0.929	0.106	900.0	1.888	7.800	0.061	0.224	0.001	0.200	0.139	
ត	+244 cm	36.40	3.55	14.19	18.95	0.22	12.39	0.07	0.09	9.33	0.32	0.01	-O.14	3.77	99.15	2.784	1.216	0.062	0.204	1.212	0.014	1.412	9000	0.013	0.910	0.077	0.001	1.921	7.835	0.071	0.281	9000	0.204	0.095	
ត	+86 cm	36.39	4.08	14.04	18.81	0.18	11.81	0.02	90.0	9.78	0.35	0.05	-0.16	3.73	99.15	2.789	1.211	0.057	0.235	1.205	0.012	1.349	0.002	0.00	0.956	0.085	9000	1.909	7.825	0.033	0.243	0.002	0.235	0.142	
- c+ cca •	+61 cm	38.11	3.58	14.59	14.63	0.11	14.83	0.03	0.09	9.60	0.10	0.07	-0.06	3.97	29.66	2.831	1.169	0.108	0.200	0.909	0.007	1.643	0.002	0.014	0.910	0.025	0.008	1.967	7.792	0.074	0.241	0.002	0.200	0.134	
์ วั															100.41	2.795	1.205	0.101	0.249	0.936	0.004	1.544	0.003	0.004	0.924	0.061	600.0	1.931	7.766	0.069	0.270	0.003	0.249	0.165	
វ៍ =	// +15 cm	36.69	7.32	13.42	17.07	0.05	11.68		0.03	9.88	0.03	0.02	-0.02	3.96	100.14	2.761	1.239	-0.049	0.414	1.074	0.003	1.310	0.00	0.004	0.948	0.008	0.003	1.989	7.706	0.048	0.286	0.000	0.414	0.247	
ត៍	90-19.5	36.29	6.63	14.04	17.30	0.04	11.10	0.01	0.09	9.71	0.43	0.01	-0.18	3.74	99.19	2.758	1.242	0.016	0.379	1.100	0.003	1.258	0.000	0.013	0.941	0.104	0.001	1.895	7.710	0.046	0.287	0.000	0.379	0.244	
ฉี		35.03														2.694	1.306	0.298	0.227	1.185	0.00	1.108	0.004	0.023	0.875	0.084	0.003	1.913	7.726	0.098	0.400	0.004	0.227	0.177	
ត	78-85	35.21	3.99	17.46	17.95	90:0	10.19	0.02	0.23	9.37	0.33	0.04	-0.15	3.75	98.46	2.694	1.306	0.268	0.230	1.148	0.004	1.162	0.002	0.034	0.915	0.079	0.005	1.916	7.764	0.049	0.354	0.002	0.230	0.187	
វ	+	36.23																	0.133											0.094	0.359	0.000	0.133	0.164	
í	85-222	33.94	2.77	18.84	22.53	0.01	5.82	0.05	0.27	8.39	0.43	0.05	-0.18	3.57	96.39	2.696	1.304	0.459	0.165	1.496	0.001	0,689	0.001	0.041	0.850	0.108	0.002	1.890	7.703	0.108					
ត៍	1-425	35.33	2.08	18.75	16.85	0.09	10.97	0.01	0.24	8.78	0.34	0.01	-0.14	3.74	97.04	2.712	1.288	0.408	0.120	1.082	9000	1.255	0.00	0.036	0.860	0.082	0.00	1.917	7.768	0.103	0.390	0.00	0.120	0.129	
í	7-218	35.55	1.37	19.40	17.89	0.11	10.18	0.03	0.30	8.76	0.38	0.01	-0.16	3.73	97.53	2.724	1.276	0.475	0.079	1.146	0.007	1.162	0.002	0.044	0.856	0.092	0.00	1.907	7.772	0.098	0.372	0.002	0.079	0.130	
์ อี	87-220	34.44	1.80	19.16	22.40	0.02	7.20	0.03	0.30	8.78	0.45	0.01	-0.19	3.63	98.02	2.689	1.311	0.453	0.106	1.463	0.001	0.838	0.002	0.045	0.875	0.110	0.00	1.889	7.783	0.077	0.386	0.002	0.106	0.139	
																S														Xtlc					

盐	AB89-41	+3cm	39.77	1.45	16.12	0.43	•	26.48	1	90.0	10.57	1.56	0.75	-0.83	3.35	99.70	2.789	1.211	0.121	0.077	0.025	0.000	2.769	0.000	0.008	0.946	0.346	0.089	1.565	7.945	0.046	0.257	0.000	0.077	0.009
ă		2															2.770	1.230	0.033	0.242	1.570	0.018	1.008	0.002	0.009	0.958	0.171	0.021	1.808	7.840	0:030	0.258	0.002	0.242	0.129
ă	AB89-41	-33 cm	35.41	2.00	13.48	24.23	0.31	8.10	0.00	0.08	9.61	0.66	0.16	-0.31	3.49	100.22	2.763	1.237	0.005	0.293	1.581	0.020	0.942	0.00	0.012	0.957	0.163	0.021	1.816	7.808	0.031	0.268	0.000	0.293	0.160
			Si02	Ti02	A1203	FeO	MnO	MgO	CaO	Na2O	K20	L	ਠ	F,CI=O	H20*	Total	S	Ali∕	Alvi	j=	Нe	Ž	Mg	Ö	Na	¥	u.	ਠ	* O	cations	Xtlc	ž	Xan	Xtispl	Xdioct

<u>a</u> .	24 cm	59.96	25.58	7.22	7.20	0.36	100.32	2.706	1.361	0.349	0.630	0.021
Kfs 89-41	-24 cm	64.82	18.94	0.14	1.51	14.38	99.79	3.026	1.042	0.007	0.137	0.856
<u>a</u>	-33 cm	59.82	25.43	6.98	7.38	0.34	99.95	2.692	1.349	0.337	0.644	0.020
Kfs //89-41	-33 cm	64.42	18.96	0.22	1.82	13.98	99.40	2.983	1.035	0.011	0.163	0.826
₫	+594 cm	55.78	27.88	10.08	5.56	0.32	99.62	2.537	1.494	0.491	0.490	0.019
颪	+244 cm	57.71	26.80	8.67	6.33	0.47	99.98	2.604	1.425	0.419	0.554	0.027
PI AB90-13	+86 cm	57.01	27.54	9.61	5.88	0.25	100.29	2.590	1.474	0.468	0.518	0.014
₫	+61 cm	57.14	27.49	9.44	5.86	0.38	100.31	2.602	1.475	0.461	0.517	0.022
PI + 18 cm	nnexsol	50.08	31.77	15.00	3.00	0.12	99.98	2.271	1.698	0.729	0.264	0.007
PI +18 cm +	reintegrate	57.42	56.09	8.36	3.81	4.27	99.95	2.635	1.411	0.411	0.339	0.250
Kfs +18 cm +	pleb	65.65	18.82	0.18	1.21	15.07	100.94	3.016	1.019	600.0	0.108	0.883
PI +18 cm	plag-host	55.48	28.49	10.72	5.38	0.25	100.33	2.494	1.509	0.516	0.469	0.015
		Si02	AI203	CaO	Na2O	Ķ S	Total	Si	₹	S S	Na	¥

Grt	AB90-13	+18 cm	38.45	0.01	21.57	25.68	2.43	6.49	5.20	0.02	98.86	2.996	0.000	1.981	0.026	1.648	0.161	0.754	0.434	0.314	0.550	0.054	0.252	44
Grt		-24 cm	37.88	90.0	21.11	26.30	4.08	2.76	8.28	0.03	100.50	2.994	0.003	1.966	0.040	1.698	0.273	0.326	0.701	0.161	0.566	0.091	0.109	700
Grt	AB89-41	-33 cm	37.99	0.04	21.32	26.68	4.41	2.51	7.75	0.00	100.69	3.002	0.002	1.986	0.005	1.758	0.295	0.296	0.656	0.144	0.585	0.098	0.098	0
Grt		89-10.3	38.51	0.04	21.59	29.76	0.62	7.60	1.59	0.00	99.71	3.008	0.002	1.987	0.000	1.943	0.041	0.885	0.133	0.313	0.647	0.014	0.295	770
Grt							0.70					3.004	0.002	1.988	0.001	2.137	0.047	0.673	0.148	0.239	0.711	0.016	0.224	0,00
Grt		81-506	38.00	0.03	20.07	25.12	10.40	3.14	2.66	0.00	99.42	3.070	0.002	1.911	0.000	1.697	0.711	0.378	0.230	0.182	0.563	0.236	0.125	0.00
Grt		78-85	38.39	0.00	20.42	32.12	1.93	5.31	1.31	0.00	99.48	3.063	0.000	1.920	0.000	2.143	0.131	0.631	0.112	0.228	0.710	0.043	0.209	7000
Grt		89-78	38.91	0.02	20.46	32.25	1.43	5.56	1.30	0.00	99.92	3.085	0.001	1.912	0.000	2.139	0.096	0.657	0.110	0.235	0.712	0.032	0.219	7600
Grt		90-19	38.87	0.03	20.24	28.44	1.56	5.77	4.58	0.00	99.49	3.067	0.002	1.883	0.000	1.877	0.104	0.679	0.387	0.266	0.616	0.034	0.223	7010
Grt		87-220	37.55	0.03	20.56	35.50	1.14	2.04	2.91	0.00	99.72	3.046	0.002	1.966	0.000	2.408	0.079	0.247	0.253	0.093	0.806	0.026	0.083	באט ט
			SiO2	Ti02	AI2O3	FeO*	Mno	MgO	CaO	xs oxy	Total	ï	=	₹	Fe3+	Fe2+	μ	Mg	Ça	₩8₩	Xalm	Xspess	Xpyr	Xaros

AB90-13 AB90-13 +61 cm +86 cm +244 cm +61 cm +86 cm +244 cm +61 cm +61 cm +244 cm +61 cm +6	Hbl Hbl 90-65 90-65		inc inc	44.09	1.71	12.44	11.98	0.05	14.62	9.65	2.02	0.40	96'96	0.32	2.08	3.26 99.36 99.44	6.360	1.640	0.475	0.185	0.692	0.754	900'0	3.129	1.491	0.268	0.297	0.073	2 2 2	1.537	0.370	0 185
Hbl Hbl Hbl AB90-13 +61 cm +86 cm +244 cm 49.63 43.07 42.77 0.68 1.62 1.43 12.18 17.50 17.30 12.18 17.50 17.30 15.24 10.25 10.62 11.59 11.23 11.34 0.26 0.41 0.41 0.89 1.33 1.28 0.05 0.15 0.16 0.15 0.16 0.22 2.10 2.01 2.01 2.10 2.01 2.01 0.05 1.00.45 99.90 1.00.54 100.45 99.90 1.00.54 1.00.45 99.90 1.00.54 1.00.45 99.90 1.00.54 1.00.45 99.90 1.00.54 1.60.45 99.90 </td <td>Hbl Hbl 90-13 89-41</td> <td>+86 cm -33</td> <td></td> <td>_</td> <td>_</td> <td></td> <td>_</td> <td></td>	Hbl Hbl 90-13 89-41	+86 cm -33																_	_												_	
Hbl Hbl Hbl AB90-13 +61 cm +86 cm +61 cm +86 cm 0.68 1.62 1.62 1.750 0.26 0.24 10.25 11.59 11.59 11.59 11.59 11.59 11.59 11.59 0.88 1.33 0.86 1.49 98.30 98.27 0.16 2.10 2.01 2.10 2.01 1.92 0.307 0.417 0.074 0.182 0.307 0.417 0.074 0.182 0.031 0.051 0.051 0.031 0.051 0.010 0.110 0.110 0.110 0.127 0.248 0.555 0.074 0.182 0.0770 1.137 0.248 0.555 0.074 0.182	<u>a</u>																															
AB90-13 +61 cm +61 cm +	롼	·																													_	_
4 W 4 10 W W W V 01 O O 01		Ŧ																														

Chu	89-12.1		37.44	1.42		5.19	0.14	53.54	0.01	2.27	100.01	1.44	96.0-	100.49	3.964	0.113		0.460	0.013	8.450	0.001	0.760	1.014	
Chond	89-41	Chond vien	34.37	2.27		2.96	0.04	54.57	0.04	4.85	99.10	2.33	-2.04	99.39	2.005	0.100		0.144	0.002	4.746	0.003	0.895	906.0	
Chu	89-41		37.54	1.47		3.86	0.09	53.40	0.08	2.53	98.97	1.27	-1.07	99.18	4.012	0.118		0.345	0.008	8.508	0.009	0.855	0.909	
ō	39-41	Dol zone	41.540	0.010	0.02	5.350	0.080	52.140	0.050		99.200				1.004	0.000	0.001	0.108	0.002	1.879	0.001			
			41.22	0.01	0.02	6.710	0.120	50.610	0.080		98.770				1.007	0.000	0.001	0.137	0.003	1.843	0.002			
			SiO2	Tios	AI2O3	FeO	MnO	MgO	CaO	ட	Subtotal	H20*	F=0	Total	Si	F	A	Fe	Mٿا	Mg	Ca	ட	동	

ă	AB89-41	-24 cm	51.03	0.05	0.67	16.06	1.04	9.10	21.35	0.21	90'0	99.58		1.982	0.018	0.013	0.002	0.018	0.504	0.034	0.524	0.889	0.016	
ă	389-41	3 cm	51.02	0.09	0.93	17.43	0.92	8.81	20.53	0.29	90.0	100.07		1.978	0.022	0.021	0.003	0.017	0.548	0.030	0.507	0.853	0.022	
хdО	B90-13	15 cm	51.36	0.11	0.79	28.69	0.50	18.71	0.77	0.01	0.21	101.16		1.949	0.051	-0.016	0.003	0.061	0.850	0.016	1.053	0.031	0.001	34 (M) N
Cpx	390-13	15 cm	51.77	0.21	1.55	10.86	0.22	13.07	21.96	0.28	0.18	100.09		1.945	0.055	0.013	9000	0.050	0.291	0.007	0.728	0.884	0.020	7
xd O	AB90-13	+18 cm	51.29	0.04	1.32	26.13	0.74	20.15	0.39	0.01	0.20	100.26		1.942	0.058	0.000	0.001	0.056	0.771	0.024	1.132	0.016	0.000	97 97 97
ă	AB90-13 AE	+61 cm	51.13	0.05	0.88	25.45	1.07	20.04	0.70	0.01	0.20	99.52		1.950	0:020	-0.010	0.001	0.058	0.754	0.035	1.134	0.029	0.000	
ă	AB90-13	+61 cm	52.13	0.13	2.09	9.11	0.50	13.52	21.87	0.28	0.05	29.62		1.953	0.047	0.046	0.004	0.014	0.271	0.016	0.751	0.878	0.020	V.
			SiO2	TiO2	AI203	FeO FeO	Mno	MgO	CaO	Na2O	(s)	Total	i	<u> </u>	۸Iiز	٩lvi	≔	-e3+	-e2+	Ę	Μg	g	۸a	

	Spl	Spl	Spl	Spl	Spl	Spl
	by Sta 1	by Sta 2		•	•	•
	83-91	83-91	83-41	89-35	AB89-41	
	inc	inc	inc	inc	Cal+Fo	Dol zone
SiO2					0.03	0.02
Ti02	0.03	0.03	0.01	0.04	90.0	0.07
AI203	60.50	60.48	60.65	59.45	68.01	80.69
Cr203					0.17	0.10
FeO*	27.85	24.99	27.16	23.80	6.86	5.51
MnO	0.05	0.10	0.05	0.03	0.07	90'0
MgO	5.08	4.50	90.9	6.26	23.69	24.32
ZuO	6.08	9.12	5.70	9.29		
O sx	0.00	0.00	0.02	0.09	0.01	0.00
	99.57	99.21	99.65	98.97	98.91	99.17
ï	0.000	0.000	0.000	0.000	0.001	0.001
F	0.001	0.001	0.000	0.001	0.001	0.001
₹	2.005	2.023	1.995	1.979	1.982	1.996
<u>්</u>	0.000	0.000	0.000	0.000	0.003	0.002
Fe3+	0.000	0.000	0.004	0.019	0.002	0.000
Fe2+	0.655	0.593	0.630	0.543	0.139	0.113
Μg	0.213	0.190	0.252	0.263	0.873	0.888
Ĕ	0.001	0.002	0.001	0.001	0.001	0.001
Zu	0.126	0.191	0.117	0.194	0.000	0.000

Sta		2	inc	25.59	0.88	57.11	12.09	0.04	2.07	1.17	0.18	1.67	100.79	7.03	0.18	18.50	0.25	2.53	0.01	0.85	0.24	0.20	3.06
Sta	/ 83-91													7.09	0.24	18.44	0.25	2.58	0.01	0.72	0.18	0.20	3.06
Sta	_													7.21									
Sta	83-41	0	inc	25.45	1.14	55.97	11.39	90.0	2.59	1.28	0.18	1.64	99.70	7.11	0.24	18.42	0.25	2.41	0.01	1.08	0.26	0.20	3.06
													100.26		0.20	18.43	0.25	2.60	0.02	1.01	0.13	0.20	3.06
													101.05		0.24	18.50	0.25	2.47	0.01	0.98	0.26	0.20	3.06
Sta	89-10.3	α	inc	25.30	1.23	57.42	10.69	0.04	2.93	1.50	0.18	1.67	100.97	6.95	0.25	18.58	0.25	2.20	0.01	1.20	0:30	0.20	3.06
Sta	//	-	inc	25.43	1.34	57.50	10.50	0.04	2.93	1.49	0.18	1.67	101.09	6.97	0.28	18.56	0.25	2.16	0.01	1.19	0.30	0.20	3.06
Sta		87-218		27.89	99.0	53.97	13.25	0.32	1.57	0.18	0.18	1.64	99.62	7.78	0.14	17.75	0.25	2.84	0.08	0.65	0.04	0.20	3.06
Sta		81-425		27.87	0.63	54.07	13.00	0.27	1.95	0.08	0.18	1.65	69.66	7.77	0.13	17.76	0.25	2.78	90'0	0.81	0.02	0.20	3.06
Sta		87-220		27.92	0.50	54.19	13.96	0.07	1.31	60.0	0.18	1.65	99.87	7.76	0.10	17.71	0.25	3.00	0.02	0.54	0.02	0.20	3.06
Sta		85-222		28.40	0.69	54.69	12.92	0.05	0.81	0.01	0.18	1.67	99.43	7.81	0.14	17.72	0.25	2.72	0.01	0.33	0.00	0.20	3.06
				SiO2	Ti02	AI203	FeO*	MnO	MgO	ZuO	Li20*	* H2O H		:S	ı=	₹	Fe3+ *	Fe2+	Ĕ	Μg	Zu	<u>*</u>	*

Appendix 3: Stable isotope mineral compositions

Stable isotope analyses were carried out on a Finnigan Mat Delta E spectrometer at Department of Geosciences, New Mexico Tech, Socorro, New Mexico. Carbonates were dissolved in phosphoric acid overnight in a 25°C water bath; silicates were reacted with ClF3 at 450°C for 10 hours, and liberated oxygen was then reacted with a glowing carbon rod. The CO2 was then isolated by standard cryogenic techniques. δ^{18} O values are reported relative to SMOW, δ^{13} C relative to PDB. One sigma precision for extraction and mass spectrometry is estimated at 0.3 ‰.

AB89-41				
	dist cm -31 -25 -18 -11 -5.1 0 0.3 0.75 1.25 1.6 2.2 2.6 3.2 3.7 4.2 4.8 5.4 5.9 6.35 11 30 244 396	18O 14.9 11.9 10.4 9.9 10.8 11.0 12.7 13.0 13.1 13.5 16.4 18.3 20.6 22.5 22.7 23.3 23.1 23.1 22.7 22.4 22.3 22.9 22.4	-2.0 -2.2 -2.3 -2.3 -1.3 -0.9 -0.5 -0.3 -0.4 -0.3 -0.4 -0.5 -0.4 -0.5	mineral fspar d18O biot fspar 6.3 fspar fspar 7.0 fspar 7.0 fspar calcite calcite calcite dolomite
AB89-62			3.3	dolonine
ALCO GE	cm 183 43 2.5 -6.35 -35.5 -63.5 -234	d18O 21.4 22.2 20.6 19.4 20.2 19.1 18.9	d13C -2.1 -1.6 -2.5	calcite calcite calcite quartz quartz quartz quartz
AB89-44	cm 55 35 3 -1 -7 -16	18.8 19.4 18.2 15.1 16.3 14.2 15.6	3.7 4.3 3.6	calcite calcite calcite quartz quartz quartz quartz
AB89-61	cm 670 366 366 366 366 135 107 102 94 71 53	d18O 24.3 23.7 23.4 23.8 24.0 20.7 19.6 19.8 19.3 19.5 18.9	d13C 0.1 -1.2 -1.2 -1.2 -1.2 -0.7 -1.3 -1.3 -1.6 -1.3 -1.1	calcite calcite calcite 1/2 hr calcite 2 hr calcite

				133	
; 2	41 18.6 33 20.1 33 20.4 15 16.9 11 16.5 10 16.6 7.6 16.9 5 16.6 2.5 16.3 24 15.9 60 16.5	-0.8		calcite dolomite calcite quartz quartz	
AB90-27	1400				
1.		-0.9 -1.0 -0.7 -1.5 -0.6		mineral calcite calcite calcite calcite calcite calcite calcite calcite calcite	
Nome Group Marble					
AB80 AB80				calcite	
AB80				calcite calcite	
AB80		4.6		calcite	
AB81	-18 15.9	4.7		calcite	
AB90-13					
38 17 8 6 5 4 3 2 1 1 1 1 1 1 1	70 15.1 36 15.1 37 14.8 37 14.8 38 16.2 23 16.1 18 16.0 15 15.7 10 16.2 0 16.2	Ox Hbld 12.1 12.2 12.2 11.7 11.9	Ox Biot 8.3 8.9 7.4 7.1 7.6 8.2 11.1 11.1	20.9 21.7 22.2 22.2	-0.9 -0.8 -1.0 -0.9
-36	O			18.1	-0.2
Kigluaik Pelites	Qtz	Biot	Wh Mica		-
85-215 89-16 89-82. 89-20	5.1 19.4 18.7	13.2 13.0 11.4 11.0	·		

89-13	15.4	7.6	
89-11.1	14.3	9.6	
87-220.1	16.3		13.9

AB90-26

cm	Ox cc	Carb cc	Ox Qtz	Ox Biot
1389			14.3	8.2
1361	28.0	-0.8		
1323	28.3	-1.6		
992	23.1	5.2		
543	27.3	0.3		
283	16.5	0.9		
104	25.0	4.7		
-28			13.1	7.2

Appendix 4: Fluid inclusion measurements

Doubly polished thin sections (100-200 μ m thick) were prepared from the sample material. Microthermometry was performed on a Fluid Inc. stage in the School of Oceanography, University of Washington, Seattle, WA. The thermocouple was calibrated by a synthetic pure CO₂ fluid inclusion. Accuracy is taken to be $\pm 0.1^{\circ}$ C for temperatures near or below 0°C increasing to $\pm 1^{\circ}$ C for temperatures above 200°C. Isochores were calculated using the programs of Nicholls and Crawford (1985).

DELITEO	Tm	Th		
PELITES OS-18	Pel I -57.1 -56.7 -57.0	28 23.5 30.2 30.2 30.2 30.2 29.3 29.5	Otz in pelite vap liq crit crit crit crit liq liq	others to vap
AB89-1.1	Pel III -57.2 -57.2 -57.1 -56.6 -57.7	26 25.9 26.5 25.9 26.1 26.1 26.2 27.8 22.4 23.7 24.6 22.9	Otz in pelite liq liq vap vap liq liq liq liq liq	
AB85-208.1		Pel IV	Qtz in pelite	
area 1	-0.3 -0.2	184	liq vap	
area 2	-7.8 -7.9	352.5 353.7	liq liq	
AB87-220.1		Pel IV	Qtz in pelite	
area 1	-58.6 -58.6 -0.7 -0.8		vap vap	
area 2	-0.5 -59.0		vap	
area 3	-0.6 -0.5	169.5 170 171 182		
AB89-33.2 area 1	-56.9 -56.8 -56.8 -4.0	Pel III 167 185	Qtz in schist vap vap vap liq liq	
area 2	-57.0	100	vap	
area 3		31 31	vap vap	
AB87-218	F	Pel IV	Qtz in pelite	

4	50.0	11 4	II.—	madium hubble at 50
area 1	-58.9 -58.6	11.4 16.7	liq liq	medium bubble at -56
	-58. 5	17.8	liq	
	-58.5	12.9	liq	small bubble at -56
	-58.4	17.1	liq	large bubble at -56
area 2	-58.1	20	vap	
	-58.1	20	vap	
	-58.1	20	vap	
area 3	-58.5	12.6	liq	most to bubble
	-58.5 -58.2	12.9 16	crit	
	-36.2	10	vap	
AB87-254.2	F	Pel IV	vap	CO2
AB87-290	F	Pel IV	Qtz in sch	nist
area 1	-0.9	256	liq	
	-1.0	200	liq	
		260	liq	
AB90-19.1		el O	Qtz in 'ch	
	-57.0 57.0	30.8	liq	others to vapor 29+
	-57.0 -56.8	30.1 29.8	liq	
	-56.8	29.6 30.6	liq liq	
	55.5	00.0	"Y	
QTZ VEINS	-)_ \/	Ot !t-	
AB87-257.2	-2.1	Pel IV 283.3	Qtz in qtz liq	vien
	-2.1 -2.2	289.8	liq	
	-2.0	277.7	liq	
	-2.1	282.7	liq	
	-2.1	283.4	liq	
	-2 .0	250.7	liq	
	-2.0	283.4	liq	
AB87-217	F	Pel IV	Qtz in qtz	: vien
plane 1	-1.0	318.6	liq	
'	-0.6	259	liq	
	-0.8	312.2	liq	
	-0.2	257.1	liq	
plane 2	-0.5	271	liq	
	-0.4	279.2	liq 	
	-0.5	265.7	liq !:-	
	-0.5 -0.4	280.3 277.3	liq liq	
	-0.4	269.5	liq	
	-0.4	277	liq	
	-0.5	285.6	liq	
	-0.5	305	liq	
AB87-212.1	F	Pel IV	Qtz in qtz	, vien
ADOR ETE.	-0.3	205.4	liq	. TIOH
	-0.5	219.5	liq	
	-0.5	214.1	liq	
	-0.6	221.8	liq	

AB87-201.1	î	Vome	Qtz in qtz vien
plane 1	-1.9	230.8	liq
	-1.7	208.5	liq
	-1.5	229.5	liq
	-1.6	228.3	liq
plane 2	-2.4	223.7	liq
		230.4	liq
		228.3	liq
	-2.3	224.9	liq
	-1.8	233.3	liq
AB87-208.3	١	Nome	Qtz in qtz vien
	-1.4	226.3	liq
	-1.5	210	liq