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René A. Wiesli
University of Tennessee

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To the Graduate Council:

I am submitting herewith a dissertation written by René A. Wiesli entitled "Geochemistry of eclogites and metapelites from the Adula nappe, Central Alps, Switzerland." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Geology.

Lawrence A. Taylor, Major Professor

We have read this dissertation and recommend its acceptance:

Claudia Mora, Theodore Labotka, Alexander VanHook

Accepted for the Council:

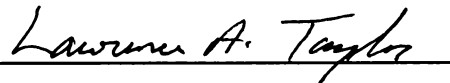
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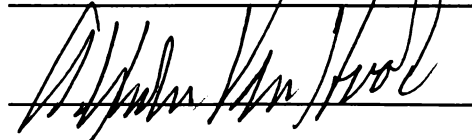
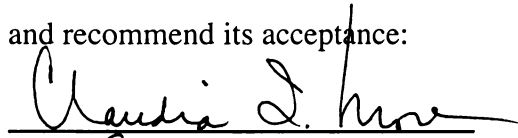
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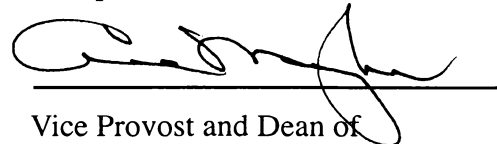


Lawrence A. Taylor, Major Professor

We have read this dissertation
and recommend its acceptance:



Accepted for the Council:



Vice Provost and Dean of

Graduate Studies

**GEOCHEMISTRY OF ECLOGITES AND METAPELITES
FROM THE ADULA NAPPE, CENTRAL ALPS, SWITZERLAND**

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

René A. Wiesli

August 2002

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ABSTRACT

Exhumed “crustal” eclogites are important recorders of physical and chemical conditions in subduction zones and allow, under favorable circumstances, evaluation of processes such as dehydration reactions, migration of fluids, mobility of elements and metasomatism. Selected group- B/C eclogites and metapelites from Trescolmen, Adula nappe, Switzerland, have been chosen for a detailed study to explore the petrogenesis and the nature and extent of fluid-rock interaction in this polymetamorphic terrane. To accomplish this objective, besides careful petrographic characterization of samples, oxygen-isotope fractionations in quartz, garnet, omphacite, kyanite, and rutile, and major- and trace-elements of the main rock-forming minerals are utilized to infer the type and magnitude of fluid-rock interaction at different scales at Trescolmen.

Major-element zonation in selected garnet porphyroblasts indicates a pre-Alpine, medium pressure growth history that has been modified under eclogite- and amphibolite-facies conditions during the Alpine orogeny. Trace-element patterns in porphyroblastic garnets show a depletion of HREE's in the rim region. Omphacites are relatively homogeneous in major elements and exhibit a LREE- and HREE-depletion. These REE-patterns can be explained by preferential partitioning of LREE into zoisite and HREE into garnet during recrystallization. In corroboration with $\delta^{18}\text{O}_{\text{WR}}$ data from eclogites (~ 5.5 to $\sim 9.5\%$), trace element patterns from whole rock analyses point to a MORB-type source as a possible protolith for the eclogites. Furthermore, the variation seen in the $\delta^{18}\text{O}_{\text{WR}}$ values in eclogites are an indication of low temperature, hydrothermal alteration in the upper oceanic crust, experienced prior to the Alpine orogeny.

Microsampling across individual garnet porphyroblasts shows a maximum zona-

tion of $\sim 0.5\%$, which indicates that the garnets grew in a closed system. Gradients in $\delta^{18}\text{O}$ of minerals in traverses across eclogite-metapelite contacts imply isotopic exchange between the two disparate lithologies. The shape of these $\delta^{18}\text{O}$ profiles across eclogite-metapelite contacts points to diffusive exchange in an at least temporarily present grain-boundary fluid. Oxygen-isotope fractionation among Qtz-Grt, Qtz-Ky, and Qtz-Rt pairs yield apparent temperatures between 550 to 750 °C. Although some mineral pairs, particularly from fine-grained samples, attain equilibrium fractionations, disequilibrium due to retention of pre-Alpine $\delta^{18}\text{O}$ values of refractory minerals such as garnet is common. Nevertheless, the overall similar fractionation values observed in minerals from eclogites and metapelites demonstrate that both lithologies experienced the last major thermal event (Alpine orogeny) together. Application of oxygen-isotope Refractory Accessory Mineral (RAM) thermometers, particularly to quartz-kyanite segregations, yields temperatures $\sim 720^\circ\text{C}$, which are higher than temperatures obtained from quartz-kyanite pairs in host rocks.

Average $\delta^{18}\text{O}$ values of quartz ($\sim 10.6\%$) from Trescolmen compare well with values of quartz from other pre-Mesozoic basement rocks in the lower Penninic nappes. This is taken as evidence that no exotic fluid, out of isotopic equilibrium, infiltrated into the Trescolmen area during Alpine metamorphism. Local $\delta^{18}\text{O}$ variation in the Trescolmen area are the result of isotopic exchange during the Alpine orogeny. This may also explain the $\delta^{18}\text{O}$ enrichment of all measured smaller ($\sim 1\text{m}$ size) eclogite boudins by interaction with a fluid derived from the metapelites during eclogite-facies metamorphism.

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PART 1

INTRODUCTION

INTRODUCTION

Exhumed and exposed high-pressure-temperature rocks, such as eclogites, in different parts of the world, allow us to extract information about physical and chemical conditions, e.g., pressure, temperature, mass- and heat transfer, during their petrogenesis. Fluids play a major role in the evolution of these metamorphic terranes. They may be carriers of chemical species and heat, and can act as a catalyst in mineral reactions.

Group B and C-type eclogites (classification after Coleman et al., 1965), embedded in metapelitic host rocks, are well exposed at Trescolmen in the polymetamorphic Adula nappe (e.g., Heinrich, 1986). Although recent studies at this locality have aimed to elucidate the structural and metamorphic evolution of this high-pressure terrane (e.g., Heinrich, 1986; Meyre and Puschig, 1993; Meyre et al., 1997; Meyre et al., 1999; Partzsch, 1998), few studies have looked in detail at the geochemistry of the eclogites and metapelites (e.g., Santini, 1992; Zack et al., 2001). Because these rocks have evidently been subducted to depth of more than 60 km during the collision of Europe with the Adriatic plate, they may provide a unique opportunity to gain insight into the behavior and interaction of fluids between the two different lithologies. Since any actual fluid phase is no longer present, suitable tracers such as oxygen isotopes or trace elements may be used to decipher past fluid-rock interaction. To get a better understanding of the oxygen-isotope systematics of this terrane, detailed sampling of the different rock types at Trescolmen was undertaken. In addition, a few other key outcrops, north and south of Trescolmen (all in the Adula nappe), have been sampled to gain a more regional picture and to put the results of Trescolmen into the proper perspective.

The results of this investigation are divided into 2 parts, which are relatively inde-

pendent from each other:

1. Geochemistry of eclogites and metapelites from Trescolmen, Central Alps, as observed from major and trace elements and oxygen isotopes.
2. Metamorphism and fluid-rock interaction in the Adula nappe: Evidence from oxygen isotopes in metamorphic minerals.

Part 1 has been published in *International Geology Review* (v. 43, 2001, p. 95-119). Part 2 has been submitted to *Contributions to Mineralogy and Petrology*.

The results of part 1 include major-element chemistry of eclogites and metapelites as well as trace-element chemistry of garnets and omphacites in eclogites from Trescolmen. It has been found that all porphyroblastic garnets from both eclogites and metapelites are zoned in terms of major elements as well as in trace elements. Specifically, garnet porphyroblasts from eclogites and metapelites in the main metapelitic zone exhibit heterogeneous zonation patterns in major elements, whereas garnets from structurally lower and higher parts (relative to the main metapelitic zone) show well developed growth zonation. In addition, oxygen-isotope systematics reveal that minerals in small eclogite boudins (< 1m) have higher $\delta^{18}\text{O}$ values (by $\sim 1\text{‰}$) than minerals in larger boudins. This difference may be attributed to fluid rock-interaction during the Alpine orogeny. Oxygen-isotope thermometry, using quartz-garnet pairs yields temperatures of approximately 600°C , consistent with estimates from phase equilibria.

Part 2 is a more detailed study of the oxygen-isotope systematics at Trescolmen and expands on the findings in part 1. Detailed traverses across eclogite-metapelite contacts revealed gradients in $\delta^{18}\text{O}$, i.e., $\delta^{18}\text{O}$ values of garnet and quartz gradually increase away from eclogites-metapelite contacts until they reach a plateau of $\sim 6.5\text{‰}$ and $\sim 11\text{‰}$

for garnet and quartz, respectively, about 1m away into the metapelites. The shape of the profile suggests diffusional exchange in an at least temporarily connected grain-boundary fluid. Furthermore, the existence of these relatively small-scale, isotopic heterogeneities imply very low fluid-rock ratios, i.e., fluids were locally derived and there was no large scale infiltration of an external “exotic” fluid. Oxygen-isotope fractionation among mineral pairs in eclogites and metapelites revealed disequilibrium in many samples. The deviation from equilibrium for some samples can be explained by diffusional resetting of $\delta^{18}\text{O}$ fractionation during cooling (Eiler et al., 1992). In addition, the quartz-garnet fractionation in coarse-grained eclogites is in many cases above 4‰. We demonstrate that these high $\Delta(\text{Qtz-Grt})$ values are due to the refractory nature of garnet and its lack of recrystallization during the Alpine orogeny. In contrast, quartz-garnet fractionation in fine grained eclogites seems to have attained oxygen-isotope equilibrium.

Application of the Fast Grain Boundary Diffusion model (Eiler et al., 1992) confirms the usefulness of oxygen-isotope Refractory Accessory Mineral (RAM) thermometers (Valley, 2001). Bi-mineralic quartz-kyanite segregations yield higher peak-metamorphic ($\sim 720^\circ\text{C}$) temperatures than previously obtained from cation partitioning.

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PART 2

**GEOCHEMISTRY OF ECLOGITES AND METAPELITES FROM
TRESCOLMEN, CENTRAL ALPS, AS OBSERVED FROM MAJOR
AND TRACE ELEMENTS AND OXYGEN ISOTOPES**

ABSTRACT

Eclogites are commonly the only tangible high-pressure evidence we have from a paleo-subduction zone, and they potentially preserve important geochemical information from the descending slab. Selected Group B/C eclogites and metapelites from the Trescolmen locality in the Adula nappe, central Swiss Alps, were chosen for a detailed investigation of oxygen isotope and major- and trace-element compositions of the main rock-forming minerals. Complex major-element zonation patterns in garnet porphyroblasts indicate a pre-Alpine, medium-pressure growth history coupled with high pressure modification during the Alpine orogeny. Garnet REE-patterns are notably HREE-depleted in rim regions, with a high overall REE content, particularly in the cores of grains. Omphacites are relatively homogeneous in major elements, and show LREE- and HREE-depleted patterns, but with overall abundances of REEs lower than in garnets. These patterns are best explained by partitioning of the HREEs into garnet and the LREEs into zoisite. Oxygen-isotope systematics indicate overall limited fluid flow in eclogites and surrounding metapelites. $\delta^{18}\text{O}$ values of quartz and garnet near the interface between eclogites and metapelites are indistinguishable and point to some isotope exchange. Oxygen-isotope fractionation among rock-forming minerals in eclogites and metapelites indicate equilibrium at $\sim 600^\circ\text{C}$. The $\delta^{18}\text{O}$ of unaltered eclogites (5.5 to 6‰) suggests a basaltic, MORB-type protolith.

INTRODUCTION

Many “crustal” eclogites are the high-pressure “dry” equivalents of rocks of basaltic composition and are usually formed in a subduction zone environment (Evans et al.,

1979, 1981). Their geologic value is that they are often the only direct evidence we have of the geochemical processes occurring in a subduction zone. The movement of fluids and the mobility of elements in this environment have been investigated by many workers, but are presently not well determined. Oxygen-isotope studies of fluid mobility indicate fluid flow on a large scale (e.g., Bebout and Barton, 1989) or restricted to, small, meter-sized domains (e.g., Nadeau et al., 1993; Getty and Selverstone, 1994).

Garnet is one of the main refractory minerals in eclogites and metapelites and can be useful in deciphering the metamorphic evolution of a rock (e.g., Selverstone et al., 1984). This is due to its occurrence in a variety of bulk compositions over a wide range of pressure-temperature conditions, its low diffusivity for major and minor cations and oxygen, its refractory nature, and its ability to form solid solutions with the main mineral-forming elements, such as Ca, Fe²⁺, Fe³⁺, Mg, Mn, Al, and Ti. Zonation in major- and trace-element contents and oxygen isotopes in garnet can give important clues about conditions under which the garnet formed (Tracy et al., 1976; Hickmott et al., 1987, 1992; Kohn et al., 1993) allowing one to reconstruct the petrogenesis of the rock.

Relict high-pressure rocks (i.e., eclogites) are found as boudins and lenses, particularly in the tectonic upper part of the Penninic Adula nappe in the central Swiss Alps (Heinrich, 1986). Recent studies have focused on its structural and metamorphic evolution (e.g., Heinrich, 1982, 1983, 1986; Meyre and Puschnig, 1993; Meyre et al., 1998, 1999). Few studies have concentrated on both the geochemistry (Santini, 1992; Bocchio et al., 2000; Zack et al., 2001) and the oxygen-isotope systematics of eclogites and metapelites (Früh-Green, 1987) in the middle part of the Adula nappe.

We focus our investigation on the middle part of the Adula nappe, particularly on

the well-exposed eclogites embedded in the metapelitic schists at Trescolmen. Several workers have reported complex-zoning patterns in garnets from this part of the nappe (e.g., Meyre et al. 1998). The present study utilizes these zonations in major, trace, and oxygen isotopes in the garnets as records of changing metamorphic conditions. Oxygen isotope and trace- and major-element data are presented for minerals in eclogites and metapelites to better determine the nature of the protoliths and their metamorphism. The objectives for this study are: (1) to characterize the mineralogy, petrography, and geochemistry of eclogites and metapelites at Trescolmen; (2) investigate the oxygen-isotope systematics between the two rock types; (3) elucidate the petrogenesis of the two rock types.

GEOLOGIC SETTING

The study area is located in the Adula nappe, with particular emphasis on the Trescolmen locale. The Adula nappe is located in the southeastern Swiss Alps (Fig. 1) and is part of the Penninic nappe stack that resulted from the convergence and collision of the southern margin of Europe with the Adriatic plate during the early Eocene (e.g., Schmidt et al., 1996). The rock types of the Adula nappe consist mainly of metagranitoid gneisses and metapelitic schists of pre-Mesozoic age, with minor mafic lenses concentrated in the metapelites (e.g., Heinrich, 1986).

At Trescolmen (Fig. 2 and 3), eclogites are particularly well exposed and usually embedded in garnet-white mica schists. The metamorphic history of these rocks includes early Tertiary high-pressure metamorphism related to the southward subduction of European margin followed by amphibolite-facies overprint during exhumation. Although both rock types may have experienced the eclogite facies event during the early Tertiary, evi-

Figure 1. Simplified tectonic map of the Adula nappe. Included is the Cima Lunga unit. The analyzed samples are from Trescolmen, located in the middle part of the nappe. Numbers on the side refer to the Swiss national grid (in km). Modified after Heinrich (1983).

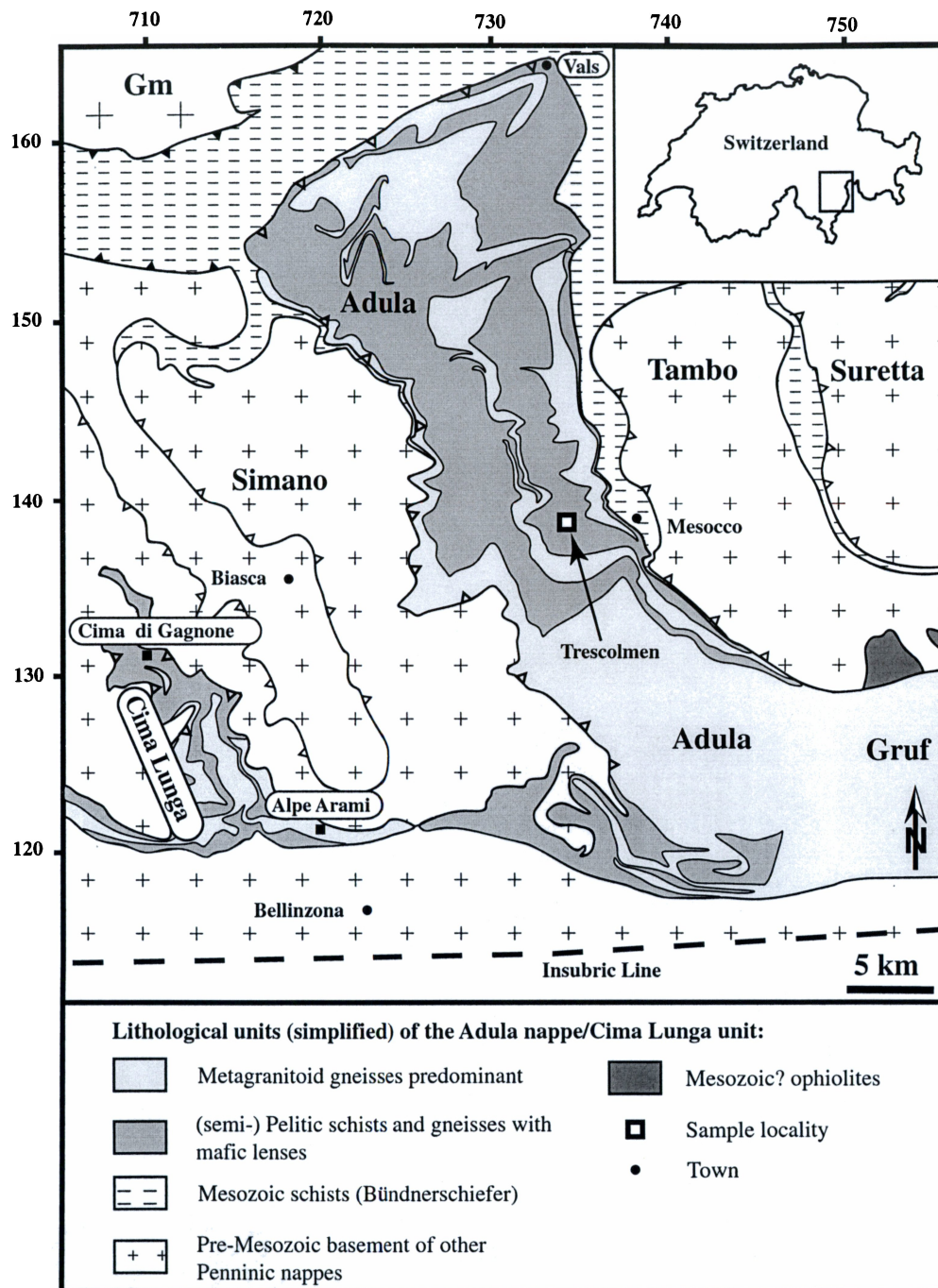
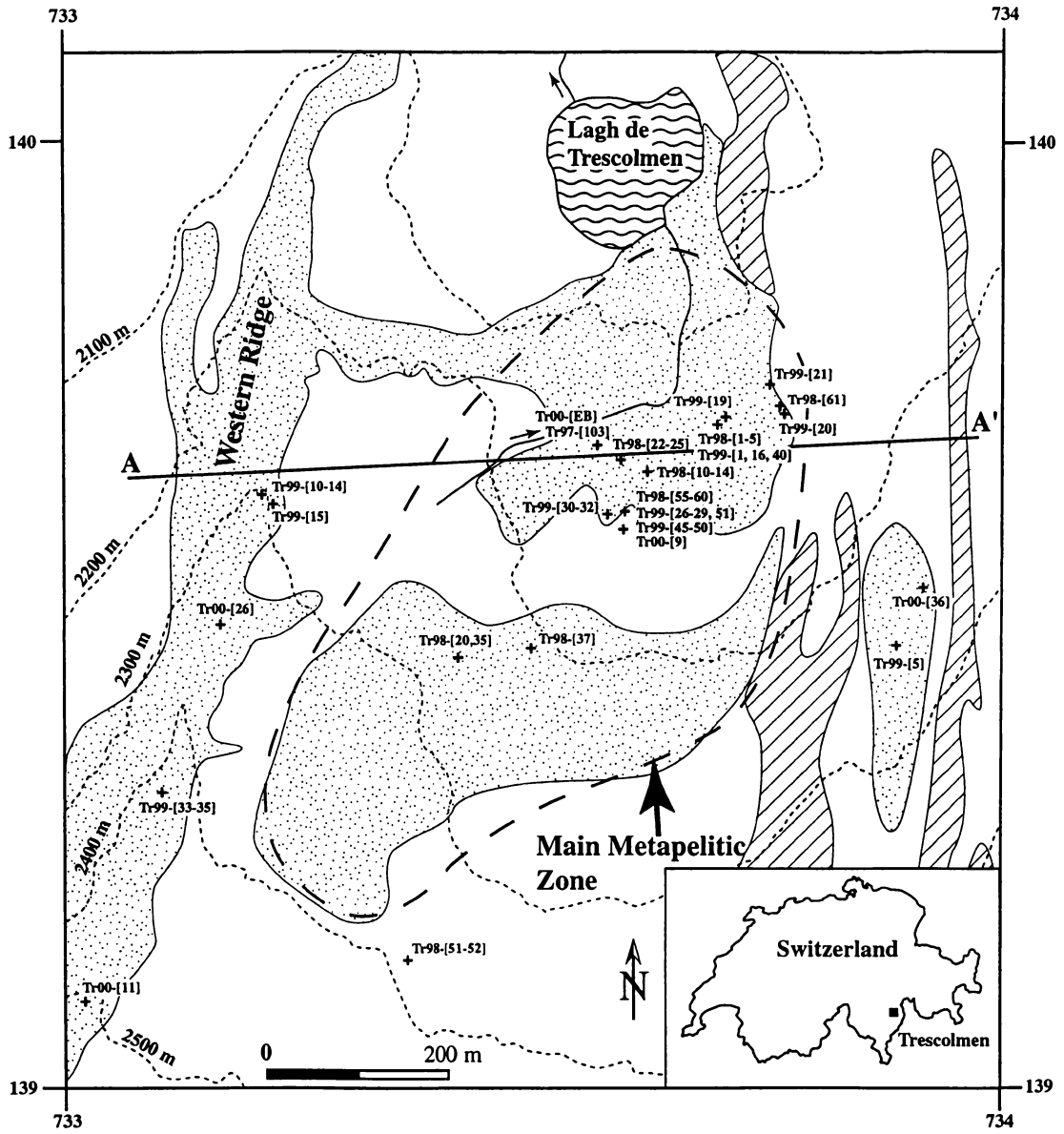


Figure 2. Simplified geologic map of the Trescolmen area with sample localities referred to in this paper. Redrawn after Puschig (1992) and Meyre (1993). Stippled areas indicate metapelite, with the numerous mafic boudins not shown. Diagonally ruled areas indicate phengite or two mica gneisses. White areas indicate debris fields, talus, or grass. The main metapelitic zone is marked with a thick, dashed line. Numbers on the side refer to the Swiss national grid (in km). Tectonic levels increase from west to east. Thin dashed lines are topographic contour lines with elevations given in meters. Cross-section A-A' is given in Figure 3.



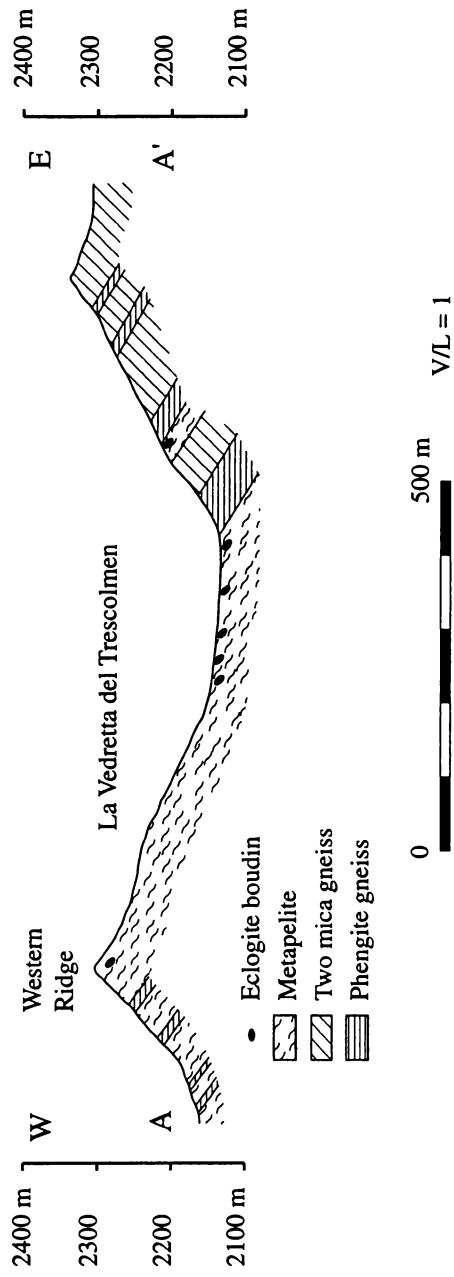


Figure 3. Schematic cross-section of the Trescolmen area. The location of the traverse A-A' can be seen on Figure 2. The main foliation dips about 35° east (S3, Zapport deformation, Partzsch, 1998).

dence of this high-pressure event is preserved mainly in the eclogite boudins. Metapelites, on the other hand, have been severely overprinted during the amphibolite facies event. Only in rare cases, as inclusions in eclogite boudins, did high pressure assemblages survive in metapelites. During decompression, dehydration of metapelites provided a fluid phase, which locally overprinted the margins of eclogite boudins to a symplectitic intergrowth of hornblende and plagioclase +/- diopside. Pressure-temperature calculations for the eclogites yield conditions of ~19-20 kbar and 650-700 °C during the early stages of exhumation, whereas some rare metapelitic assemblages yield peak conditions of ~24 kbar and ~600 °C (Meyre et al., 1999).

A MORB-type source has been suggested as a possible protolith for the eclogites (Santini, 1992), based on trace-element data. However, unlike the mafic rocks within the Cima Lunga unit, for which an oceanic affinity has been firmly established (Evans et al., 1979), this interpretation is not certain for some eclogite samples from Trescolmen, as shown later in this study. Several possibilities have been suggested for the mechanism and timing of emplacement of the mafic rocks into the metapelites. One possibility is the disruption and imbrication of oceanic crust during the Alpine orogeny, producing exotic blocks in pelitic material of continental affinity (Trommsdorff, 1990). Another is emplacement of dikes, lava flows and/or tuffs on the thinned continental European margin, before the collision of Europe with the Adriatic plate (Zack et al., 2001). In light of the different types of mafic rocks (e.g., eclogites, garnetites), and the wide range of geochemical signatures observed in them, the second alternative is favored at the moment.

Quartz veins at Trescolmen are abundant and give ample evidence for the presence of a fluid during the evolution of this metamorphic terrane, similar to other eclogitic

terrane (e.g., Barnicoat, 1988). Many eclogites are crosscut by irregular quartz veins and veinlets (Heinrich, 1986). The size of these quartz features varies from millimeters to meters in width or length. Minerals at the vein-host rock interface suggest that not all veins are in equilibrium with the host rock. However, kyanite, phengite, omphacite, and rutile are found as inclusions in the veins. Some of the larger veins (i.e., width < 0.5 m, length < 25 m) that crosscut eclogites and metapelites are probably related to amphibolite-facies metamorphism during exhumation, as quartz in these veins is enriched in $\delta^{18}\text{O}$ relative to smaller veins in eclogites (Wiesli et al., 2002).

Age dating using U-Pb zircon and Sm-Nd (Grt, Cpx, and whole rock) methods in the Cima Lunga unit (Becker, 1993; Gebauer et al., 1992, Gebauer, 1996) indicated a Tertiary age for the high-pressure metamorphic event. Additional information on the geology of the Adula nappe can be found in Frischknecht (1923), Heinrich (1982, 1986), Löw (1987), and Partzsch (1998).

ANALYTICAL TECHNIQUES

Modal Analysis

Modal analyses were obtained using a point-counter. Depending on grain size, up to 8000 points per thin section were counted. However, the modal contents are only valid for a particular thin section since abundances of phases vary within a given hand-specimen, even on a centimeter scale.

Major elements

Chemical analyses of major elements were performed on polished thin (30 μm) and thick ($\sim 600 \mu\text{m}$) sections by electron microprobe using the automated CAMECA SX-

50 electron microprobe (EMP) at the University of Tennessee. The accelerating voltage used was 15 kV, with a beam current of 20 or 30 nA. The beam size employed, depending on grain size, was either 5, 10, or 50 μm , with counting times of 20 seconds for each element. For glass-bead analyses, a beam size of 30 μm and a current of 20 nA were employed. Data were corrected applying the CAMECA PAP (Poucheau and Pichoir, 1985) correction procedure.

Bulk-rock fused-beads were prepared for EMP analyses following a procedure similar to that of Jezek et al. (1978), whereby rock powder was fused on a Mo strip-heater in a nitrogen atmosphere. A representative composition for a sample was obtained by at least 14 EMP analyses, from which the mean is reported. The loss of volatiles during the ~ 25 second heating is a potential problem but from previous experience with this technique in our lab, the volatile loss is at most 1%.

Trace elements

In-situ trace-element analyses on garnet porphyroblasts and coexisting omphacites were performed by laser-ablation inductively coupled-plasma, mass spectrometry (LA-ICP-MS) at the Department of Geological Sciences, Tsukuba University, Japan. Details of the analytical procedures can be found in Longerich et al. (1996). Detection limits for 80 μm spot size were in the range from 0.2 to 2 ng/g for most heavy elements ($Z > 80$), and 1 to 10 ng/g for light elements, except for Si, Ca, and Ti. For these elements, detection limits were 1, 6, and 100 $\mu\text{g/g}$, respectively. The software package LAMTRACE (Jackson et al., 1992) was used for data reduction to obtain concentrations in ppm.

Oxygen isotopes

Oxygen-isotope analyses were performed on mineral separates or chips (usually

weighing between 1 to 2 mg) by heating samples in BrF_5 , using a 32 W CO_2 laser mounted on-line to a dual-inlet Finnigan MAT 251 mass spectrometer at the University of Wisconsin at Madison. Every day, prior to analysis of samples, at least 4 aliquots of UWG-2 garnet standard were analyzed, yielding an average of $5.77 \pm 0.1\text{‰}$ (1 SD, $1 \sigma = 0.01 \text{‰}$) over the 13 day period in which these samples were measured. All analyses were corrected to University of Wisconsin Gore Mountain garnet standard (UWG-2) which has a recommended value of $\delta^{18}\text{O}$ of $5.8 \pm 0.1\text{‰}$ (1σ), yielding $\delta^{18}\text{O} = 9.59\text{‰}$ for NBS-28 African Sand (Valley et al., 1995). The average correction based on each day's analyses of UWG-2 was 0.03‰ . NBS-28 analyzed on the same day as UWG-2 yielded 9.33‰ , and 5.76‰ , respectively, making $\Delta^{18}\text{O}_{\text{NBS28-UWG2}} = 3.57\text{‰}$. Replicate analyses were performed on many samples, and for those the average is reported. Microsampling with a spatial resolution of about 0.5 mm, using the thin-saw blade technique (Kohn et al., 1993), was utilized to check for possible zonation in $\delta^{18}\text{O}$ in garnet porphyroblasts. Mineral separates were obtained by crushing about 0.5 cm^3 of a sample and handpicking using a binocular microscope. Only inclusion-free minerals were analyzed. Small discrepancies up to 0.3‰ have been reported for the analysis of clinopyroxene by laser fluorination and conventional technique because of analytical difficulties. Kohn and Valley (1998) suggested that clinopyroxene should either be uncorrected or corrected upwards by at most 0.3‰ , using the laser-fluorination technique. Also, analysis of fine grained quartz has caused some problems using lower powered CO_2 lasers (Sharp and Kirschner, 1995; Fouillac and Girard, 1996). This potential problem is obviated by operating the CO_2 laser at the University of Wisconsin at a higher power setting (Spicuzza et al., 1998). All analyses are reported with respect to V-SMOW.

PETROGRAPHY

For the present study, 5 eclogite and 4 metapelite samples from Trescolmen were chosen from our larger collection. These samples were selected for freshness and contain a variety of minerals in different proportions. Consideration was also given to the size of the garnet porphyroblasts because of the intended analyses by LA-ICP-MS. The following convention has been applied to accommodate the spatial relationships among the different samples: metapelites within 20 cm of the contact with an eclogite boudin will be labeled Mp1; metapelites anywhere from 20 cm to several 100 m away from eclogite boudins will be labeled Mp2; metapelites close to the structural boundary of the Trescolmen cirque will be labeled Mp3; eclogites from small boudins, i.e., less than 3 m in size and samples from rims of larger boudins will be labeled E2; eclogites from the core regions of larger boudins, i.e., more than 3 m in size, will be labeled E1. All mineral abbreviations used in this paper are after Kretz (1983).

The investigated eclogites consist of a variety of assemblages: kyanite + zoisite + white mica + amphibole, clinozoisite + kyanite + white mica + amphibole + ankerite, and clinozoisite + amphibole. All assemblages also contain quartz, omphacite, garnet, rutile, ilmenite, and apatite (Table 1). The metapelites at Trescolmen contain the assemblages: quartz + white mica + garnet + chlorite + kyanite + plagioclase + biotite + epidote (Mp1 and Mp2) and quartz + white mica + chlorite + staurolite + kyanite + garnet + plagioclase + biotite (Mp3). Both assemblages also contain apatite, rutile, zircon, monazite, and magnetite (Table 1).

The most visible characteristics of the metapelites are the axial planar S3 foliation (Zapport deformation phase, see Partzsch 1998) and the reddish-brown garnet porphyro-

Table 1. Modal abundances and whole-rock chemistry.

Sample Assemblage	Tr99-19B eclogite	Tr98- 20b eclogite	Tr98-5c eclogite	Tr97-103 eclogite
<i>Modal abundances (vol.%)¹</i>				
Grt	33.6	34.3	38.6	29.7
Omp	58.9	42.6	48.9	52.7
Qtz	3.3	4.3	5.3	4.7
Cam	<1	1.3	<1	1.5
Zo/Czo	1	<1	<1	5.3
Ky	-	-	-	4.5
St	-	-	-	-
Rt	1.6	2.8	1.5	1.2
Ap	<1	1.1	<1	<1
White mica	-	6.2	-	<1
Symplectite	2.2	6.7	2.9	<1
Bt	-	-	-	-
Chl	-	-	-	-
Zrn	<1	<1	<1	<1
Mag	-	-	-	-
Py	-	-	-	-
Pl	-	-	-	-
<i>Whole-rock analyses (wt.%)²</i>				
SiO ₂	48.6	46.5	48.3	48.8
TiO ₂	1.59	2.25	0.74	1.03
Al ₂ O ₃	15.2	15.7	15.0	15.4
Cr ₂ O ₃	0.04	0.06	0.10	0.15
MgO	7.78	5.94	7.93	9.41
CaO	11.4	10.8	11.52	12.5
MnO	0.19	0.21	0.22	0.17
FeO ³	10.6	12.7	11.8	7.86
Na ₂ O	2.29	3.27	2.86	2.57
K ₂ O	<0.03	0.29	<0.03	<0.03
P ₂ O ₅	0.11	0.34	0.11	0.14
Total ⁴	97.9	98.1	98.5	98.3
Mg # ⁵	56.6	45.4	54.5	68.1

(continues)

Table 1. (continued)

Sample Assemblage	Tr99-35 metapelite	Tr99-58 metapelite	Tr99-20b metapelite	Tr99-5aa metapelite
<i>Modal abundances (vol.%)</i>				
Grt	16.0	23.1	6.7	8.6
Omp	-	-	-	-
Qtz	18.5	46.7	64.1	35.5
Cam	-	-	-	-
Zo/Czo	-	<1	-	<1
Ky	<1	7.2	<1	<1
St	1.2	<1	-	<1
Rt	<1	<1	<1	<1
Ap	<1	<1	<1	<1
White mica	55.0	15.5	24.0	37.8
Symplectite	-	-	-	-
Bt	4.3	3.6	1.7	3.0
Chl	1.7	1.8	<1	8.6
Zrn	<1	<1	<1	<1
Mag	<1	<1	<1	<1
Py	-	-	-	<1
Pl	1.1	1.0	2.9	7.3
<i>Whole-rock analyses (wt.%)</i>				
SiO ₂	55.5	67.2	67.3	60.5
TiO ₂	1.13	0.73	0.94	0.89
Al ₂ O ₃	23.1	16.3	16.2	19.7
Cr ₂ O ₃	<0.03	<0.03	0.03	<0.03
MgO	2.30	2.32	1.91	2.43
CaO	0.77	1.11	0.84	0.83
MnO	0.26	0.10	0.06	0.23
FeO	8.75	6.39	5.82	8.24
Na ₂ O	1.44	1.05	3.03	1.15
K ₂ O	3.95	2.18	2.01	3.07
P ₂ O ₅	0.25	0.09	0.03	0.17
Total	97.5	97.4	98.2	97.3
Mg #	31.9	39.3	36.9	34.4

¹ Determined by point counting, up to 8000 points per thin section.

² Each analysis represents the average of at least 14 EMP analyses of a fused bead.

³ Iron was analyzed as Fe and calculated as FeO.

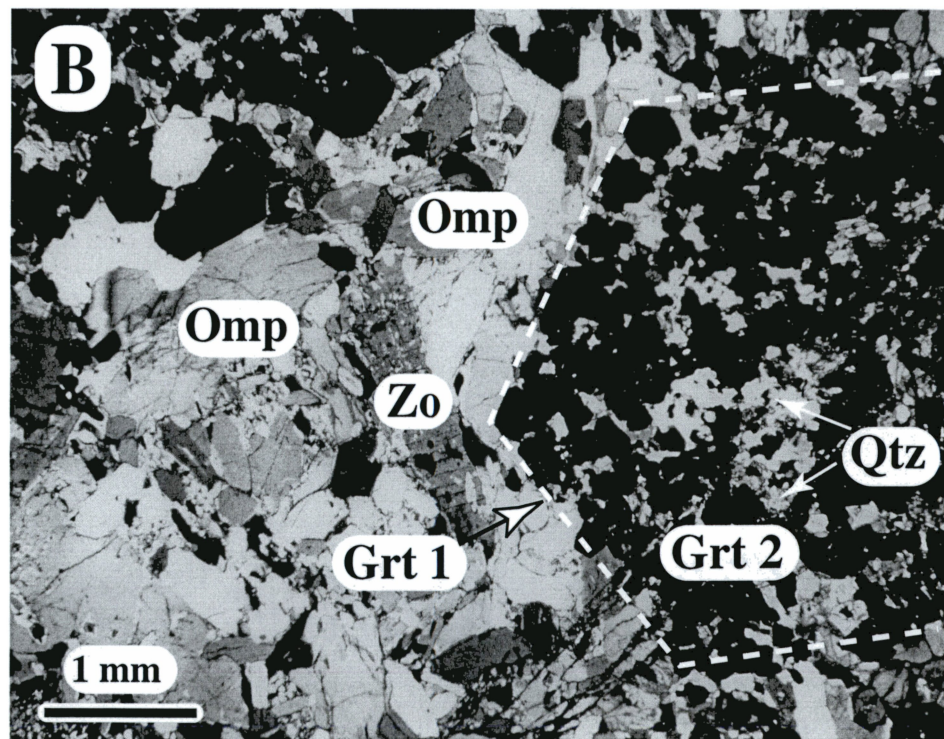
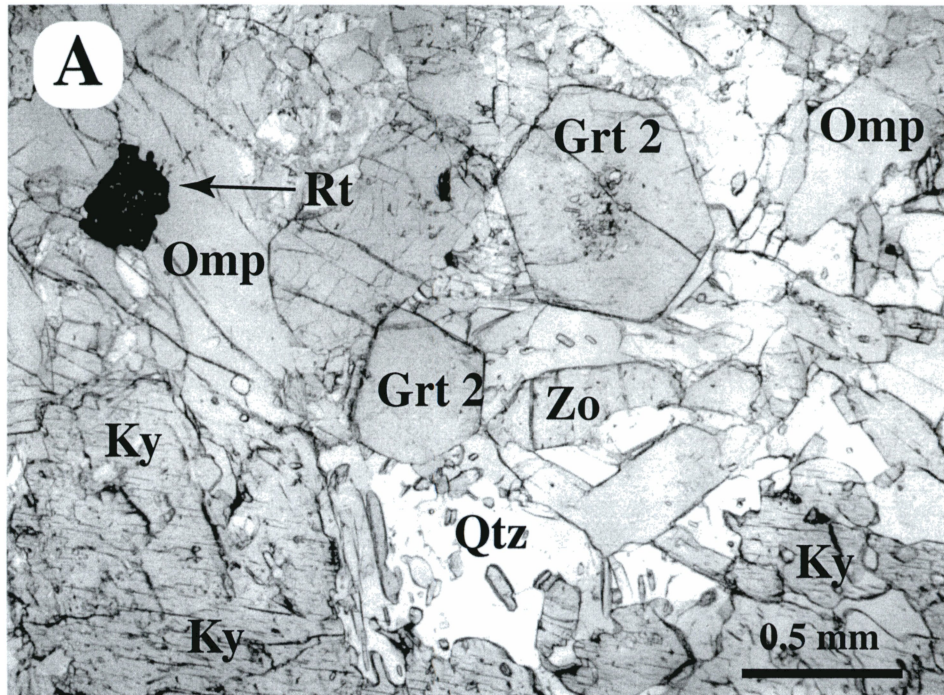
⁴ The low totals represent the loss of water and other volatiles during preparation of the fused bead.

⁵ $[\text{Mg}/(\text{Mg} + \text{Fe})]_{\text{moles}} \times 100$.

blasts. The penetrative foliation is defined by alignment of white mica and quartz ribbons. Other minerals in the matrix are plagioclase, kyanite, staurolite, epidote, apatite, monazite, zircon, magnetite, and allanite. Garnet porphyroblasts can reach sizes of more than 2 cm and contain inclusions of quartz, kyanite, staurolite, apatite, zircon, mica, rutile, and some have traces of plagioclase.

Eclogite specimens have a pale-green and pink color in hand samples, with a porphyroblastic, granular texture. Eclogites with porphyroblastic textures (i.e., garnet diameter > 2 mm) predominantly occur in boudins larger than ~ 1.5 m in size. Garnet porphyroblasts can reach sizes of up to 15 mm and are usually anhedral- to subhedral (Fig. 4a). Some of the garnet porphyroblasts appear to have been shattered and disaggregated, and the rims recrystallized to smaller, subhedral to euhedral garnet grains (Fig. 4b). The outline of the original, euhedral garnet can in many cases still be observed (Fig. 4b). From these textural observations, garnets are subdivided into two generations. The large, older porphyroblastic garnets are labeled Grt 1, whereas the smaller, younger garnets are labeled Grt2. These garnet porphyroblasts contain inclusions of quartz, rutile (sometimes intergrown with ilmenite), zircon, amphibole, apatite, paragonite, and epidote-group minerals. Some of the smaller, euhedral Grt 2 garnets, with few or no inclusions can also be found in the omphacite matrix (cf., Meyre et al., 1998). The matrix of the eclogites is to a large part made up of anhedral to subhedral omphacite, with grain size up to several millimeters, but on average less than a millimeter and often recrystallized. In some sections, omphacite displays a weakly aligned fabric (Fig. 5). In general, the omphacites from the larger boudins appear unaltered. However, when observed in thin sections in reflected light, they always have a symplectitic texture along grain boundaries. This symplectitic

Figure 4. Photomicrographs of representative textures in eclogites. **A.** Sample Tr97-103 with a granoblastic texture (plane polarized light). **B.** Same sample as in A but showing relict garnet Grt 1 (crossed-polarized light).



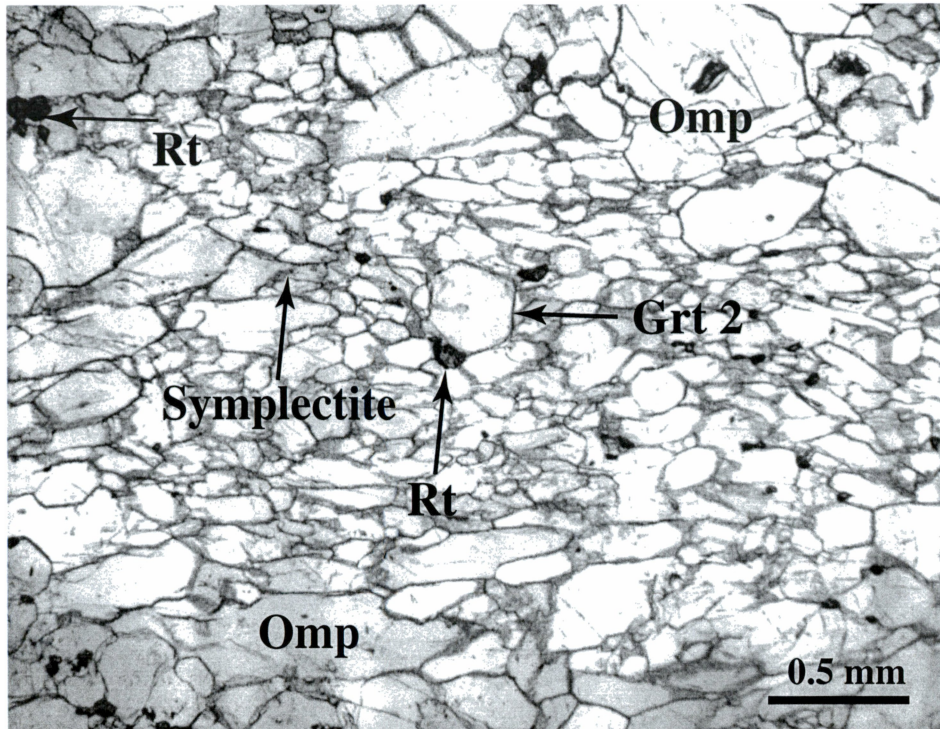


Figure 5. Photomicrograph of slightly aligned and recrystallized omphacites. Boundaries of omphacites in this sample consist of symplectite, i.e., an intergrowth of plagioclase, amphibole and clinopyroxene (sample Tr98-3, plane-polarized light).

texture consists of a small scale (~10 to 40 μm), wormlike intergrowth of clinopyroxene, albite-rich feldspar, and amphibole.

Epidote-group minerals occur in all eclogite samples. Typically, they are small (< 300 μm), subhedral, and are observed at the interface between garnet and omphacite. In sample Tr97-103, bladed zoisite, with minute (< 25 μm) inclusions of quartz, reach a length of over 3 mm. This eclogite also contains kyanite. Amphibole and apatite, usually anhedral, have been observed in all the samples. Rutile, sometimes intergrown with il-

menite and rarely rimmed by sphene (in sample Tr98-20b), occurs randomly distributed in all sections.

BULK CHEMISTRY

Eclogites

Bulk-rock analyses were performed on samples Tr97-103, Tr98-20b, Tr98-5c, and Tr99-19B (Table 1). The results are comparable to modern basalts described in the literature (e.g., Sun et al., 1979) and compare well to bulk-rock analyses of eclogites from Cima di Gagnone (Fig. 1; Evans et al., 1979). In particular, low concentrations of K_2O measured in the Cima di Gagnone eclogites can also be observed in eclogites from Trescolmen.

Metapelites

The metapelitic samples chosen for bulk-rock analyses are from the main metapelitic zone (samples Tr99-20b and Tr99-58) and from the border region of the cirque of Trescolmen (Tr99-5aa and Tr99-35). Major-element compositions of the four samples are presented in Table 1. These values compare well with compilations of shales and pelites given by Taylor and McLennan (1985).

MINERAL CHEMISTRY

Eclogites

Garnets. The eclogite garnets from Trescolmen display a wide compositional range (Fig. 6). Heinrich (1983) has also reported on their wide range in compositions and zonations. The various X-ray maps (e.g., Fig. 8 and others) performed in this study reveal

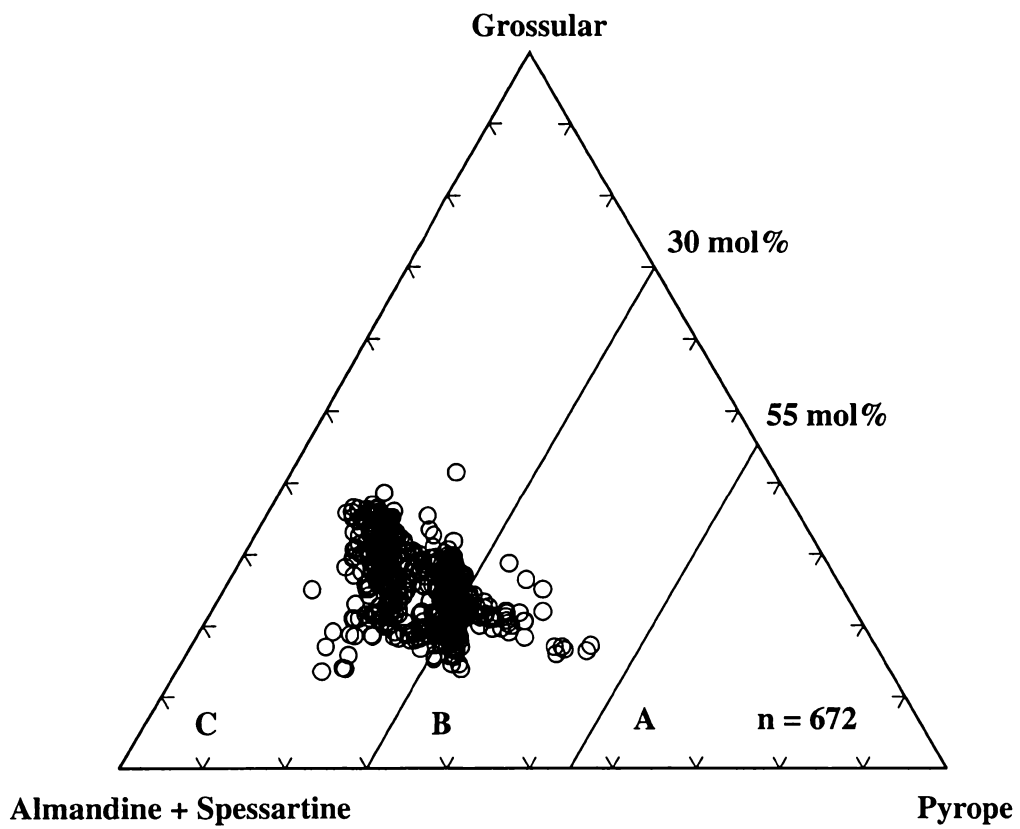


Figure 6. Ternary diagram for garnets in eclogites from Trescolmen. Group boundaries are after Coleman (1965).

subtleties in composition that would not have been detected with conventional line traverses. The compositions of garnets from four representative eclogite samples from our study can be seen in Figure 7. In the chemical classification scheme adapted from Coleman et al. (1965), the garnets plot mainly in the group C field, with some in the group B field. Within single garnet porphyroblast, e.g., Tr98-3-3-1, a considerable variation exists, as large as in all other garnets combined.

Garnet porphyroblasts from the eclogites all exhibit complex-zoning patterns, as seen in compositional maps. Sample Tr98-3-3-1, which is from a large boudin (i.e., > 20 m exposed), exhibits typical zoning patterns, as depicted with a Ca X-ray map (Fig. 8). The most obvious feature in the X-ray map are the distinct domains of Ca concentration. Ca concentration changes by up to 4 wt.% within a distance of 20 μm . The actual compositional variation from the line traverse A-B is shown in Figure 9. Optically, the garnet is homogeneous, i.e., no physical cracks are visible where some of the Ca-rich zones occur in fracture-like arrays in the core. The boundaries of the different zones in the garnet are well-defined in the Ca X-ray map, but are poorly shown by Mg and Fe X-ray maps.

In contrast to Tr98-3-3-1, garnet in sample Tr98-5c is only about 3.5 mm in diameter (Fig. 10). The Ca X-ray map reveals that this garnet is relatively homogeneous and has a smaller compositional range (Fig. 11). The average composition of the inner region of this garnet is similar to the rim composition in the garnet of sample Tr98-3-3-1 (see Figures 9 and 11).

The euhedral porphyroblastic garnet from sample Tr98-20b has a diameter of about 13 mm. This garnet possesses a concentric zoning pattern in major elements, is relatively homogeneous in its interior (Fig. 12), and the compositional change is limited to the rim

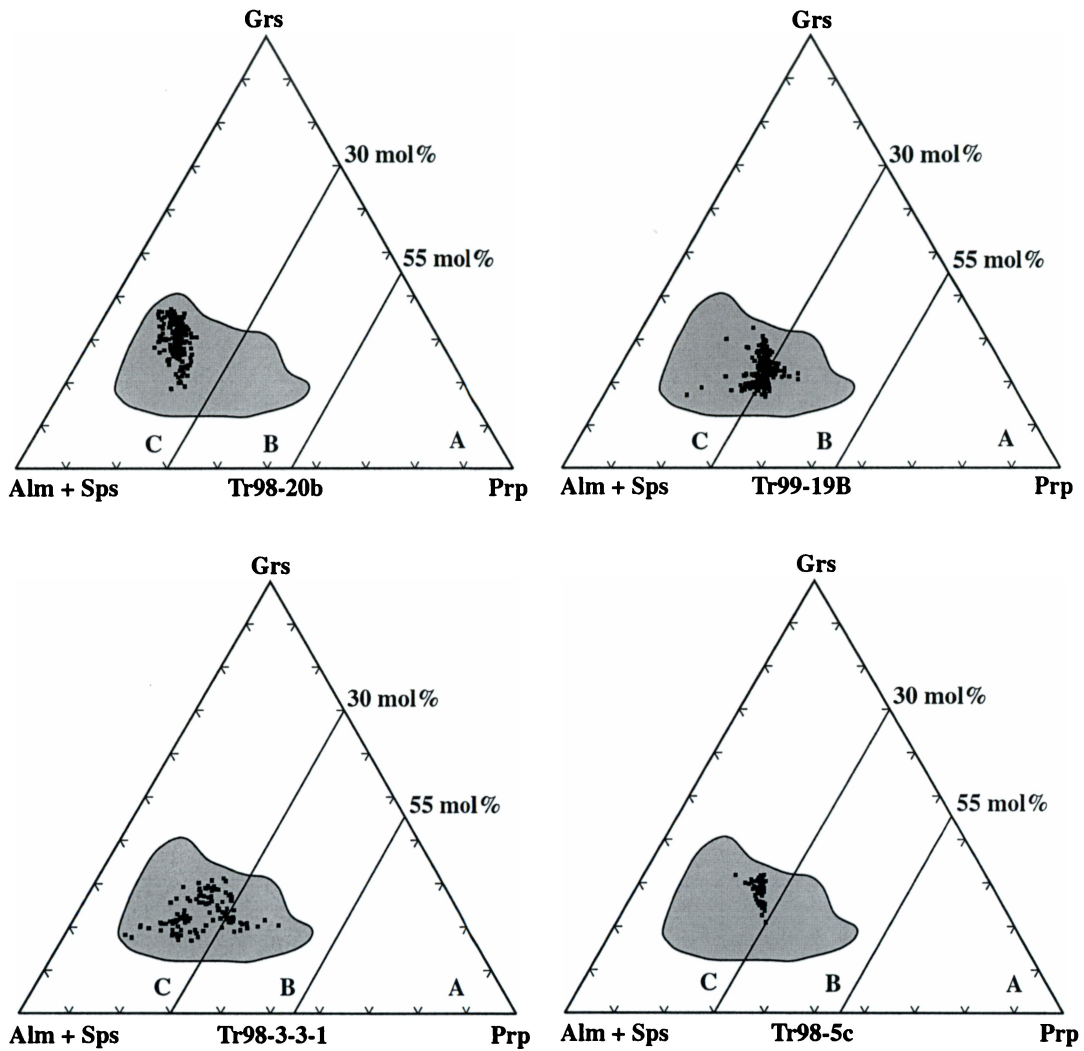


Figure 7. Compositional variations in selected garnets from eclogites. Samples considered are Tr98-20b, Tr99-19B, Tr98-3-3-1, and Tr98-5c. The shaded region encloses all garnet analyses of eclogites from Trescolmen. Group boundaries are after Coleman et al. (1965).

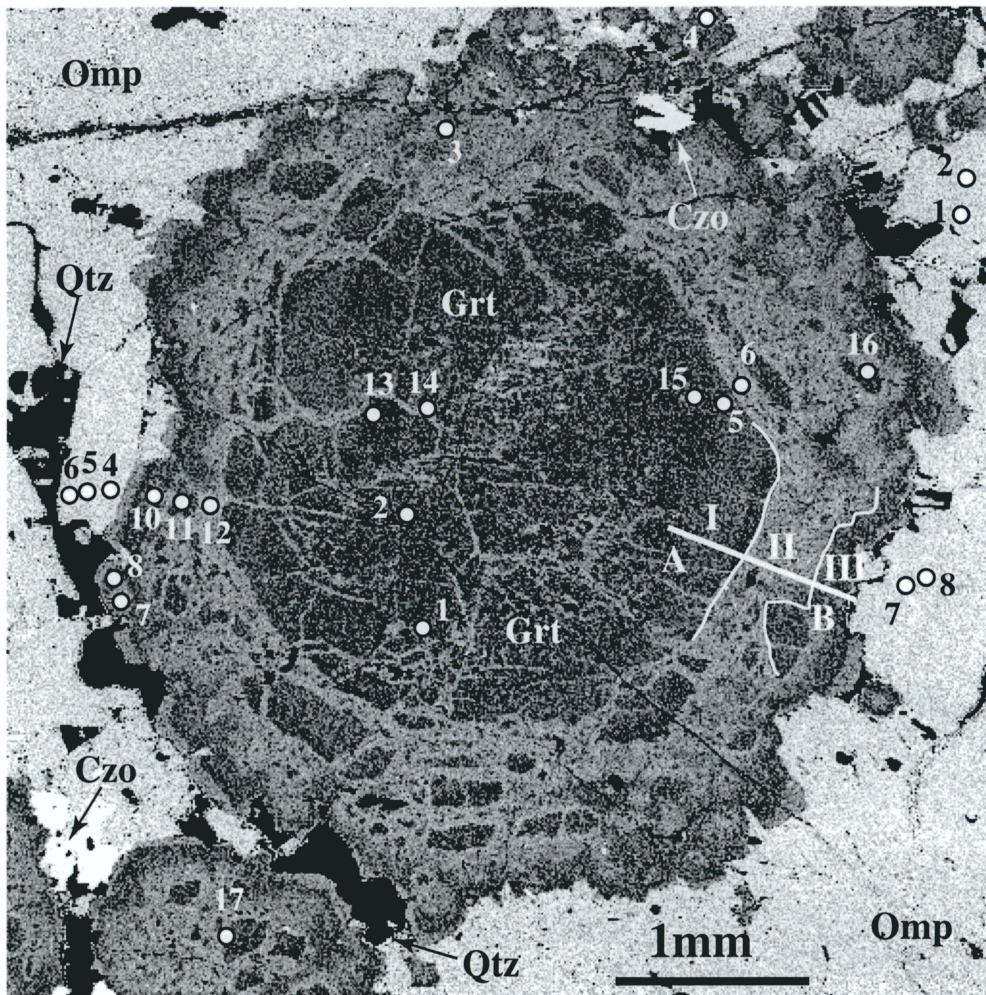
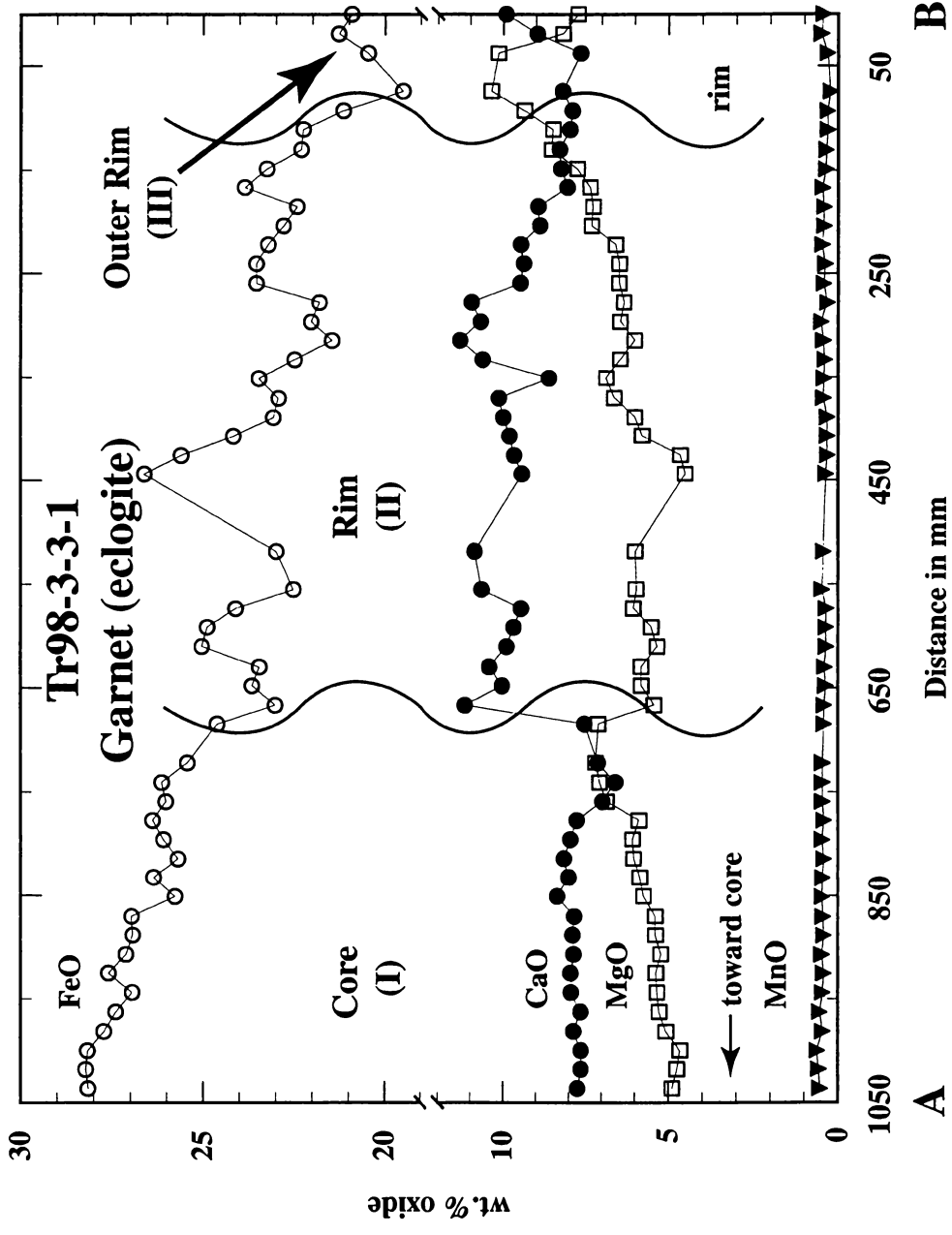


Figure 8. Calcium X-ray map of a garnet in sample Tr98-3-3-1 (eclogite). Lighter shades of gray indicate higher Ca abundance. The EMP traverse A-B is given in Figure 9. Roman numerals I, II, and III on the traverse refer to the different domains given in Figure 9. The overall compositional variation can also be seen in Figure 7. The boundaries in the vicinity of the traverse have been emphasized. Notice the subhedral morphology of the original garnet (low Ca, i.e., high Fe) in the central region. Circles indicate points of LA-ICP-MS analyses and the associated numbers refer to the number of the analyses given in Tables 2 and 3.

Figure 9. Line traverse A-B in a garnet from sample Tr98-3-3-1 (eclogite). Notice the sharp change in the composition of the remnant garnet toward the rim region. The positions of the different domains (core I, rim II, and outer rim III) can be seen in Figure 8.



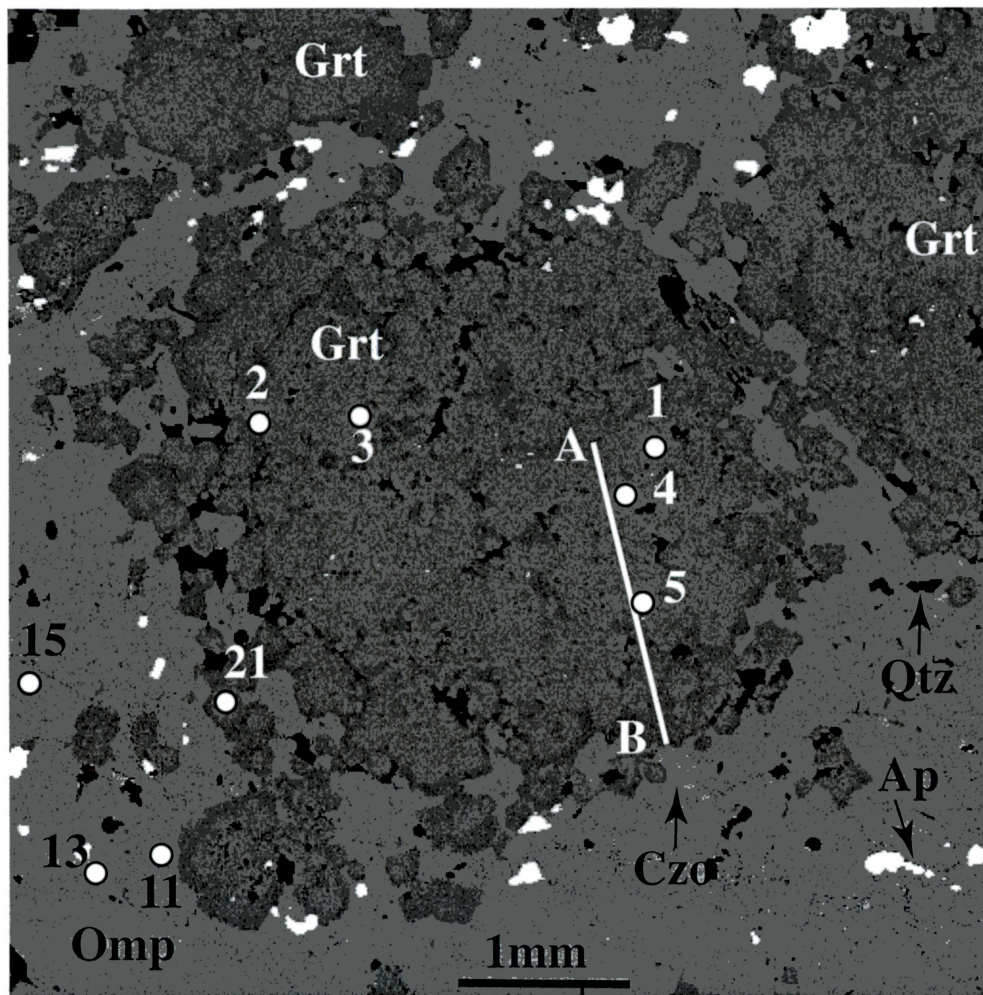
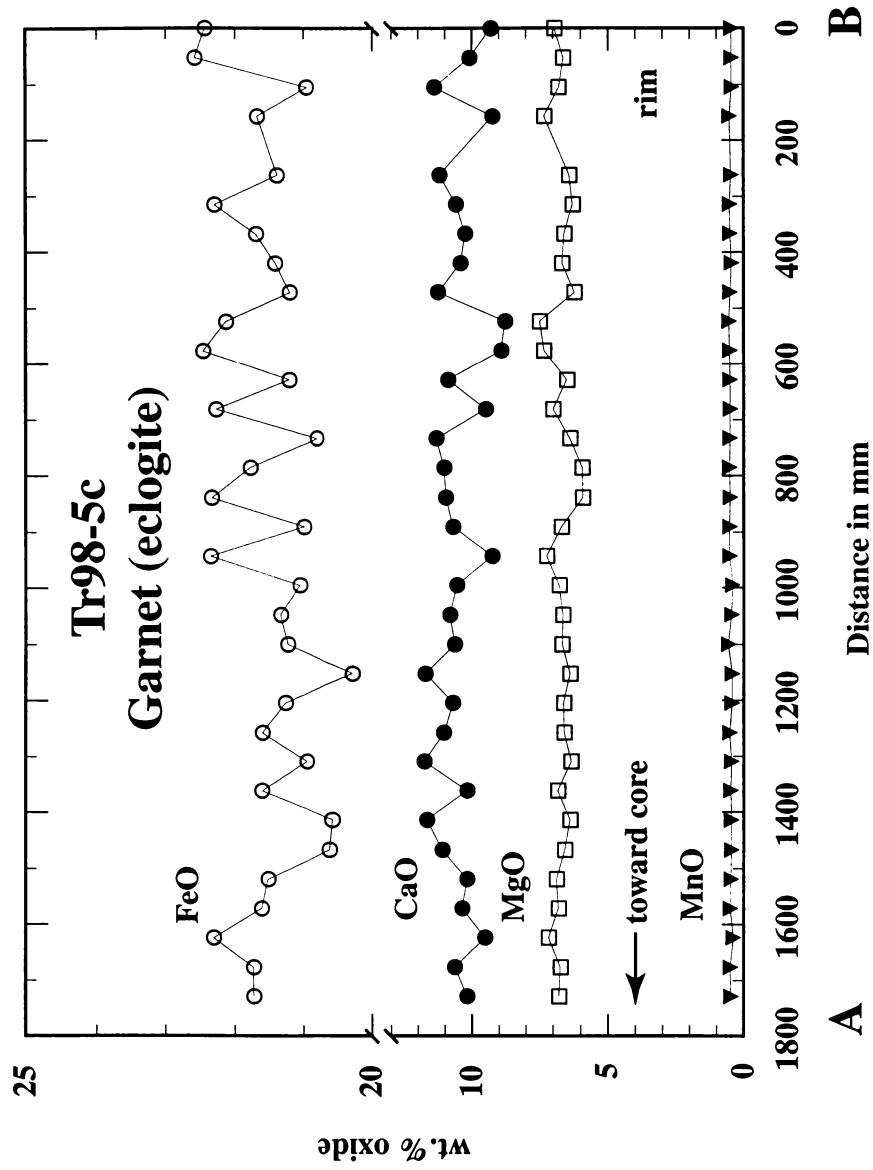


Figure 10. Calcium X-ray map of a garnet in sample Tr98-5c (eclogite). Lighter shades of gray indicate higher Ca abundance. Circles indicate points of LA-ICP-MS analyses and the associated numbers refer to the analyses given in Tables 2 and 3. Notice the lack of zonation in the interior region of the garnet and the drop in concentration at the rim. The EMP traverse A-B is given in Figure 11.

Figure 11. Line traverse A-B in a garnet from sample Tr98-5c (eclogite). Notice the relatively homogeneous Ca concentration in comparison to sample Tr98-3-3-1.



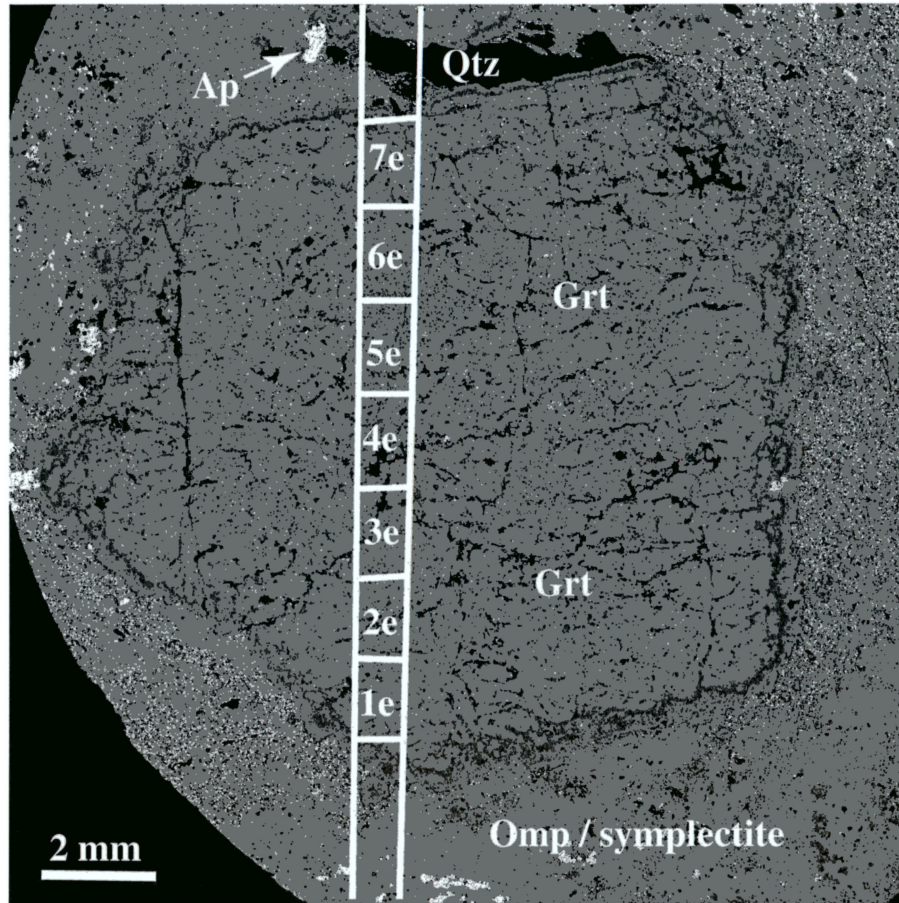


Figure 12. Calcium X-ray map of a garnet in sample Tr98-20b (eclogite). Lighter shades of gray indicate higher Ca abundance. Superimposed are the locations of microsampling for oxygen isotopes. $\delta^{18}\text{O}$ values are given in Table 5. Symplectite refers to an intergrowth of plagioclase, amphibole, and clinopyroxene.

region (about 2 mm). From EMP analyses, CaO changes from ~ 6.7 wt.% at the rim to ~14 wt.% at ~1.5 mm inside the garnet. Qualitatively this can also be observed in Figure 12. The overall compositional variation can be seen in Figure 7.

The garnet from sample Tr99-19B is anhedral and similar in size to Tr98-3-3-1. A subhedral, almandine-rich core is not visible; rather, Ca-rich zones are pervasively present throughout the garnet (Fig. 13). There is not a Ca-rich rim surrounding the core as in Tr98-3-3-1. The overall compositional variation can be seen in Figure 7. Most analyses straddle the boundary between group B and C eclogites. The highest pyrope content occurs within about 300 μm of the rim, similar to the garnet in sample Tr98-3-3-1.

Pyroxenes. Pyroxenes from Trescolmen are omphacitic, i.e., mainly a solid solution between jadeite and diopside, with minor hedenbergite (Fig. 14). No attempt has been made to assess the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios due to uncertainty in Fe^{3+} calculations from EMP analyses, as well demonstrated by Sobolev et al. (1999). The end-members are calculated with a set of linear equations following Spear et al. (1982). In the calculations, the aegirine component has been omitted with the result that the jadeite end-member is maximized. In general, omphacites display little inter- and intra-granular chemical variations on the scale of a thin section.

Omphacite in sample Tr98-20b is relatively fine-grained (i.e., 200 to 400 μm), and surrounded by abundant fine-grained symplectite. In this sample, the symplectite consists of an intricate intergrowth of plagioclase (An_{10}), omphacite (Jd_{35-50}), and sodic-pargasitic hornblende. Omphacite analyses for this sample are distinct from the other samples studied. The jadeite contents are higher by about 10 mol.% (i.e., Jd_{50} ; Fig. 14) in larger omphacite grains (i.e., ~ 200 μm) but decreases to Jd_{35} in omphacite grains in the symplec-

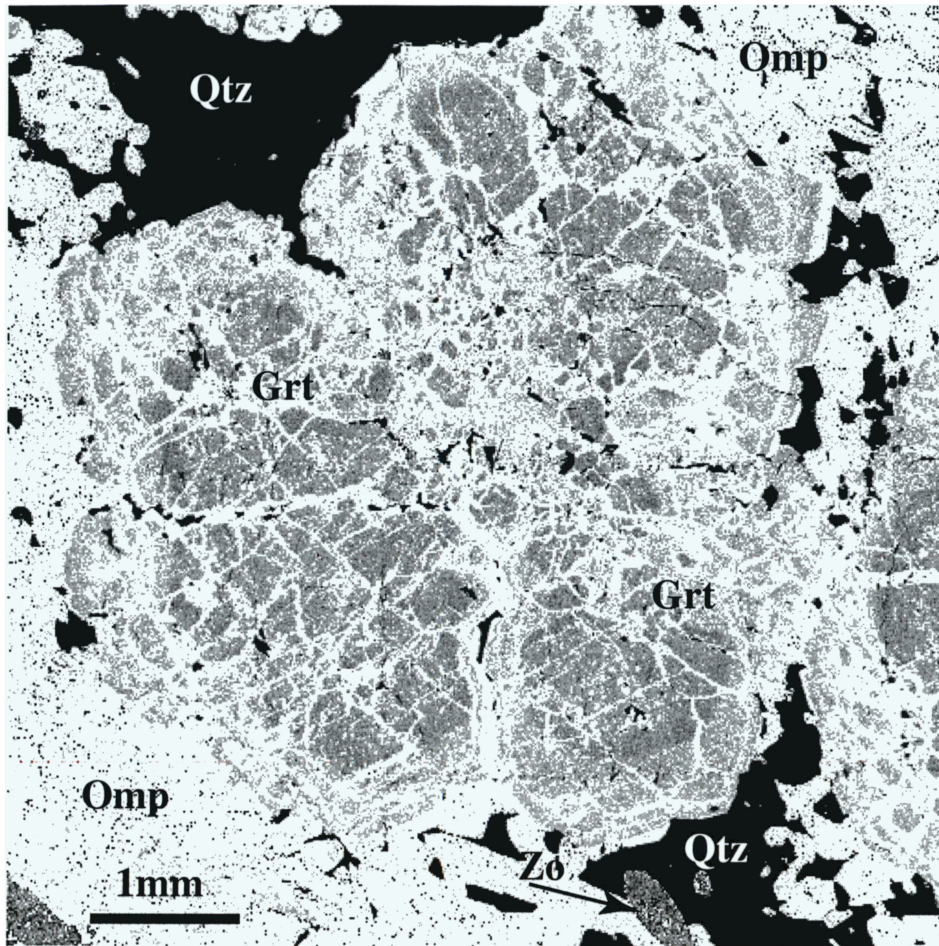


Figure 13. Calcium X-ray map of a garnet in sample Tr99-19B (eclogite). Lighter shades of gray indicate higher Ca abundance.

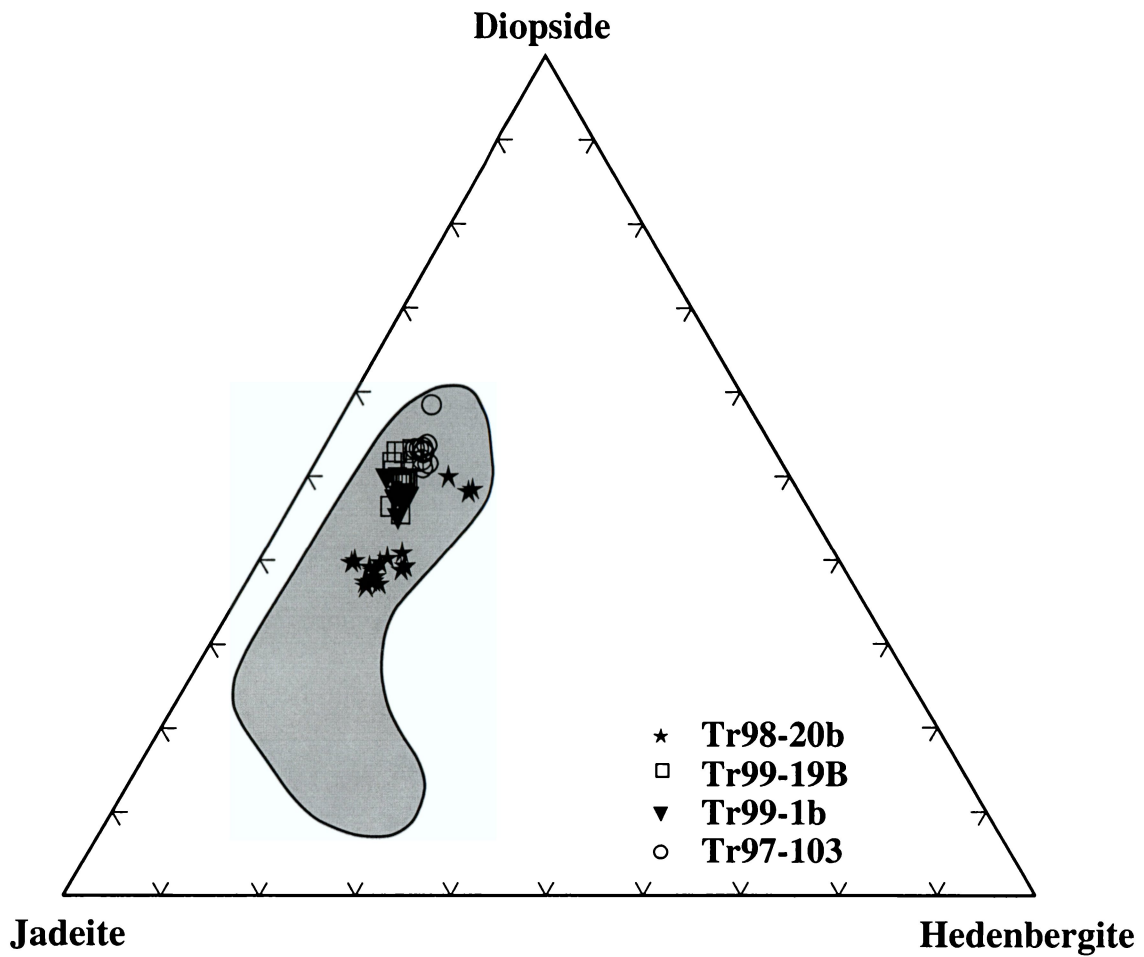


Figure 14. Ternary plot of omphacite compositions from Trescolmen. The analyzed pyroxenes are normalized to the three end-members jadeite, hedenbergite, and diopside. The shaded envelope encloses additional analyses of Trescolmen omphacites from the literature (Heinrich, 1986; Santini, 1992; Meyre et al., 1998). Notice the compositional gap in the omphacites from sample Tr98-20b.

tite. In the other samples, omphacite from interior of large boudins (>10 m) is more coarse-grained, with Jd_{40} . The Ca-Tschermak component in omphacite in sample Tr98-20b is negligible, unlike in the other samples, where it reaches up to 3 mol.%. All grain boundaries of omphacites, even from these relatively unaltered samples are marked by symplectite, up to 40 μm in width, consisting of a wormlike intergrowth of plagioclase and amphibole.

In the classification scheme of Taylor and Neal (1989), most omphacites plot in the Group B field (Fig. 15), except omphacite from sample Tr98-20b, which straddles the B-C boundary. The compositions in the shaded region in Group C, i.e., high Na_2O (9 to 11 wt.%) and low MgO (3 to 7 wt.%), were not observed in the analyzed samples. Overall, the classification of omphacites using the division of Taylor and Neal (1989) agrees with the classification from garnets, i.e., Coleman et al. (1965).

Other minerals. Epidote-group minerals occur in most eclogitic samples, as inclusions in garnet, or interstitially. In sample Tr98-3-3-1, most of the clinozoisite occurs at the garnet-omphacite interface and attains $\sim 300 \mu\text{m}$ in size. Back-scatter-electron (BSE) images reveal these grains to be zoned. Most of these grains show an enrichment of LREE in the core, with a substantial and abrupt change in concentration in the rim region. The abundances of some of the LREEs, as determined by EMP, reach 3.24 and 2.36 wt.% CeO_2 and Nd_2O_3 , respectively.

Metapelites

The garnets in the metapelites also show a wide range in composition. All of the garnet porphyroblasts (> 3 mm) show some type of zonation in major elements. Depending on their structural position, the zonation patterns are either well-developed, i.e., con-

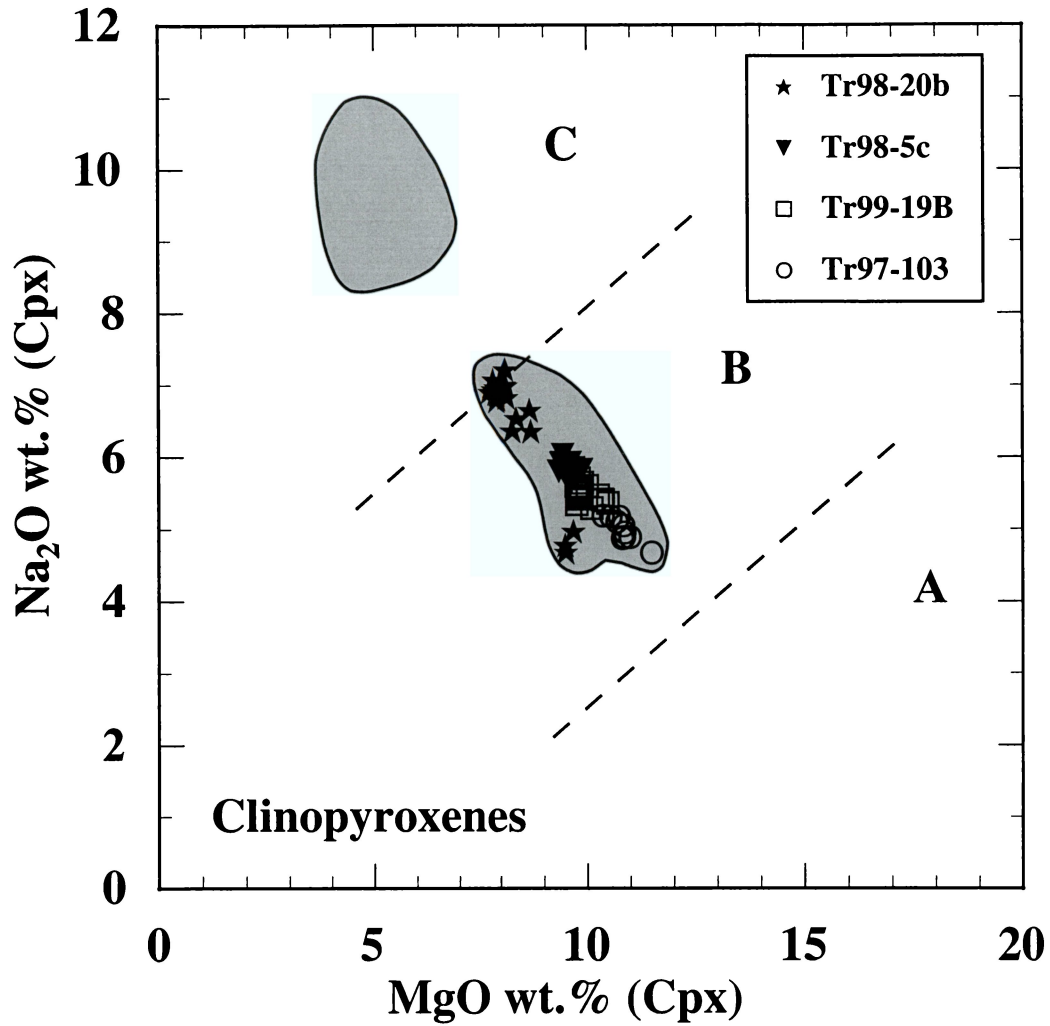


Figure 15. Na₂O versus MgO in clinopyroxenes from Trescolmen. Classification after the scheme of Taylor and Neal (1989). The shaded areas enclose additional analyses of omphacites from Trescolmen from the literature (Heinrich, 1986; Santini, 1992; Meyre, 1998). Notice the compositional gap in the clinopyroxenes from sample Tr98-20b.

centric as seen in Figure 16a, or patchy-irregular (similar in style to eclogitic garnets, e.g., Figure 13) as seen in Figure 16b. It is interesting to note that the irregular zoned garnets from Mp1- and Mp2-type metapelites are from the main metapelitic zone in the Trescolmen cirque. In contrast, Mp3 metapelites from the lowest structural level (i.e., western ridge, see Figure 2) and from the structural highest position of the metapelitic zone show well-developed growth zonation.

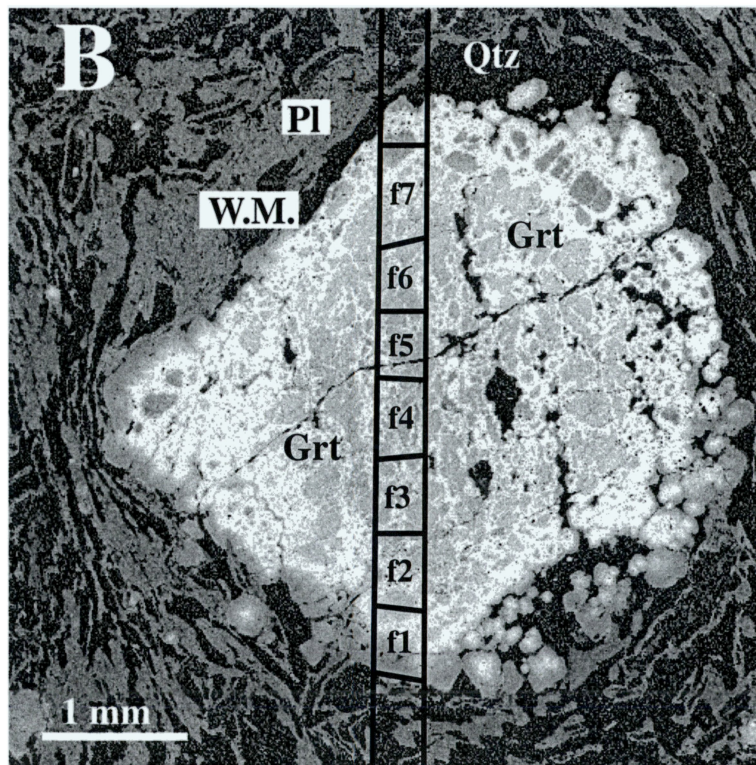
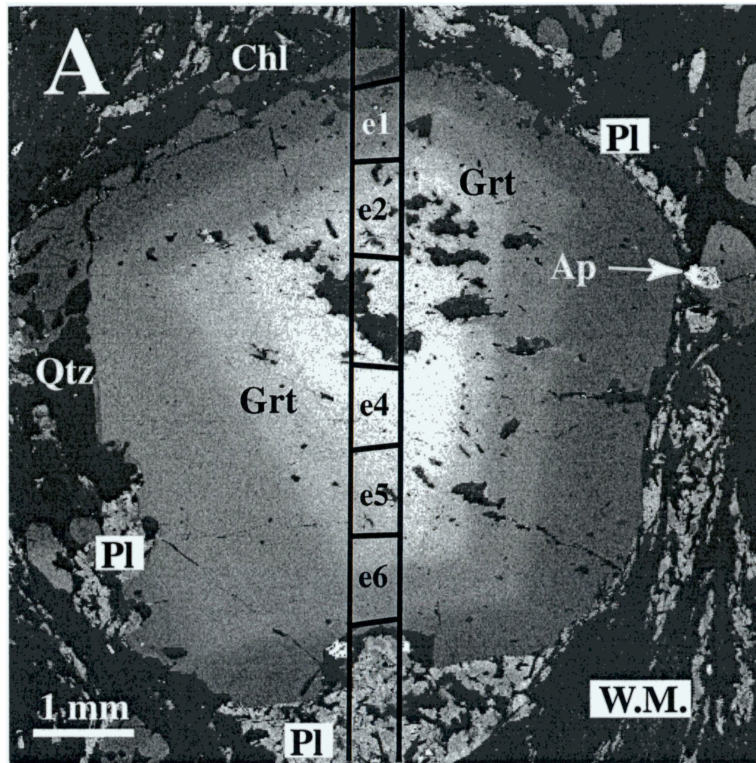
The overall composition of garnets from the metapelitic rocks from Trescolmen is shown in Figure 17. The growth zonation shown by a Ca X-ray map in a garnet from sample Tr99-5aa, is typical for the Mp3-type metapelites (Fig. 16a). As determined by numerous (175) EMP analyses, the garnet in Tr98-5aa has the following overall composition: $(\text{Alm} + \text{Spess})_{66-77}$, Grs_{2-14} , and Prp_{12-29} (Fig. 18).

The other type of zonation typical for garnet porphyroblasts from Mp2 metapelites is patchy and irregular, similar to the zonation observed in garnet porphyroblasts in the eclogites. The garnet porphyroblast from sample Tr99-20b exemplifies this type of zonation. The irregular zonation is best seen in a Ca X-ray map (Fig. 16b). Garnets in Tr99-20b have the following overall compositional variation of $(\text{Alm} + \text{Sps})_{63-71}$, Grs_{3-14} , and Prp_{18-29} (Fig. 18).

TRACE ELEMENTS

Trace-element compositions of garnet and omphacite from selected eclogite specimens were determined by LA-ICP-MS. Previous to these analyses, the concentration of Ca (used as an internal standard in the LA-ICP-MS analyses) was determined by EMP on selected spots on thick (~ 600 μm) sections.

Figure 16. Calcium X-ray maps of metapelitic garnets from Trescolmen. Lighter shades of gray indicate higher Ca concentration. Superimposed are the locations of microsampling for oxygen isotopes with the ratios given in Table 5. **A** Garnet from sample Tr99-5aa (Mp3, boundary of of metapelitic zone); **B** Garnet from sample Tr99-20a (Mp2, vicinity of eclogites). W.M. = white mica (mainly paragonite and phengite).



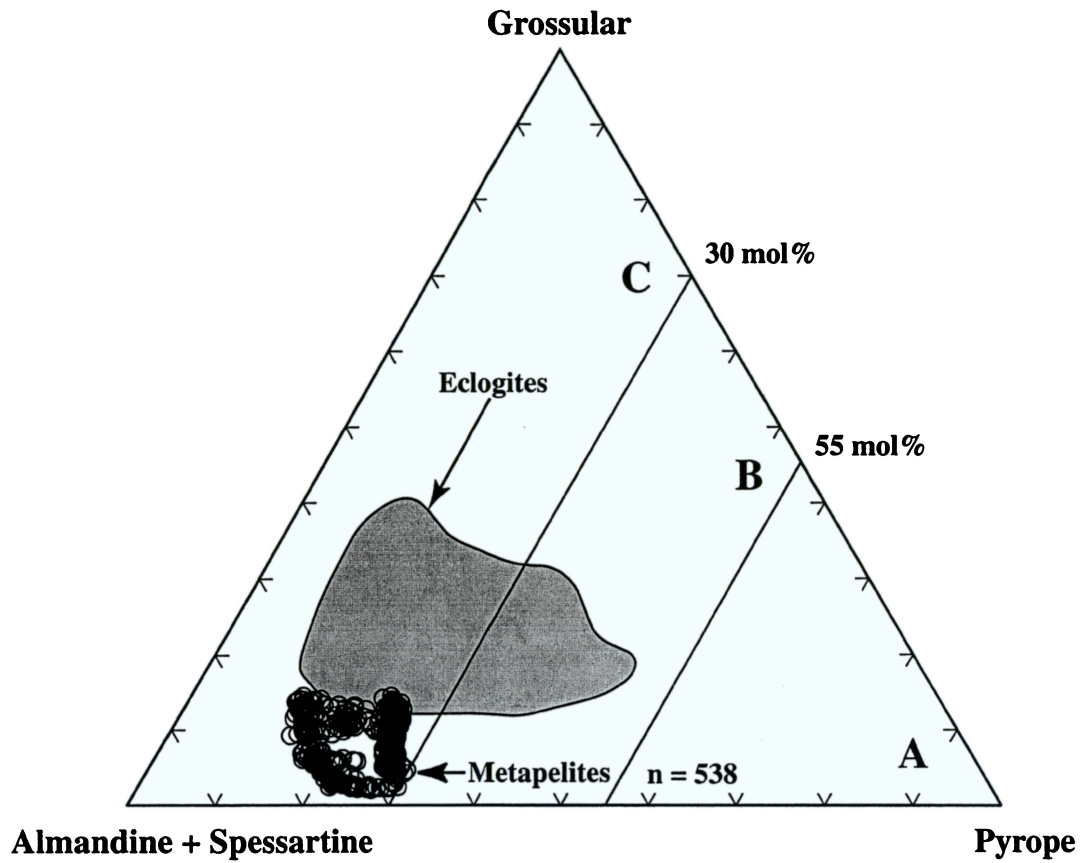


Figure 17. Ternary diagram for all garnets analyzed in metapelites from Trescolmen. For reference, the shaded region gives the compositional variation of the eclogitic garnets from Trescolmen. Group boundaries for the eclogitic garnets are after Coleman et al. (1965).

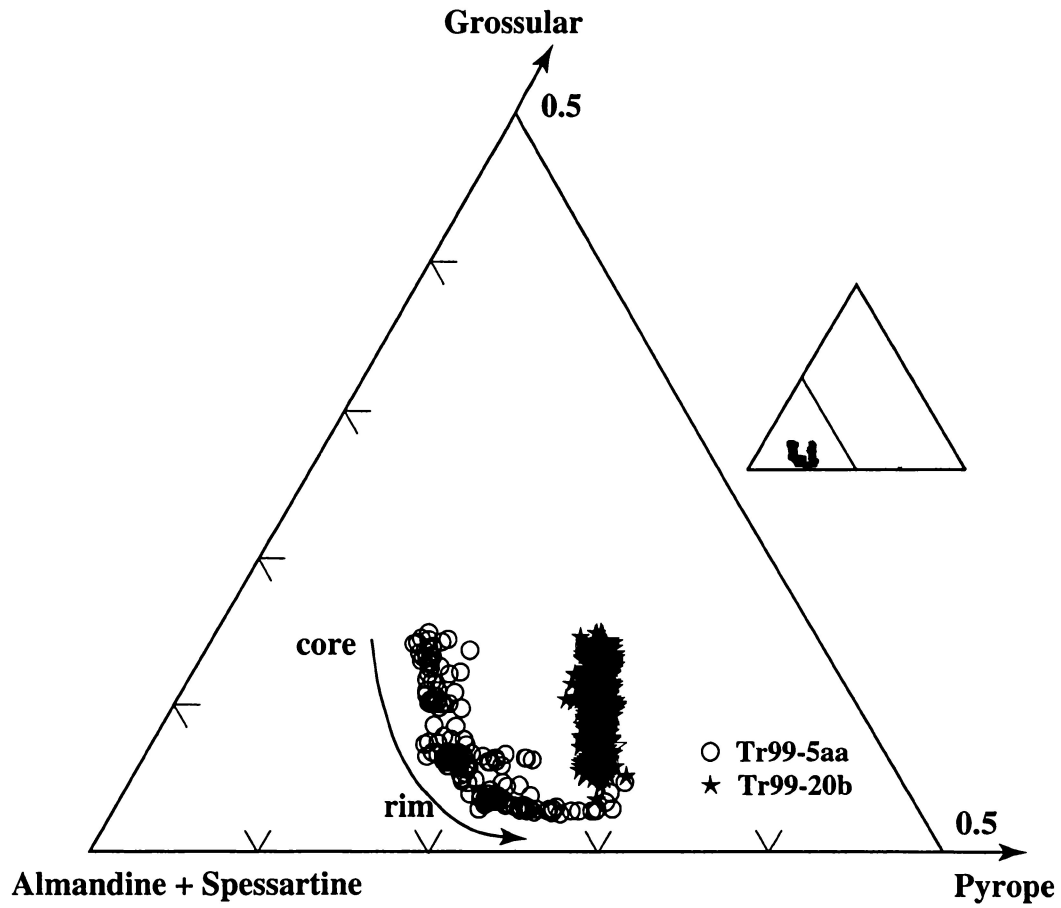


Figure 18. Compositional variations in two garnets from metapelites. Tr99-5aa is from the structurally uppermost part of the metapelitic zone of Trescolmen, whereas the garnet from sample Tr99-20b is from the main metapelitic zone. Both garnets have similar diameters but have different types of zonation (cf. Fig. 16).

The garnet from sample Tr98-5c (see Fig. 10) is light-rare-earth-element (LREE)-depleted with chondrite normalized Sm_n contents from 0.87 to 5.03 (Fig. 19a; Table 2). The heavy-rare-earth-elements (HREE) are slightly depleted with $[Dy/Yb]_n > 1$, ranging from 1.02 to 2.82. The variations among the analyses are smallest in the middle-rare-earth-element (MREE)-region and show the widest variations for HREEs, i.e., Yb_n ranges from 28 to 97 (Fig. 19a). The Y contents (in ppm) range from 83.7 to 147. Omphacite grains in contact with garnet (analysis # 11) and close (within 1 mm; analyses # 13,14, and 15) to it have REE patterns that are convex upwards with a maximum at $Eu_n \sim 8$ (Fig. 19b; Table 3). The LREEs and the HREEs are depleted, i.e., $[Ce/Sm]_n$ and $[Eu/Dy]_n$ range from 0.05 to 0.06 and 4.86 to 7.28, respectively.

Garnet in eclogite Tr98-3-3-1 shows similar patterns to those just described, although the range in concentration is greater, particularly for the HREEs (Fig. 20; Table 2). The HREEs are depleted as well as enriched, depending on the location of the analysis. $[Dy/Yb]_n$ ranges from 0.44 to 3.72, and Yb_n varies from ~ 8 to ~ 166 . The highest HREE concentrations occur in the central region of the garnet that has the lowest Ca content. Interestingly, the discontinuity in Ca concentration between the core region and the Ca-rich rim is also reflected in the concentration of the REEs. The concentration of the HREEs drops by a factor of ~ 4 , whereas the lighter REEs remain about the same. Omphacite analyses in Tr98-3-3-1, in contact with garnet (analysis # 4; Table 3) and within 1 mm of the garnet interface have convex-upwards REE patterns, with a maximum at Eu_n of ~ 5.7 (Fig. 20; Table 3). The LREEs, as well as the HREEs, are depleted, i.e., $[Ce/Sm]_n$ ranges from 0.05 to 0.032, $[Eu/Dy]_n$ varies from 1.74 to 5.38.

Figure 19. Chondrite-normalized REE abundances in garnet and omphacite from sample Tr98-5c (normalization after McDonough and Sun, 1995). **A** Garnet with various negatively sloped HREEs; **B** Omphacite with convex upwards LREE patterns. Analyses locations are shown on Figure 10.

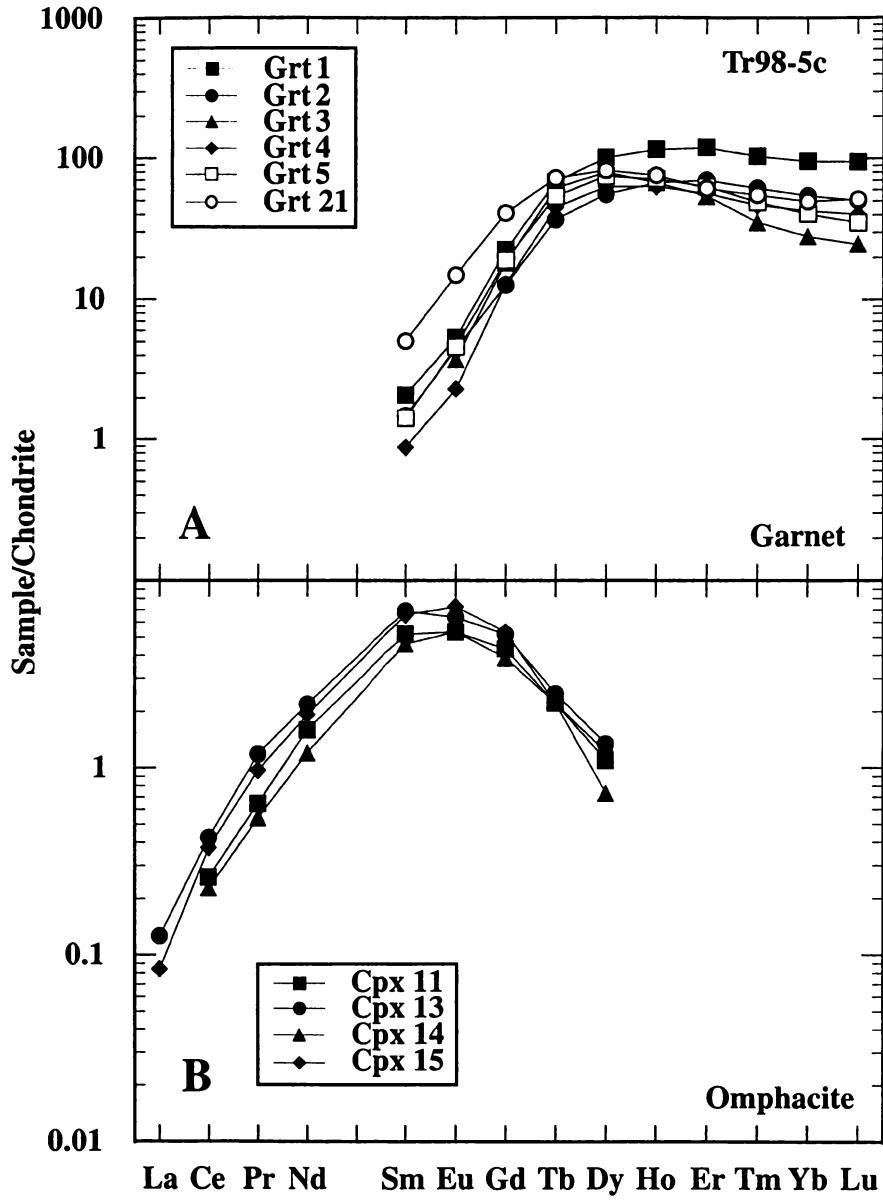


Table 2. REE concentrations¹ in garnets from Trescolmen eclogites.

Sample	Sm	Eu	Gd	Tb	Dy	Er	Yb	Lu	[Dy/Yb] _n ⁵	Y
Garnet										
Tr98-5c										
1 ²	0.31 ³	0.30	4.50	2.48	25.0	19.2	15.4	2.34	1.05	147
2	0.22	0.25	2.53	1.34	13.8	11.3	8.75	1.24	1.02	88.3
3	n.d. ⁴	0.21	3.64	2.25	19.6	8.66	4.52	0.61	2.82	90.2
4	0.13	0.13	2.58	1.64	15.6	9.08	6.81	0.99	1.48	83.7
5	0.21	0.26	3.80	1.96	18.5	10.1	6.53	0.87	1.84	98.1
21	0.75	0.84	8.22	2.64	20.3	9.85	7.96	1.27	1.65	101
Tr98-3-3-1										
1	1.79	1.85	11.21	2.75	21.2	16.4	17.5	2.62	0.78	115
2	1.24	1.23	9.37	3.12	27.3	23.1	25.0	3.97	0.70	163
5	n.d.	0.31	2.82	1.86	27.6	30.1	26.4	3.98	0.67	213
15	1.10	1.14	8.71	2.64	21.4	15.5	13.8	2.12	1.00	120
10	0.66	0.74	5.25	1.42	7.34	2.20	1.28	0.12	3.72	26.4
11	0.49	0.85	5.73	1.42	8.19	4.26	3.66	0.59	1.45	37.1
12	n.d.	0.30	3.79	1.83	14.1	5.61	2.93	0.37	3.13	63.3

¹ Determined by LA-ICP-MS.² Analysis #.³ Concentration in ppm.⁴ Not detected.⁵ [Dy/Yb]_n is normalized to chondrite.

Table 3. REE- and trace-element concentrations¹ in omphacites from Trescolmen.

Sample	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Sr	V	Ni	Cr
Omphacite												
Tr98-5c												
11 ²	0.16 ³	0.06	0.73	0.77	0.30	0.86	0.08	0.27	127	509	149	356
13	0.26	0.11	1.00	1.02	0.36	1.03	0.09	0.33	149	551	175	427
14	0.14	0.05	0.55	0.68	0.30	0.77	0.08	0.18	131	550	154	456
15	0.23	0.09	0.88	0.97	0.41	1.06	0.08	0.30	144	523	162	340
Tr98-3-3-1												
1	0.10	0.04	0.49	0.55	0.31	0.87	0.09	0.33	118	465	140	239
2	0.09	0.04	0.30	0.50	0.30	1.01	0.09	0.25	118	456	142	265
4	0.09	0.04	0.35	0.68	0.28	0.95	0.10	0.36	117	486	155	267
5	0.09	0.03	0.41	0.44	0.32	0.84	0.09	0.26	121	516	175	241
6	0.06	0.03	n.d. ⁴	0.44	0.20	0.80	0.12	0.43	104	471	145	296
7	0.06	0.02	n.d.	0.31	0.18	0.67	0.09	0.27	84	488	176	201
8	0.08	0.02	0.36	0.47	0.23	0.71	0.10	0.21	113	498	157	304

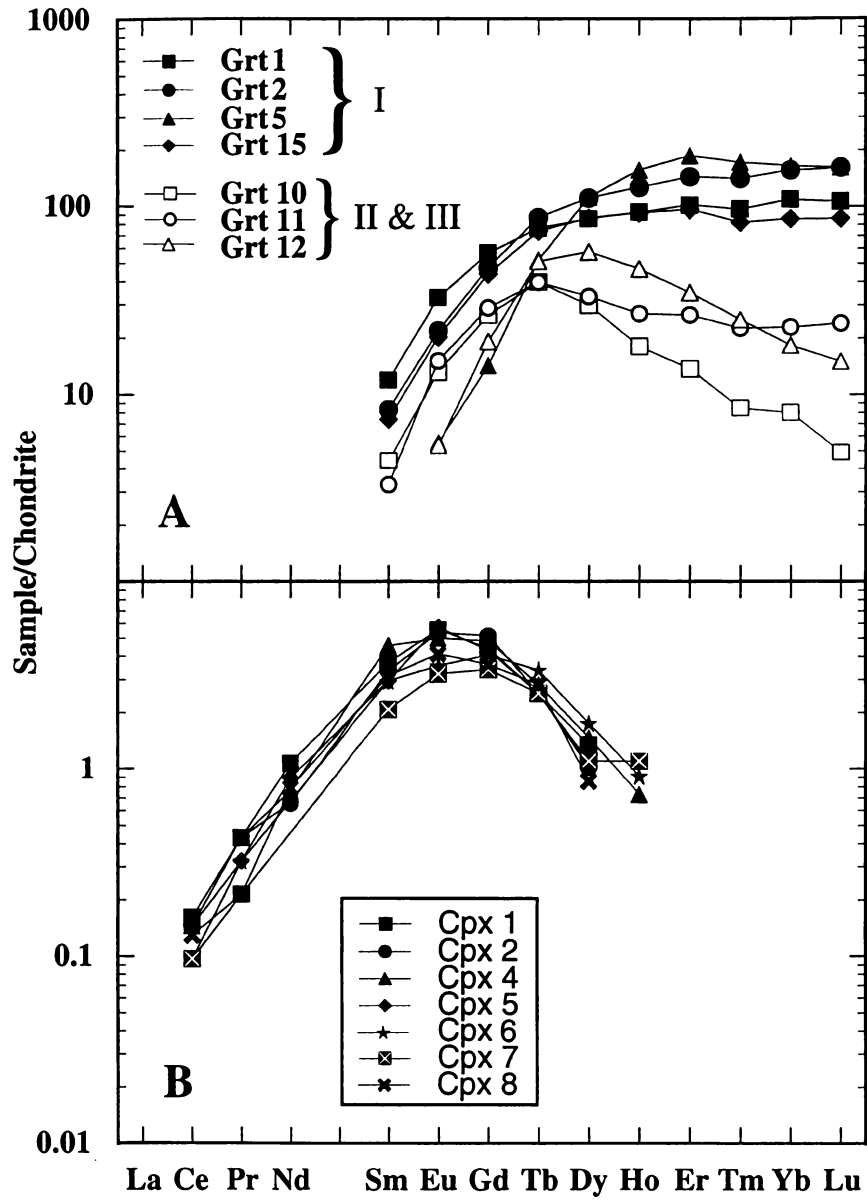
¹ Determined by LA-ICP-MS.

² Analysis #.

³ Concentration in ppm.

⁴ Not detected.

Figure 20. Chondrite-normalized REE abundances in garnet and omphacite from sample Tr98-3-3-1 (normalization after McDonough and Sun, 1995). Analyses locations are shown in Figure 8. **A** Garnet with various negatively sloped HREEs. Abundances for some HREE vary by more than one order of magnitude. The roman numerals I, II and III refer to the domains given in Figure 8. **B** Omphacites with convex-upward LREE patterns, similar to sample Tr98-5c.



OXYGEN ISOTOPES

The oxygen-isotope ratios are all from mineral separates and “thin strip” (Kohn et al., 1993) microsampling. Mineral separates were obtained from eclogites (i.e., garnet, omphacite, quartz, kyanite, and rutile) and metapelites (i.e., garnet, quartz, and kyanite) to evaluate any systematic variation and possible zonation of $\delta^{18}\text{O}$ within the eclogites and metapelites and between these two rock types. Special attention was given to the chemical zonations within garnet porphyroblasts in eclogites and metapelites. The results for the mineral separates from Trescolmen are given in Table 4.

Oxygen isotope composition of eclogites

Calculated whole-rock $\delta^{18}\text{O}$ (from mineral analyses and mode) from unaltered eclogites from Trescolmen cover a range of ~ 5.5 to 7.5 ‰. These values are typical for mid-ocean ridge basalts that have been altered by seafloor “weathering” at ambient temperatures or by low temperature hydrothermal systems (Muehlenbachs, 1986). Oxygen-isotope ratios for minerals in eclogites correlate with boudin size, i.e., minerals in larger boudins, in general, show lower $\delta^{18}\text{O}$ values, whereas minerals in smaller boudins have higher $\delta^{18}\text{O}$ (Table 4). Other minerals analyzed from E1 boudins include kyanite and rutile with values of 6.75 and 3.33 ‰ (not listed in Table 4), respectively. The garnet, omphacite, and rutile $\delta^{18}\text{O}$ values are within range of previously reported analyses from Trescolmen eclogites (Kohn and Valley, 1998).

Oxygen-isotope composition of metapelites

Calculated whole rock $\delta^{18}\text{O}$ (from mineral analyses and mode) for Mp2 metapelites give ratios ~ 9 ‰, whereas Mp3 metapelites have $\delta^{18}\text{O}$ ratios of ~ 10.5 ‰. These whole-rock values are within the range reported from similar metamorphic terrains (e.g., Garlick

Table 4. Oxygen isotope ratios¹ for mineral separates from Trescolmen.

Sample	$\delta^{18}\text{O}$ Grt	$\delta^{18}\text{O}$ Qtz	$\delta^{18}\text{O}$ Omp	$\Delta(\text{Qtz-Grt})$	$\Delta(\text{Grt-Omp})$	T (Qtz-Grt)
Eclogite (E1)						
Tr99-16	5.46	9.46(± 0.15)		4.01		535
Tr99-19a	5.37	9.47	6.50	4.10	1.13	525
Tr99-19B	5.28(± 0.06)	9.43(± 0.15)	6.43 (± 0.08)	4.15	1.15	520
Tr99-40	5.31	9.52	6.78	4.21	1.47	510
Tr00-EB	5.86	8.90	6.20	3.04	0.34	650
Eclogite (E2)						
Tr98-10	6.21 (± 0.05)	9.72		3.51		590
Tr98-13	6.46 (± 0.10)	9.85 (± 0.06)	7.11 (± 0.08)	3.39	0.65	605
Tr98-61	6.33 (± 0.07)	9.69	7.10	3.36	0.77	605
Tr99-1b	6.22	9.96	7.05	3.74	0.83	560
Tr99-31	6.30	10.23	7.37	3.93	1.07	540
Tr99-47m	5.94	10.45		4.51		485
Metapelite (Mp1)						
Tr98-37	6.74 (± 0.03)	10.32 (± 0.06)		3.58		580
Tr98-56	6.11	10.55		4.44		490
Tr99-26	6.55 (± 0.03)	10.33 (± 0.08)		3.78		555
Tr99-45	6.30	10.07		3.77		555
Tr99-48	5.94	10.17		4.77		465
Tr99-51	6.46	10.18		3.72		565
Metapelite (Mp2)						
Tr98-22	7.37 (± 0.03)	10.23		2.86		680
Tr98-52	7.57 (± 0.10)	10.54 (± 0.04)		2.97		660
Tr99-20a	7.56	10.51		2.95		665
Tr99-21	7.12	10.86		3.74		560
Tr99-27	7.16	10.55		3.39		605
Tr99-28	7.30 (± 0.01)	10.68		3.38		605
Tr99-50	7.43	11.05		3.62		575

(continues)

Table 4. (continued)

Sample	$\delta^{18}\text{O}$ Grt	$\delta^{18}\text{O}$ Qtz	$\delta^{18}\text{O}$ Omp	Δ (Qtz-Grt)	Δ (Grt-Omp)	T (Qtz-Grt)
Metapelite (Mp3)						
Tr99-15a	8.82 (± 0.20)	12.21 (± 0.04)		3.39		605
Tr99-15b A	8.49	12.31		3.82		550
Tr99-15b M	8.85	12.40		3.55		585
Tr99-33	9.48	12.20		2.72		705
Tr99-35	9.29	12.56		3.27		620
Tr00-11a	9.58	13.12		3.54		585
Tr00-26	8.39	12.43		4.04		530
Tr00-36b	9.72	12.41		2.69		710

¹ All analyses are given in ‰ (V-SMOW) and are corrected to UWG-2 = 5.8‰. Numbers followed by parenthesis are averages from two analyses with the variation about the mean (1sd). E1 samples are from large boudins (> 3 m), E2 samples are from small boudins (< 3 m) and rims of large boudins. Mp1 samples are at the contact with eclogite boudins, Mp2 specimens are at least 0.2 m away from eclogites, and Mp3 samples are distant, i.e., occur at the structural boundary of the Trescolmen cirque. Temperatures are in °C. Simple error propagation of uncertainties in the “A” factor and the analytical precision yield temperatures uncertainties of ± 25 °C.

and Epstein, 1967). Mineral separates of garnet and quartz from metapelites of different structural levels have been analyzed (Table 4). The lowest $\delta^{18}\text{O}$ values for minerals are found in Mp1 metapelites, whereas the highest values occur in Mp3 metapelites. Oxygen-isotope data for Mp2 samples are intermediate to data from Mp1 and Mp3 samples.

Oxygen-isotope composition of garnets (microsampling)

A few relatively large (> 4 mm) garnet porphyroblasts from eclogites and metapelites were selected for microsampling using the thin-sawblade technique of Kohn et al. (1993). The location of the microsampling can be seen in Figures 11 and 16, the corresponding analyses are given in Table 5. The two metapelitic garnets show no consistent trend in terms of $\delta^{18}\text{O}$. There is a possibility that some of the higher values could be caused by quartz inclusions. The majority of “fresh” eclogitic garnets display an increase in $\delta^{18}\text{O}$ from core to rim. An exception is sample Tr98-20b that has the heaviest $\delta^{18}\text{O}$ values in the core region.

Table 5. Oxygen-isotope ratios¹ from microsampling of selected garnets from Trescolmen.

Tr98-20b (eclogite, E2)		Tr99-5aa (metapelite, Mp3)		Tr99-20a (metapelite, Mp2)	
Analysis no.	$\delta^{18}\text{O}$	Analysis no.	$\delta^{18}\text{O}$	Analysis no.	$\delta^{18}\text{O}$
E7	7.07	E1	8.58	F7	7.21
E6	7.16	E2	8.33	F6	7.44
E5	7.20	E4	8.47	F5	7.25
E4	7.54	E5	8.34	F4	7.27
E3	7.18	E6	8.38	F3	7.35
E2	6.97			F2	7.16
E1	6.92			F1	7.18

¹ All analyses are given in ‰ (V-SMOW) and are corrected to UWG-2 = 5.8‰. Analyses # refers to the locations given on Figures 12 and 16.

DISCUSSION

Major-element chemistry

The zonation in major elements observed in both eclogitic and metapelitic garnets reflects variations in P-T-X conditions during their prolonged evolution. Compositional X-ray maps of garnet porphyroblasts document several stages of garnet growth, overprint and deformation. This is particularly well seen in the Ca X-ray maps of the eclogite sample Tr98-3-3-1 (Fig. 7). At least three events probably affected this garnet. The almandine-rich (pre-Alpine ?) core, with inclusions of paragonite, quartz, Ca-Na amphibole, and epidote might suggest an amphibolite as a potential protolith of the current assemblage (cf., Heinrich, 1986; Plas, 1959). During Alpine metamorphism, the break down of plagioclase to grossular + kyanite + quartz may have been a source of Ca for the higher grossular content in domain II (Fig. 8). The break down of plagioclase could have taken place either with increasing P or with decreasing T. Alternatively, another source for the increased grossular content might be the break down of zoisite to grossular + kyanite + quartz + H₂O. In contrast to the plagioclase break down reaction, the demise of clinzoisite will take place with increasing P and with increasing T. Deformation may also have been involved during that period, as the Ca-enriched stringers also penetrate the core region of the garnet. Increased availability of Mg for garnet growth in domain III (see Fig. 7 and 8) may be the result of a possible breakdown of amphibole and/or augite to pyroxene. It is interesting to note that both eclogitic and metapelitic garnets from the main metapelitic zone at Trescolmen display this heterogeneous Ca zonation. This similar type of zonation indicates deformation in both rock types during garnet recrystallization.

In sharp contrast to the garnet porphyroblasts from inside the cirque of Trescol-

men, X-ray maps for garnets from the border region of the cirque show euhedral elemental growth-zoning patterns (Fig. 16a) typical of prograde metamorphism. This observed contrast might be due to different deformational styles or due to the juxtaposition of different units during the Alpine orogeny.

Several studies have documented that garnet preserves major-element zonation patterns during metamorphic or tectonic reworking (e.g., Tuccillo et al., 1992; Argles et al., 1999). Many of the garnets from eclogites and metapelites at Trescolmen are poly-metamorphic, i.e., they have undergone the high-pressure eclogite-facies event and/or the later amphibolite-facies overprint during exhumation (e.g., Heinrich, 1983). From the zonation pattern in sample Tr98-3-3-1, an even more complex metamorphic evolution is possible. If the garnet core is indeed pre-Alpine, i.e., Variscan or even older, it would imply that the garnet core had a medium-pressure, pre-alpine growth history and that some metabasic rocks at Trescolmen have a pre-Tethys age. Although we consider that scenario more likely, there is still the possibility that the garnet cores experienced a prograde growth history during eclogite-facies metamorphism with the consequence that the metabasic rocks of Trescolmen have a Tethys age.

Oxygen-isotope fractionations

Oxygen-isotope ratios of analyzed minerals in eclogites and metapelites from Trescolmen define a distinct spatial trend. The highest values in metapelites are encountered in samples from the structurally lowest horizon (western ridge of the Trescolmen cirque, see Fig. 2 and 3), as well as in the structurally highest position already imbricated in the gneiss layers. In the interior of the cirque of Trescolmen, metapelites have lower $\delta^{18}\text{O}$, the lowest values encountered near the contact with the eclogite boudins. The variation of

isotopic fractionations between quartz and garnet for the different groups of eclogites and metapelites can be seen in Figure 21. The relationship between isotopic fractionation between two minerals and temperature is approximated by the equation $\Delta_{I,J} = A_{I,J} * 10^6/T^2$ (T in K), where I = mineral 1, J = mineral 2, and A is a constant (e.g., Bottinga and Javoy, 1973). Cation substitutions in garnet exert a considerable effect on the fractionation of oxygen isotopes (Kohn and Valley, 1998). Using Kohn and Valley's (1998) A factor of 2.2 ± 0.25 for Ca-poor garnet (< 20 mol.% Grs) in combination with the experimental results of Clayton et al. (1989), $A = 2.60$. This value was used for temperature calculations. Figure 21 suggests that equilibrium was closely approached without being significantly reset during cooling and that equilibrium temperatures of ~ 600 °C agree reasonably well with estimates from consideration of phase equilibria (e.g., Heinrich, 1986; Meyre et al., 1999). It is interesting to note that $\delta^{18}\text{O}$ values from minerals in metapelites and eclogites overlap at the interface of the two rock types. Furthermore, since both rock types lie on the same isotherm, it is likely that they all experienced the last thermal event together. However, the Mp3 samples have higher whole-rock values and display different patterns in compositional X-ray maps (growth zonation versus heterogeneous zonation) suggesting that the two groups experienced different tectonic histories previous to the last thermal event. Another possibility might be different protoliths or different degrees of post-metamorphic alteration.

The oxygen-isotope fractionations between garnet and omphacite are shown in Figure 22. The two groups plot in two distinct regions. Unlike quartz-garnet fractionations, the omphacite-garnet fractionations indicate a lack of isotopic equilibrium. Diffusional resetting of oxygen could be a potential problem, but inasmuch as the crystalliza-

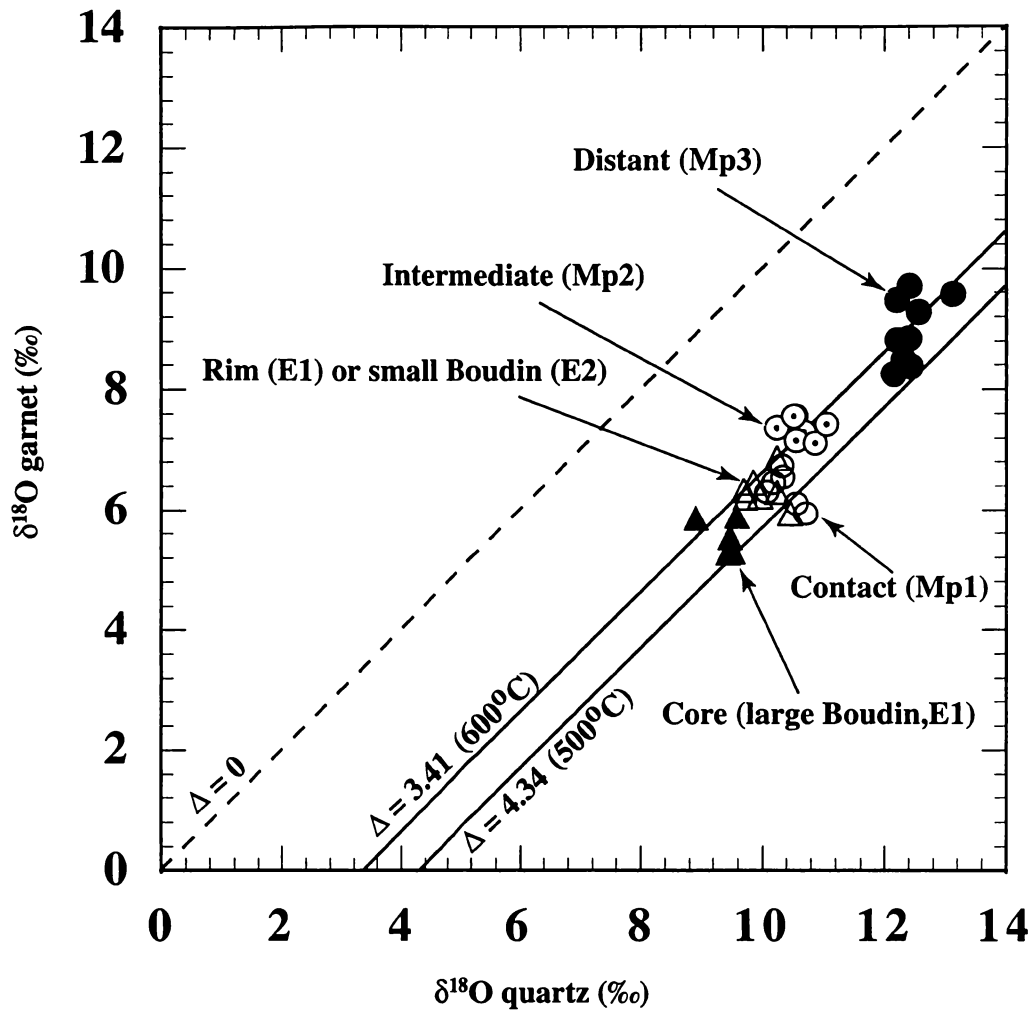


Figure 21. δ - δ plot of oxygen-isotope compositions of quartz and coexisting garnet from Trescolmen. Triangles correspond to eclogitic, circles to metapelitic garnets, respectively. The dashed diagonal line is $\Delta = 0$. The solid lines are the isotherms for temperatures of 500 and 600°C. Uncertainty in δ 's are less than the size of the symbols used.

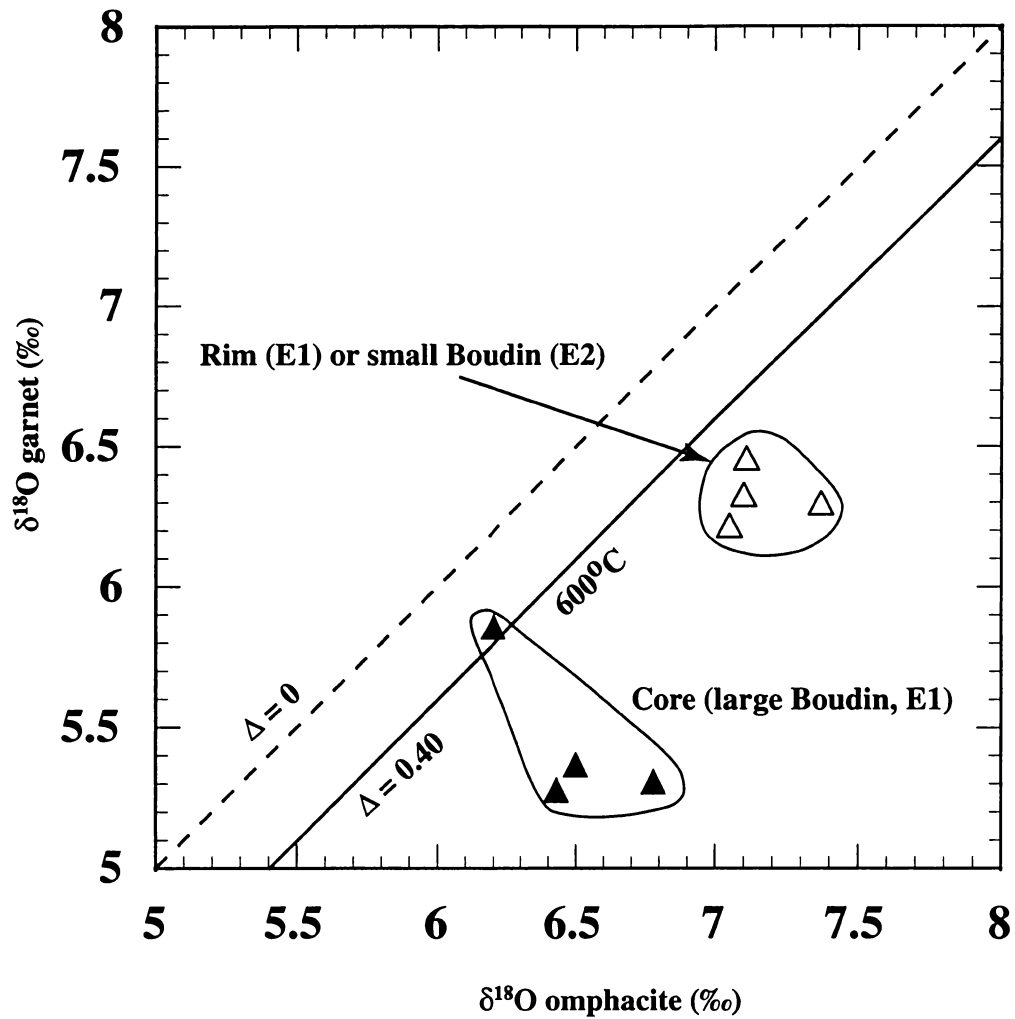
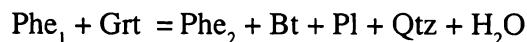


Figure 22. δ - δ plot of oxygen-isotope compositions of omphacite and coexisting garnet from Trescolmen. The dashed diagonal line marks the $\Delta = 0$ fractionation. The solid diagonal line indicates the 600°C isotherm. Uncertainty in δ 's are less than the size of the symbols used.

tion temperature was relatively low and diffusion rates for oxygen are slow in garnet and omphacite (Farver, 1989; Coghlan, 1990), this complication is probably negligible. Another contributing factor might be analytical problems with oxygen extraction from omphacites, as previously discussed (Kohn and Valley, 1998). However, adding the suggested 0.3 ‰ correction to omphacite values makes the fractionation even larger. There is a strong possibility that the oxygen isotopes of omphacite and garnet (at least for some larger grains) did not equilibrate with each other during the Alpine orogeny. Alternatively, growth zonation in garnet and omphacite and changing water fugacity (Edwards and Valley, 1998) also might have contributed to the observed disequilibrium.

Fluid exchange between eclogites and metapelites

Devolatilization of the eclogite protolith during its metamorphic history is unlikely to have changed the whole-rock $\delta^{18}\text{O}$ values, because fractionations among minerals at high temperature are small, and most of the oxygen remains in the rock despite some loss due to volatiles (Valley, 1986). Considering also the much larger abundance of the metapelitic rocks at Trescolmen, devolatilization of the eclogite protolith could not produce a major isotopic shift in the metapelites. Loss of volatiles in the eclogites, however, might have contributed to the low $\delta^{18}\text{O}$ values observed in minerals in metapelites adjacent to eclogite boudins. In contrast to the eclogites, Heinrich (1982) showed that devolatilization of the metapelitic rocks (the dominant lithology in the cirque of Trescolmen) may be accomplished by the reaction:



which, during the amphibolite facies event, could have produced enough fluid to potentially alter all eclogites into amphibolites.

Preliminary oxygen-isotope data from traverses across eclogite-metapelite contacts indicate a gradient in $\delta^{18}\text{O}$ between minerals in E2 and Mp1, and Mp2 samples. This gradient of $\delta^{18}\text{O}$ values in minerals along the traverse indicates localized advective or diffusional processes during (re)crystallization of the minerals (Wiesli et al., 2001). It is noted that minerals in parts of large boudins have elevated $\delta^{18}\text{O}$ signatures which suggest a localized influx of fluid with a $\delta^{18}\text{O}$ value out of equilibrium with the original eclogite. Fluid access was probably strongly influenced by deformation. Similar conclusions have been reached from oxygen-isotope studies in other eclogite bearing terranes (e.g., Nadeau et al., 1993; Getty and Selverstone, 1994).

Zonation in oxygen isotopes in garnet has been reported by Kohn et al. (1993). Changes in $\delta^{18}\text{O}$ are susceptible to variations in temperature, reaction history, and fluid interaction (Valley, 1986). Isotopic shifts caused by net-transfer reaction are expected to be small (i.e., $< \sim 1\text{‰}$, Kohn, 1993), and oxygen diffusion in garnet is low (Coghlan, 1990) such that growth zonation in $\delta^{18}\text{O}$ might be preserved. Kohn et al. (1993) and Kohn and Valley (1994) suggested that oxygen-isotope zonation in garnets from mafic rocks are insensitive to the P-T evolution of the rock and could be used as an indicator for fluid infiltration. Garnets from Mp3 metapelites (e.g., sample Tr99-5aa) are unzoned with respect to oxygen isotopes, within analytical uncertainty, indicating a closed system or complete equilibration with an external fluid with respect to oxygen. Zonation of $\delta^{18}\text{O}$ in garnets from eclogites is small, i.e., $\sim 0.6\text{‰}$ for the garnet in sample Tr98-20b (Fig. 16), but would allow the presence of an external fluid.

Trace elements

Trace elements can provide important constraints for deciphering the petrogenesis of subducted rocks. In addition, they are susceptible to influences from fluid infiltration and metasomatism, and can provide important clues about fluid-rock interactions (e.g., Hickmott, 1987). Studies have repeatedly demonstrated that REEs, HFSEs, Y, and Zr are relatively immobile during subduction-type metamorphism (e.g., Bernards et al., 1985). However, in certain situations, Zr and Ti may be mobile even in a subduction-zone environment (Ayers and Watson, 1991; Philippot and Selverstone, 1991). Hickmott et al. (1987, 1992) suggested that REEs and Y in garnet could be modified by local metamorphic reactions (“internal metasomatism”) or by an influx of an outside fluid (“external metasomatism”). Concentration of trace elements at the interface of a growing garnet is governed by the bulk composition of the rock and the bulk distribution coefficient (D) for allocation of elements between the matrix and the garnet. Variations in D are caused by changes in intensive parameters, such as P and T . Also, bulk composition can be significantly modified by the break down of a refractory phase such as ilmenite (Hollister, 1969). Another possibility is the introduction of an external, trace-element-rich fluid.

The eclogitic garnets investigated in this study are from a polymetamorphic terrane that has undergone at least two alpine-metamorphic events (Heinrich, 1986). The Ca X-ray map of sample Tr98-3-3-1 (Fig. 8) reveals well-defined compositional variations between an older, pre-Alpine-generation garnet core (Ca-poor and Fe-enriched), and a younger (Ca- and Mg-enriched) rim region. The compositional zonation in Fe and Mg are less pronounced, implying diffusional movement of these element during cooling and uplift. The abundance of REEs in the rim region (in Tr98-3-3-1) is notably less; in par-

ticular, HREE abundances decrease by an order of magnitude. This coupled zonation in REEs and major elements is indicative of changes in growth condition of the garnet. Such variations can be caused by a change in bulk composition or in the bulk-distribution coefficient. Other elements, particularly Ti, do not change significantly across that boundary and are obviously buffered by the presence of Ti-phases in the garnet and the matrix (Ghent and Stout, 1984). This indicates that there was probably no major change in the bulk-distribution coefficient due to variation in pressure.

A possible cause for the change in trace-element concentrations near the rim of the garnet could be due to metasomatic fluids or a change in the reactants. Evidence for the presence of fluids include primary quartz veins in the eclogites and the amphibolite rims surrounding the eclogite boudins. Another cause for the concentration change might be the resorption of refractory minerals (e.g., zoisite/clinozoisite) rich in trace elements during garnet growth (Hollister, 1969).

The depletion of HREEs in garnets from eclogites is unusual, but has been observed by a number of investigators (e.g., Jerde et al., 1993; Messiga et al., 1995). Messiga et al. (1995) reported a zoned-garnet grain with decreasing HREE concentrations from core to rim, as observed in our samples. There are several possibilities for this change in concentration, including the influence of major-element chemistry and crystallography. Caporuscio and Smyth (1990) found a positive correlation of grossular content and the incorporation of MREE into garnets. They attributed this to the size of both the cations and the crystallographic site in the garnet structure. The variation in grossular content in a single eclogitic garnet from Trescolmen is about 12 mol.%. Because of the complicated zoning pattern, the trend observed by Caporuscio and Smyth (1990) is not visible in sample

in Tr98-3-3-1. The sharp increase in Ca concentration at the at the compositional break between domain I and II (Fig. 9) could indicate the resorption of a Ca-rich phase, such as plagioclase or zoisite/clinozoisite that has relatively low HREE concentrations. It is also possible that the HREE-garnet zoning might be a function of metasomatism. However, this seems unlikely because other trace elements such as Sr, or V, remain unchanged in the Ca-rich zone.

All omphacites analyzed for REEs display a bell-shaped pattern, i.e., a strong depletion in both LREEs + HREEs. The overall abundance of REEs in the omphacites in comparison with the garnets is smaller by a factor of ~ 10 . Caporuscio and Smyth (1990), from an investigation of mantle eclogites, suggested that the overall abundance of REEs in clinopyroxenes might depend on charge-balance involvement of the jadeite component. The strong depletion of the LREEs in omphacite is unusual, but has been reported to occur in the Adula nappe at Soazza (Bocchio et al. 2000) and from eclogitized Fe-Ti gabbros from the Ligurian Alps (Messiga et al., 1995; Tribuzio et al., 1996). Several other studies (e.g., Gromet and Silver, 1983; Thöni and Jagoutz, 1992; Tribuzio et al., 1996) indicated that major amounts of REEs commonly reside in accessory phases, such as apatite, allanite, zoisite etc. These accessory phases can control the abundance of trace-element patterns in the residual rock (e.g., Sorensen and Grossman, 1989; Sorensen et al., 1997). Some of these minor-mineral chemistries can completely dominate the REE abundances of a rock. Since the eclogites investigated in this study contain apatite and zoisite, it is suggested that the bell-shaped REE curves of the omphacites are caused by preferential incorporation of the LREEs into zoisite and the HREEs into garnet.

CONCLUSIONS

1. Garnets from eclogites and metapelites at Trescolmen show a wide range in chemical composition. The compositional X-ray maps of garnet porphyroblasts show that many garnets are at least Alpine in age and have undergone eclogite-facies metamorphism followed by amphibolite-facies overprinting during exhumation. We speculate though that some garnet cores are pre-Alpine.

Garnets from the structural lowest part (western ridge) and the structural highest part of the metapelitic zone have concentric major-element zoning patterns, whereas all the larger garnet porphyroblasts from the actual cirque have complex zoning patterns due to deformation and overprinting. There is a possibility that the border region of the Trescolmen cirque experienced a different tectonic history before the amphibolite-facies metamorphism.

2. Oxygen-isotope compositions for eclogites (especially for the larger boudins), in addition to bulk-rock chemistry, point to a basaltic precursor that has preserved its oxygen-isotope signature during eclogite-facies metamorphism. The slightly higher whole-rock $\delta^{18}\text{O}$ values in comparison with the signature of MORB ($5.7 \pm 0.2\text{‰}$; Harmon and Hoefs, 1995) may be a result of seafloor “weathering” at ambient temperatures or by low temperature hydrothermal alteration (Muehlenbachs, 1986). Alternatively, the higher $\delta^{18}\text{O}$ values could have been derived from continental-type basaltic protoliths, which have a higher $\delta^{18}\text{O}$ values than MORB (Harmon and Hoefs, 1995). In general, the smaller eclogite boudins have higher $\delta^{18}\text{O}$ values than the larger boudins (e.g., Grt $\delta^{18}\text{O}$ of $\sim 6.5\text{‰}$ vs. 5.6‰ , respectively). Assuming that both small and large boudins had the same protolith,

the easiest explanation for the elevated $\delta^{18}\text{O}$ values for the smaller boudins is the infiltration of fluid with a higher $\delta^{18}\text{O}$ than the bulk eclogites, perhaps derived from dehydration of the metapelites.

3. Garnet and quartz $\delta^{18}\text{O}$ values at the interface of the two lithologies overlap, and both gradually increase towards the metapelite, indicating fluid exchange. These systematic $\delta^{18}\text{O}$ gradients have been observed from several traverses across eclogite-metapelite contacts. Dehydration of the eclogites might have caused this gradient in the metapelites in the close vicinity of the eclogites.

4. Fractionation of oxygen isotopes between quartz and garnet in metapelites and eclogites points to a close approach to oxygen-isotope equilibrium, at least at the scale of a thin section. The obtained fractionation temperatures reach $\sim 600^\circ\text{C}$, which is in agreement with temperatures estimated from phase-equilibria considerations. In addition, the close approach to equilibrium fractionation between garnet and quartz suggests that fluid flow occurred before the growth of garnet. Oxygen-isotope fractionation between omphacite and garnet points to disequilibrium that might be a result of slow diffusion of oxygen in these minerals.

5. Trace-element chemistry of garnet porphyroblasts in eclogites shows a depletion of the HREEs in the Ca-overprinting zone. This might have been caused by a Ca-rich reactant with low HREE content such as plagioclase or zoisite/ clinozoisite. REE patterns of omphacite grains are LREE and HREE depleted, probably caused by preferential partitioning of the LREEs into minerals such as zoisite or apatite and the HREEs into garnet.

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PART 3

**METAMORPHISM AND FLUID-ROCK INTERACTION IN THE
ADULA NAPPE: EVIDENCE FROM OXYGEN ISOTOPES IN
METAMORPHIC MINERALS**

ABSTRACT

Fluid-rock interaction can be recorded in the stable-isotope systematics of a metamorphic terrane. At Trescolmen (Adula nappe, central Alps), systematic variations of oxygen-isotope ratios in quartz, garnet, kyanite, and rutile have been used to determine the nature and extent of fluid-rock interactions, as well as to determine peak-metamorphic temperatures in a polymetamorphic terrane. Detailed traverses across eclogite-metapelite contacts reveal a systematic gradient in $\delta^{18}\text{O}$ on a meter scale in the eclogite and metapelite adjacent to the eclogite. At the interface of the two disparate rock types, quartz and garnet $\delta^{18}\text{O}$ values from both rock types are indistinguishable but increase farther into the metapelites. The width of these boundary zones seem to have a positive correlation with the size of the eclogite boudin. The shape of the $\delta^{18}\text{O}$ gradient with an inflection point close to the interface between the two rock types suggests diffusional exchange in a static, at least temporarily connected, grain-boundary fluid. Oxygen-isotope fractionation of Qtz-Grt, Qtz-Ky, and Qtz-Rt pairs yield apparent temperatures in the range between 550 to 750°C. Although oxygen-isotope fractionation among minerals approach equilibrium, Qtz-Grt pairs from coarse-grained eclogites record disequilibrium due to inherited $\delta^{18}\text{O}$ values in garnets, possibly acquired during pre-Alpine, amphibolite-facies crystallization. The range of $\delta^{18}\text{O}$ signatures observed in eclogites points to basaltic protoliths, which have experienced different types of hydrothermal alteration prior to Alpine metamorphism. Furthermore, the preservation of isotopic heterogeneities at Trescolmen precludes any large scale-fluid infiltration during the Alpine orogeny.

INTRODUCTION

Oxygen isotopes have been extensively used to document fluid-rock interaction, as well as to determine paleo temperatures of geologic terranes. Oxygen-isotope studies of meta-basalts and gabbros in exhumed high-pressure terranes have been used to document the scale of fluid-rock interaction, as well as the nature of fluid flow in subduction zones (Bebout, 1997; Cartwright and Barnicoat, 1999). For example, homogeneous $\delta^{18}\text{O}$ values over a wide area from a variety of lithologies in the Catalina Schist (California), which underwent high-pressure metamorphism during subduction, have been taken as evidence for large scale fluid-rock interaction (Bebout, 1991a). In contrast, oxygen-isotope studies in Alpine eclogites point to restricted fluid flow (centimeter to meter scale) under high-pressure metamorphism (e.g., Philippot and Selverstone, 1991; Nadeau et al., 1993; Getty and Selverstone, 1994; Barnicoat and Cartwright, 1997; Putlitz et al., 2000). Possible mechanisms for mass transport include diffusion along grain boundaries and fluid films, and through crystal lattices, as well as by advection or infiltration along fractures and zones weakness via a moving fluid (e.g., Bebout, 1991b; Joesten, 1991). Following the modeling of Bickle and McKenzie (1987), several investigators fitted 1-D transport equations to compositional profiles to gain insight into the nature of the fluid flow, i.e., diffusion versus advection. Thereby, it was possible to extract quantitative information such as fluid flux, porosity, diffusivity, and timing (e.g., Bickle and Baker, 1990; Cartwright and Valley, 1991; Nabelek and Labotka, 1993; Graham et al., 1997). Many of the compositional profiles have been measured across silicate-marble contacts because of large isotopic contrasts (e.g., Bickle and Baker, 1990; Cartwright and Valley, 1991; Baker and Spiegelman, 1995; Gerdes et al., 1995). However, few profiles have been performed

across silicate-silicate contacts because of smaller isotopic contrasts and generally lower reactivity of silicates with a H₂O-rich fluid in comparison with marble (Cartwright and Valley, 1992; Puris and Wickham, 1994; Skelton et al., 1997).

Fractionations of oxygen isotopes among coexisting minerals are sensitive to temperature; however, it has been widely recognized that oxygen-isotope thermometry yields apparent temperatures that are reset or discordant because of diffusion during cooling (e.g., Deines, 1977; Javoy, 1977; Gilletti, 1986; Valley, 2001) or because of retrograde net-transfer reactions (Kohn, 1993; Young, 1993). Models have been developed to assess these apparent temperatures in terms of diffusional resetting (Dodson, 1973; Gilletti, 1986; Jenkin et al., 1991; Eiler et al., 1992).

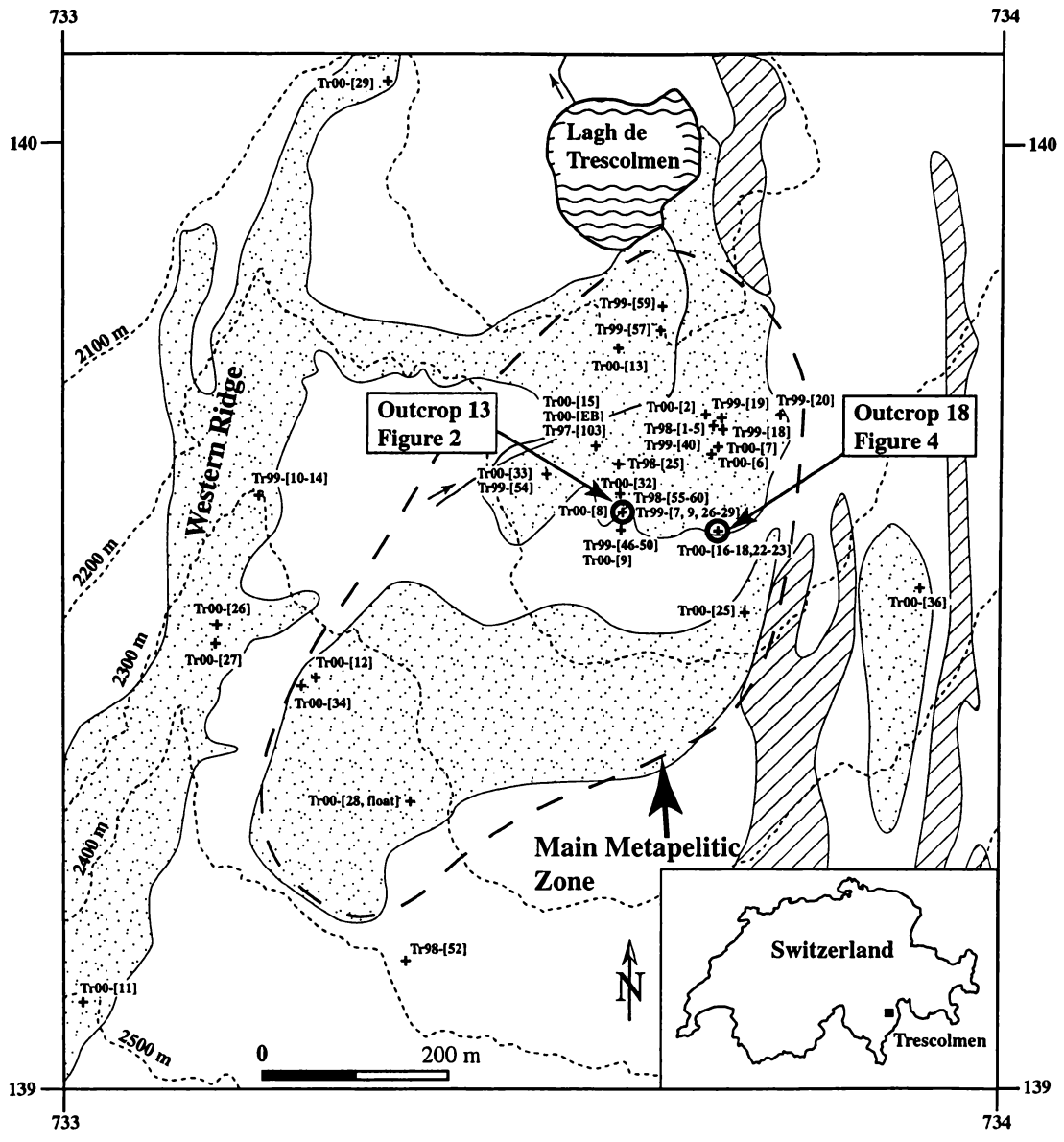
This paper utilizes oxygen isotopes to infer fluid sources and the nature of fluid-rock interaction at different scales at Trescolmen. Oxygen-isotope gradients between metapelites and eclogites at this locality were first recognized by Wiesli et al. (2001). Well exposed eclogite-metapelite contacts have permitted detailed sampling traverses with an assessment of the nature of fluid-rock interaction between the two lithologies in a high-pressure terrane. On a larger scale, the more regional implications of the oxygen-isotope results are addressed. In addition, to gain independent estimates from conventional thermometry (cation partitioning), we have used oxygen-isotope fractionation between Qtz-Grt, Qtz-Ky, and Qtz-Rt pairs to calculate apparent temperatures. These temperatures are evaluated for possible diffusional resetting using the Fast Grain Boundary (FGB) diffusion model of Eiler et al. (1992).

GEOLOGIC SETTING

Trescolmen (Fig. 1) is the region of the present study, located in the lower Penninic Adula nappe in the southeastern Swiss Alps. At Trescolmen, well-exposed eclogite boudins ranging from less than a meter to several 10s of meters in size are embedded in metamorphosed, pre-Mesozoic pelitic host-rocks (Heinrich, 1986). Although the timing and process of juxtaposition of the two rock types remains uncertain, both rock types shared the early Alpine eclogite-facies metamorphism followed by amphibolite overprinting during decompression (Heinrich, 1986). Inclusions of epidote, amphibole, and paragonite in garnet porphyroblasts from eclogites suggest a pre-eclogite-facies metamorphic stage (Variscan ?) for some of the Trescolmen eclogites (Heinrich, 1983; Wiesli et al., 2001). Quartz-bearing veins in both eclogites and metapelites bear evidence of the presence of fluids during the evolution of this metamorphic terrane. Peak-metamorphic conditions for the Trescolmen area have been estimated from a sodic white-schist sample to be 2.4 GPa at 600°C (Meyre et al., 1999). In addition, five deformation phases related to the Alpine orogeny have been recognized at Trescolmen (e.g., Meyre and Puschignig, 1993; Partzsch, 1998). The most visible phase is the Zapport phase that manifests itself as an axial-planar foliation.

Eclogite boudins at Trescolmen were subjected to amphibolite-facies conditions as a result of fluid infiltration during decompression (Heinrich, 1982). Some of the smaller boudins have been completely overprinted by amphibolite-facies mineralogy, whereas larger boudins were only affected at their rims, the alteration zone ranging from few millimeters to more than half a meter. The alteration manifests itself as replacement of omphacite by a symplectitic intergrowth of hornblende + plagioclase ± diopside and of gar-

Figure 1. Simplified geologic map of the Trescolmen area, showing sample localities referred to in this paper. Stippled areas indicate metapelites, with the numerous mafic boudins embedded in them (not shown). Diagonally ruled areas show phengite or two mica gneisses. White areas indicate debris fields, grass, and talus. Numbers on the side refer to the Swiss national grid (in km). Thin dashed lines are topographic contour lines with elevation given in meters. The main metapelitic zone is marked with a thick dashed line. Structural levels increase from west to east (modified after Puschig, 1992, and Meyre, 1993).



net by chlorite \pm epidote (Heinrich, 1982). Heinrich (1982) suggested that infiltration of hydrous fluids from dehydrating metapelites nearby were responsible for the alteration. Interior parts of eclogite boudins remain mostly unaltered except for incipient, symplectitic overgrowth (about 10 μm thick) at omphacite grain boundaries. The amphibolite-facies overprint in the metapelites is evidenced by epitactic overgrowth of biotite on phengite grains, a decrease of the celadonite component toward the rim of phengite grains, and fine-grained reaction products of the generalized reaction $\text{Pa} + \text{WM1}$ (WM = white mica) $+ \text{Grt} = \text{WM2} + \text{Bt} + \text{Pl} + \text{Qtz} + \text{H}_2\text{O}$ (Heinrich, 1982).

ANALYTICAL METHODS

Analyses of major elements were performed on polished thin sections of eclogite and metapelite samples using a CAMECA SX-50 electron microprobe (EMP) at the University of Tennessee. Accelerating voltage was 15 kV, with a beam current of 20nA (Faraday cup). The beam diameter employed, depending on the grain size, was either 5 μm (Grt, Cpx, Pl) or 10 μm (mica), with counting times of 20 seconds for each element. All data were corrected applying the CAMECA PAP correction procedure (Pouchou and Pichoir, 1985). Modal abundances of minerals were determined by point counting with an automated stage. Depending on grain size, up to 8000 points were counted per thin section. Grain sizes were estimated using a calibrated eyepiece reticule.

Oxygen isotope analyses were performed, using ~ 1 to 2 mg single grains or splits of minerals by laser-fluorination technique, at the University of Wisconsin, Madison. On each of the 12 analysis days, prior to analysis of samples, at least four aliquots of UWG-2 garnet standard were analyzed, yielding an average of $5.73 \pm 0.09\text{‰}$ (1sd, $n = 55$, $1\sigma =$

0.01). All analyses were corrected to University of Wisconsin Gore Mountain garnet standard (UWG-2) that has a recommended value of $5.8 \pm 0.1\text{‰}$ (1σ), yielding $\delta^{18}\text{O} = 9.59\text{‰}$ for NBS-28 African sand (Valley et al., 1995). The average correction based on each day's analysis of UWG-2 was 0.07‰ . NBS-28 analyzed on the same day as UWG-2 yielded $9.55 \pm 0.06\text{‰}$ (1sd, $n = 3$), making $\Delta^{18}\text{O}_{\text{NBS28-UWG2}} = 3.75\text{‰}$. Mineral separates were obtained by crushing about 0.5 cm^3 of a sample and by handpicking, using a binocular microscope. For accurate sampling of two adjacent minerals, as well as assessment of individual larger grains for homogeneity, the thin-saw-blade technique of Kohn et al. (1993) was utilized. Only inclusion-free minerals were analyzed. All analyses are reported with respect to V-SMOW.

Oxygen-isotope temperatures between mineral pairs (Qtz-Grt, Qtz-Ky, and Qtz-Rt) were calculated using the equation $\Delta_{i,j} = A \times 10^6/T^2$ (T in K), except for the Qtz-Ky calibration of Zheng (1993) and the Qtz-Rt calibration of Chacko et al. (1996). These use a second- and third degree polynomial, respectively, to approximate the temperature-dependent equilibrium fractionation. Simple error propagation of uncertainties in the A factor and the analytical precision give temperature uncertainties of $\pm 35 \text{ °C}$ for Qtz-Ky pairs, $\pm 25 \text{ °C}$ for Qtz-Grt pairs, and $\pm 15 \text{ °C}$ for Qtz-Rt pairs.

SAMPLING

For the present study, samples were collected from eclogites, metapelites, and quartz veins and segregations in the Trescolmen area (Fig. 1). Most samples are from the main metapelitic zone, which hosts numerous eclogite boudins. Additional samples were obtained from the western ridge (the structurally lowest level of the Trescolmen cirque) and

from a metapelitic band already imbricated into the eastern gneiss layers (the structurally highest part of the Trescolmen cirque, see Fig. 1). Detailed traverses across eclogite-metapelite contacts, employing a core drill, have been performed to investigate the oxygen-isotope systematics in the vicinity of eclogite boudins. Spatial relationships among collected samples from Trescolmen are described in Table 1 (cf., Wiesli et al., 2001). Characterization of representative samples of eclogites and metapelites are given in Wiesli et al. (2001) and in the appendix. All mineral abbreviations in this paper are after Kretz (1983).

RESULTS

Traverses across eclogite-metapelite contacts

Wiesli et al. (2001) noticed a systematic variation of $\delta^{18}\text{O}$ values of minerals from eclogites and metapelites. In particular, garnets in larger eclogite boudins have lower $\delta^{18}\text{O}$ values (~ 5.3 to 6.0‰) than garnets in smaller boudins (~ 5.9 to 6.7‰). In addition, $\delta^{18}\text{O}$ values of minerals in metapelites close to eclogite boudins are lower than in metapelites farther away. We performed detailed core sampling across eclogite-metapelite contacts

Table 1. Spatial relationships among collected samples from Trescolmen.

Code	Comments
Mp1	Metapelites within 20 cm from an eclogite contact (main metapelitic zone)
Mp2	Metapelites at least 20 cm away from an eclogite contact (main metapelitic zone)
Mp3	Metapelites from the western ridge and metapelites imbricated into gneiss layers (eastern part of Trescolmen)
E1	Core of eclogite boudins > 3m in size (main metapelitic zone)
E2	Eclogite boudins < 3m in size and rims of larger E1 boudins (main metapelitic zone)
E3	Eclogite boudins embedded in Mp3 metapelites

from a small boudin (1 m) and a larger boudin (> 10 m) to determine the extent of oxygen-isotope variation in minerals, particularly quartz and garnet. Both traverses are approximately 90° to strike and perpendicular to the S3 foliation. Outcrop #13 (Fig. 2, Swiss coordinates: 733.600/139.600) is the same as described by Heinrich (1982), Meyre and Puschig (1993), Partzsch (1998), and Meyre et al. (1999). It contains two eclogite boudins, the northern one has been folded under eclogite-facies conditions (Meyre and Puschig, 1993). The core of the lens consists of a quartz-rich metapelite with jadeite-rich ($\sim\text{Jd}_{63}$) omphacite grains that are completely surrounded by a symplectite rim of sodic plagioclase and amphibole (cf., Meyre et al., 1999). In a traverse across the contact, sample Tr98-56 (Fig. 3 and Table 2) reveals similar $\delta^{18}\text{O}$ values for garnets from the quartz-rich metapelite in the fold hinge of the northern eclogite boudin and the metapelite right at the contact with the eclogite. Oxygen-isotope values of garnets increase to average values of $\sim 7\text{‰}$, about 20 cm away from the eclogite-metapelite contact. Oxygen-isotope values of quartz are slightly lower in the quartz-rich metapelite in the core of the northern eclogite boudin, but increase outside the eclogite boudin to $\sim 11\text{‰}$ (Fig. 3, Table 2).

An outcrop sketch of a traverse into a larger boudin is shown in Figure 4. Unlike the traverse across the small eclogite boudin, which indicated narrow zones of isotopic depletion (≤ 20 cm), the $\delta^{18}\text{O}$ values for garnet and quartz do not reach the typical plateau ($\sim 7.9\text{‰}$; $\sim 11.5\text{‰}$; respectively) observed in garnets and quartz in Mp2 metapelites (Fig. 5 and Table 2) until ≥ 1 m from the contact. In addition, oxygen-isotope fractionation between quartz and garnet ($\Delta^{18}\text{O}$) is relatively constant in the metapelitic part ($\sim 3.6\text{‰}$) but increases in the eclogitic part of the traverse ($\sim 3.8\text{‰}$, Fig. 5).

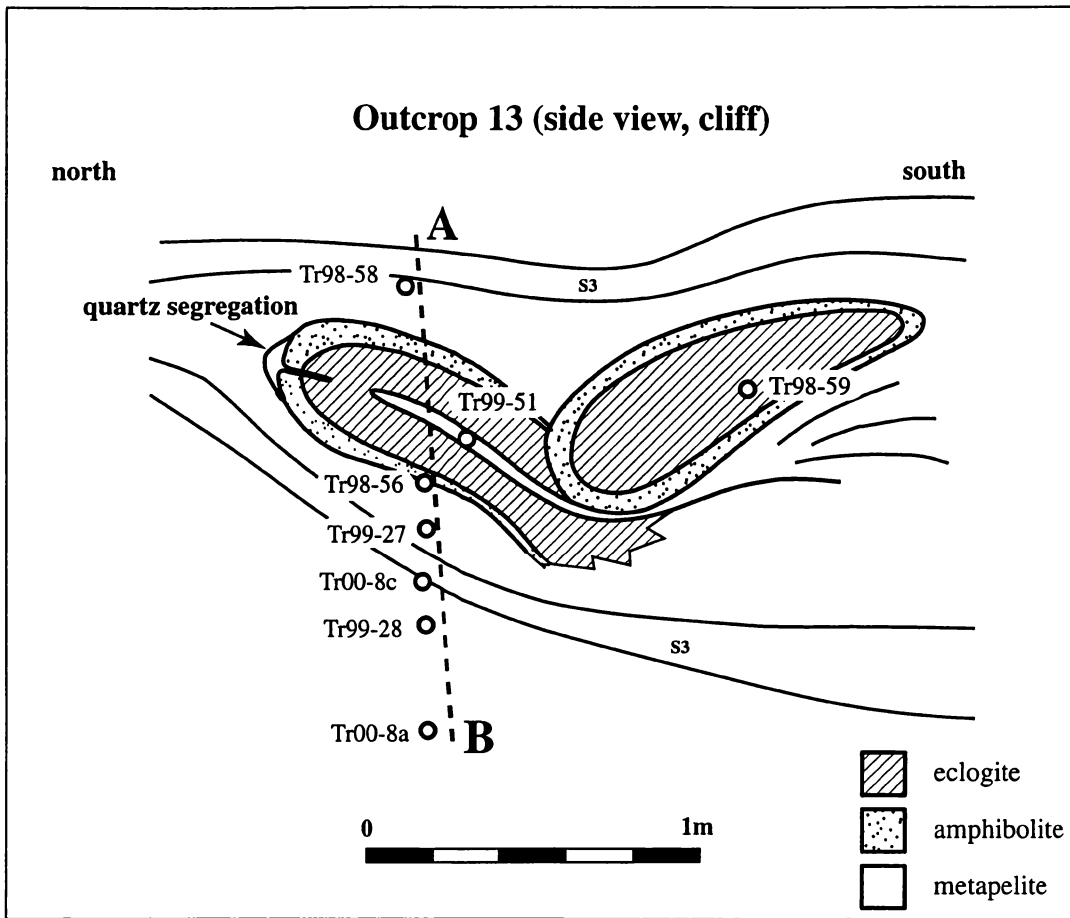


Figure 2. Schematic sketch of outcrop 13. Two eclogite boudins with amphibolite rims surrounded by metapelite. Notice the core of the northern, isoclinally folded boudin consists of metapelite. Typical for many boudins from Trescolmen are quartz segregations at boudin necks as seen at the north side of the isoclinally folded boudin (see Partzsch, 1998). Black circles indicate sample localities. S3 indicates the main axial-planar foliation observed at Trescolmen (Zapport phase, see Partzsch, 1998). The dashed line marks the traverse A-B which can be seen in Figure 3.

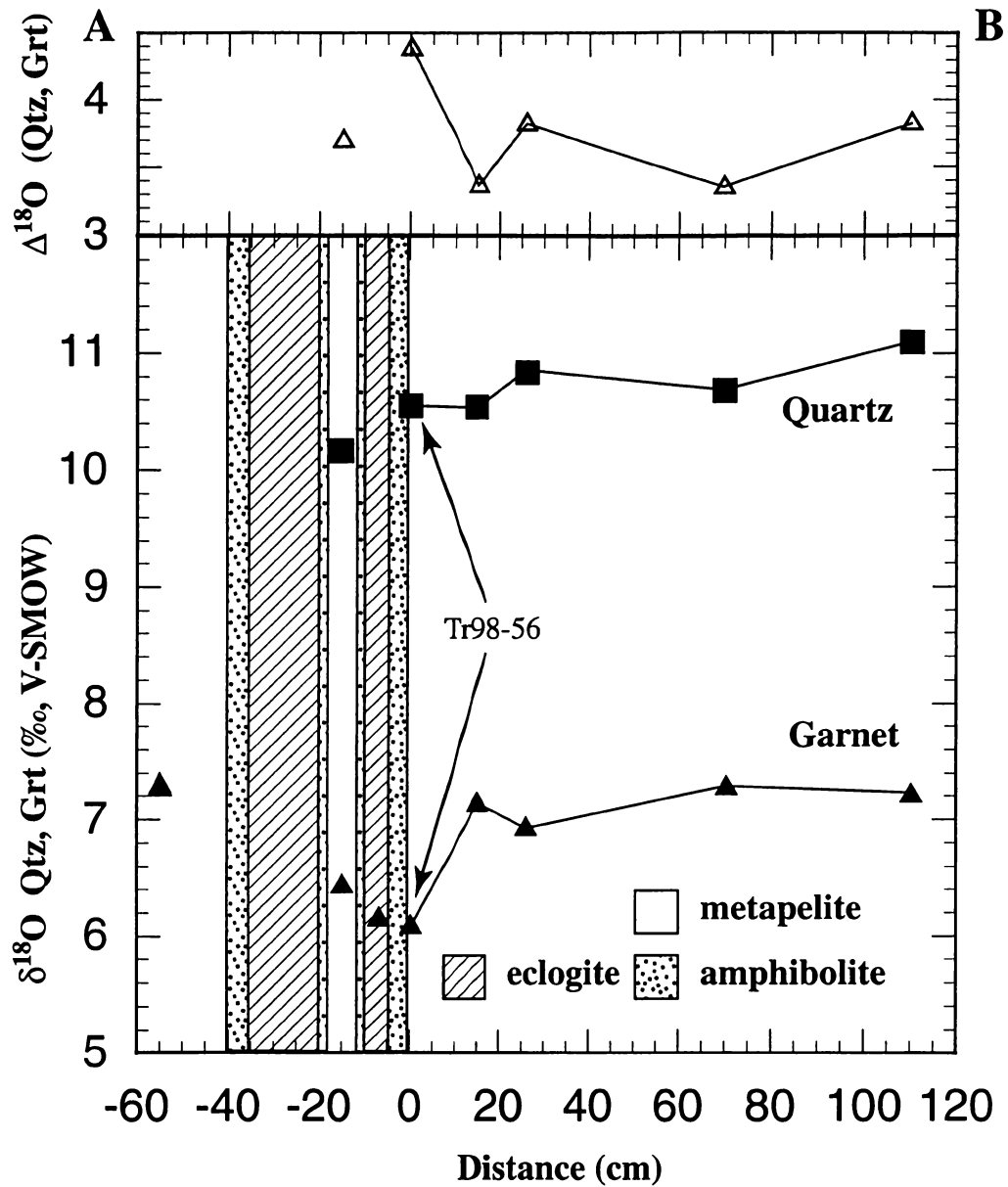


Figure 3. Oxygen-isotope composition of garnet and quartz versus distance across an eclogite-metapelite contact at outcrop 13. Sample Tr98-56 is a metapelite, about 6 mm from the contact. The upper part of the graph shows fractionation between quartz and garnet ($\Delta^{18}\text{O}$). Analytical uncertainty (1sd) in $\delta^{18}\text{O}$ values is less than the size of the symbols used. See Figure 2 for location.

Table 2. Oxygen-isotope values¹ of quartz-garnet pairs from Trescolmen. Included are calculated oxygen-isotope temperatures using different calibrations.

Sample	assemblage	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$	$\Delta^{18}\text{O}$	A=3.03	A=2.6	
		‰	‰		‰	T°C	T°C
		Qtz	Grt	‰	(M) ²	(Z) ³	(K) ⁴
Tr00-17b	E1	9.32	6.05	3.27	690	715	620
Tr00-22a	E1	9.57	5.89	3.68	635	650	565
Tr00-EB ⁵	E1	8.90	5.86	3.04	725	755	650
Tr98-59	E2	-	6.19	-	-	-	-
Tr00-2c	E2	10.39	6.79	3.60	645	660	575
Tr00-6a	E2	10.12	5.96	4.16	580	585	515
Tr00-12e	E2	10.56	6.27	4.29	565	570	505
Tr00-18a	E2	9.88 (± 0.06) ⁶	6.03 (± 0.09)	3.85	615	625	550
Tr00-18b	E2	9.98	6.07	3.91	605	615	540
Tr00-18c	E2	10.20 (± 0.09)	6.48 (± 0.03)	3.72	630	640	565
Tr00-25a1	E2	-	6.70 (± 0.01)	-	-	-	-
Tr00-25a2	E2	-	6.53 (± 0.01)	-	-	-	-
Tr00-25a3	E2	-	6.56 (± 0.10)	-	-	-	-
Tr00-27	E3	-	8.18	-	-	-	-
Tr00-36a	E3	12.57	9.07	3.50	655	675	590
Tr99-51 ⁵	Mp1	10.18	6.46	3.72	630	640	565
Tr98-58	Mp1	-	7.31	-	-	-	-
Tr98-56	Mp1	10.55	6.11	4.44	555	550	490
Tr00-9a	Mp1	10.07	6.55	3.52	655	670	585
Tr98-52b	Mp2	10.36	7.05 (± 0.06)	3.31	685	710	615
Tr99-27 ⁵	Mp2	10.55	7.16	3.39	670	690	600
Tr99-28 ⁵	Mp2	10.68	7.30 (± 0.01)	3.38	675	695	605
Tr00-2e	Mp2	10.85	7.40	3.45	665	685	595
Tr00-8a	Mp2	11.10	7.24	3.86	615	625	548
Tr00-8b	Mp2	10.73	7.47	3.26	690	715	620
Tr00-8c	Mp2	10.83	6.97	3.86	610	625	550
Tr00-13c	Mp2	10.82	7.45	3.37	675	695	605
Tr00-18d	Mp2	10.80 (± 0.15)	7.10 (± 0.06)	3.70	630	645	565
Tr00-18e	Mp2	11.51 (± 0.05)	7.91 (± 0.03)	3.60	645	660	575
Tr00-18f	Mp2	11.50 (± 0.06)	7.95 (± 0.03)	3.55	650	670	580
Tr00-25b	Mp2	10.90	7.23	3.67	635	650	569
Tr00-28	Mp3	14.32 (± 0.16)	10.94 (± 0.00)	3.38	675	695	605
Tr00-29	Mp3	12.80	8.67	4.13	585	590	520

¹ All analyses are given in ‰ (V-SMOW) and are corrected to UWG-2 = 5.8‰. Calibrations of: ² Matthews (1994), ³ Zeng (1993), ⁴ Kohn and Valley (1998). ⁵ Data from Wiesli et al. (2001). ⁶ Average of three analyses with the variation about the mean given in parenthesis. Two analyses were performed on separates obtained from different parts of the core sample (~5 cm distance).

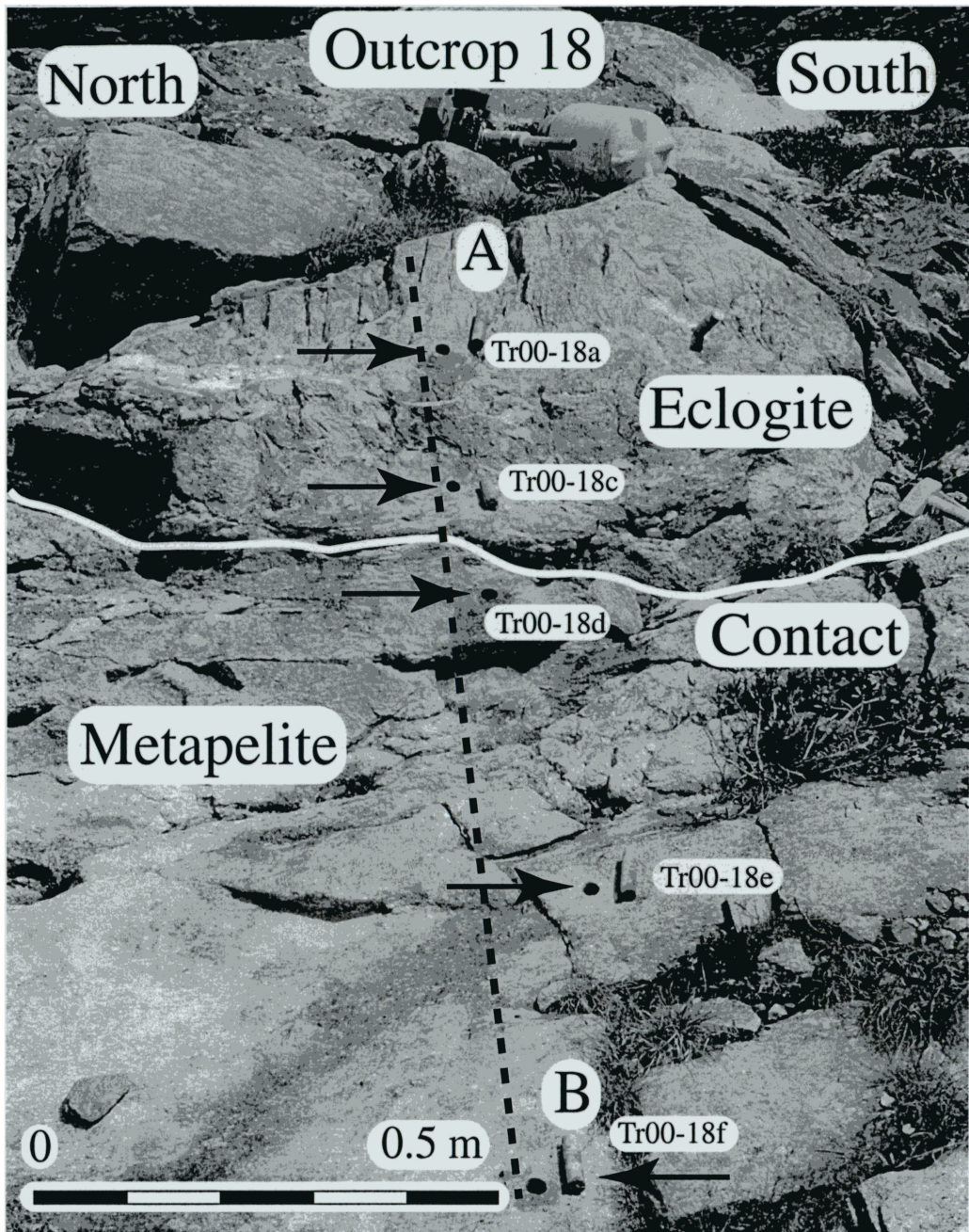


Figure 4. Picture of outcrop 18, showing sampling locations and the contact region between eclogite and metapelite. The exposed area of this eclogite indicates a boudin size of at least 10m in diameter. Notice the sample locations marked by black arrows. The dashed line marks the traverse A-B, seen in Figure 5.

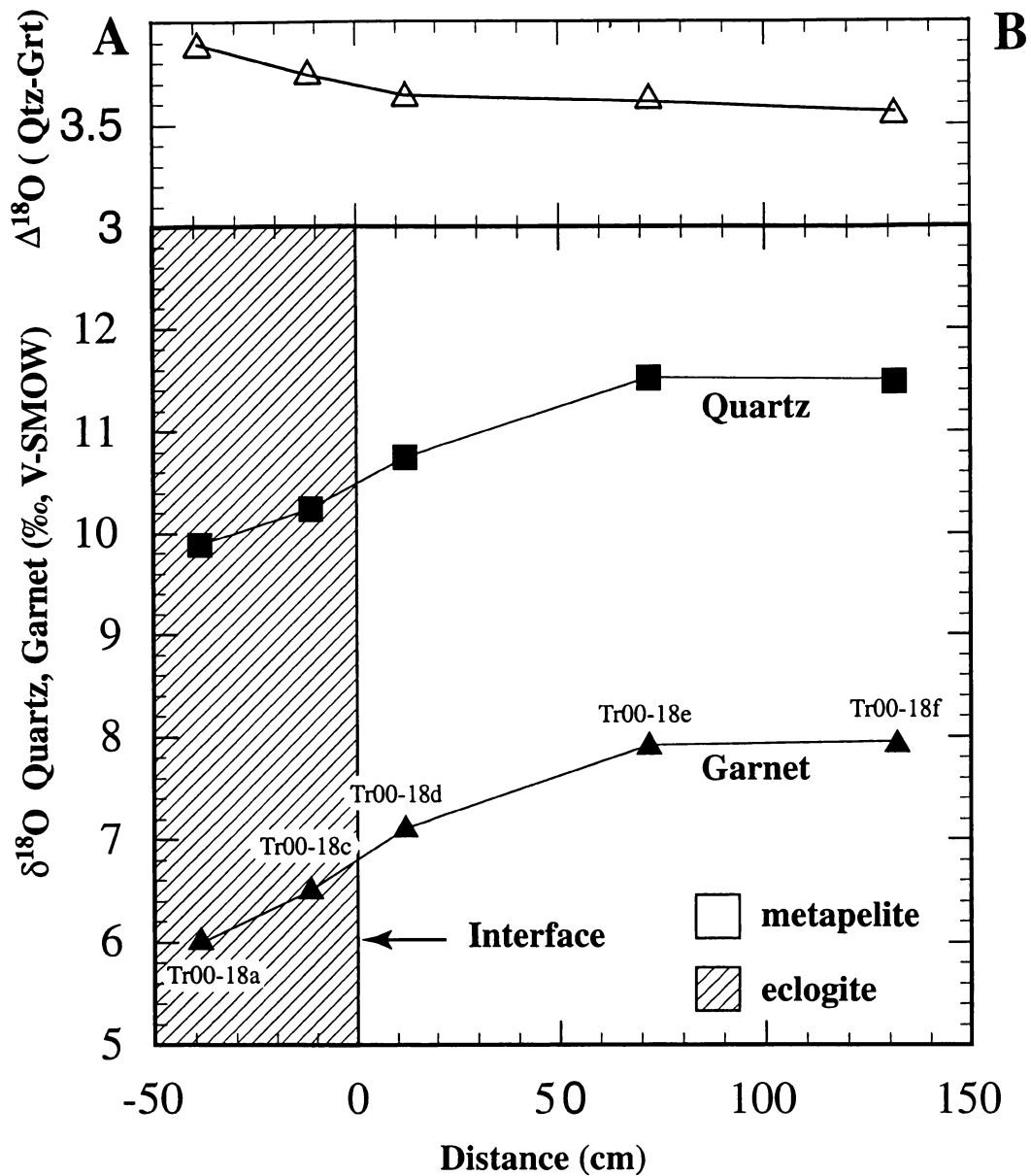


Figure 5. Oxygen-isotope composition of garnet and quartz versus distance across an eclogite-metapelite contact at outcrop 18. Notice the increase in $\delta^{18}\text{O}$ for both garnet and quartz from the eclogite into the metapelite. Omphacite close to the interface in the eclogite is altered to symplectite. The analytical uncertainty (1sd) in $\delta^{18}\text{O}$ values is less than the size of the symbols used.

Traverse across an amphibolite-eclogite contact

Rims of the eclogite boudins have been hydrated due to an influx of fluids during decompression (Heinrich, 1982). The width of the amphibolite rims vary from a few millimeters to completely overprinted, smaller eclogite boudins. A 140 mm long, 2.5 cm core has been drilled into a 3 m sized boudin at the sample locality Tr00-25a. This core consists of about 80 mm amphibolite and approximately 60 mm fresh eclogite. Different parts of the core have been sampled. The results are shown on Figure 6. The “Omp” sample closest to the surface (erosional contact) is a mixture of amphibole and Na-rich plagioclase (retrograde minerals); however, this does not seem to have any major effect on $\delta^{18}\text{O}$, in comparison with fresh omphacite values. Essentially, the isotopic compositions of garnet and omphacite from the fresh part of the boudin and the amphibolitized rim are indistinguishable, within analytical error. Similar results have been reported by Baker et al. (1997) from overprinted eclogites in the Dabie Shan, China.

Oxygen-isotope fractionation and thermometry of selected mineral pairs

Oxygen-isotope fractionation among coexisting minerals can be used to evaluate equilibrium conditions and constrain metamorphic temperatures independent of cation partitioning (e.g., Valley, 2001). In particular, oxygen-isotope fractionation between Refractory Accessory Minerals (RAM) such as garnet, kyanite, and rutile and modally dominant, faster oxygen-diffusing minerals (e.g., quartz) can provide accurate temperatures (Valley, 2001). Below, we use mineral-pair thermometry and compare it with the Qtz-Ky and Qtz-Rt RAM thermometers to obtain metamorphic temperatures for the Trescolmen area. An assessment of the calculated temperatures in terms of resetting is given in the discussion.

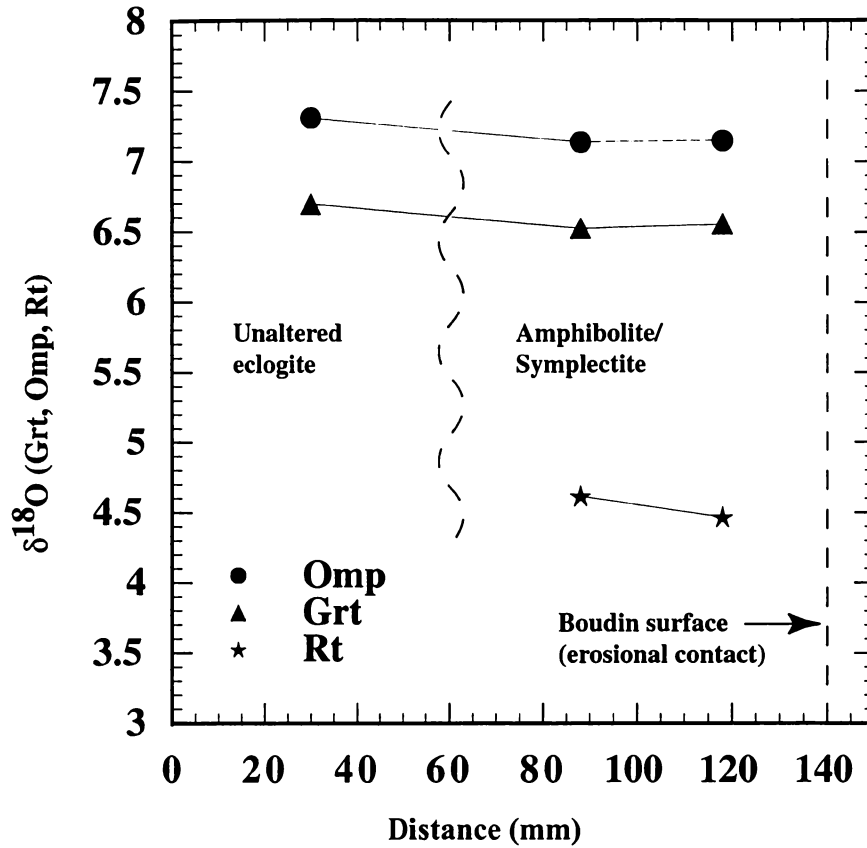


Figure 6. Oxygen-isotope composition of garnet, omphacite, and rutile from sample Tr00-25a versus distance across the rim of an eclogite boudin with an amphibolite rim. The mineral separates were derived from a 2.5 cm diameter core that has been drilled into the boudin. Analytical uncertainties (1sd) in $\delta^{18}\text{O}$ values are about the size of the symbols used.

Quartz-Garnet. Both eclogites as well as metapelites at Trescolmen contain these two minerals, allowing a comparison of the Qtz-Grt oxygen-isotope fractionation in the two rock types. The results of the analyses of mineral separates and the calculated temperatures can be seen in Table 2. The oxygen-isotope calibration of Matthews (1994), Zheng (1993), and Kohn and Valley (1998) have been employed for thermometry. The different calibrations yield reasonable and similar temperatures, although for some samples (e.g., Tr00-EB, Tr98-56), the obtained temperatures seem too high or low (see discussion below).

Quartz-Rutile. Rutile is a common mineral in crustal eclogites, and at Trescolmen, rutile occurs as a minor phase in all eclogites, as well as in eclogite-hosted, quartz-rich veins. Some of the rutile grains in these quartz veins reach a size of more than 10 mm. The results of analyses of mineral separates and the calculated temperatures are reported in Table 3. The calibrations used are from Matthews (1994) and Chacko et al. (1996). The calibration of Matthews (1994) yields slightly higher temperatures by about 45 °C. Quartz-rutile pairs from quartz veins in eclogites and quartz-rutile pairs from eclogite-host rocks give almost identical temperatures. Two samples (Tr00-EB and Tr00-15b1) yield significantly higher temperatures, which will be discussed below.

Quartz-Kyanite. Kyanite is a common high-pressure mineral in Al-rich metapelites, eclogites, and in eclogite-facies quartz veins (e.g., Moecher and Sharp, 1999; Philippot and Rumble, 2000; Widmer and Thompson, 2001). Kyanite at Trescolmen occurs in eclogites, metapelites, as well as in quartz-kyanite segregations associated with eclogite boudins. We have employed the empirical calibration of Sharp (1995) and the incremental method of Zheng (1993) in this study. Application of the calibration of Tennie

Table 3. Oxygen-isotope values¹ of quartz-rutile pairs from Trescolmen. Included are calculated oxygen-isotope temperatures using different calibrations.

Sample	assemblage	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$	$\Delta^{18}\text{O}$	$T^\circ\text{C}$	$T^\circ\text{C}$
		‰ Qtz	‰ Rt	‰	(M) ²	(C) ³
Tr99-14	E3, vein	12.09 (± 0.05) ⁴	6.07 (± 0.02)	6.02	640	600
Tr99-40	E1, vein	9.53 (± 0.15)	3.33 (± 0.04)	6.20	625	585
Tr00-15b 1	E1, vein	8.90	3.12	5.78	660	615
Tr00-7b	E2, vein	9.90 (± 0.02)	4.10	5.80	660	615
Tr00-18b	E2, vein	9.54	3.41	6.13	630	590
Tr00-EB	E1	8.90	3.53	5.37	695	650
Tr00-18b	E2	9.98	3.64	6.34	615	570
Tr00-2c	E2	10.39	4.21	6.18	630	585
Tr00-18c	E2	10.12	3.64 (± 0.07)	6.45	610	565
Tr00-25a 2	E2	-	4.62	-	-	-
Tr00-25a 3	E2	-	4.47	-	-	-

¹All analyses are given in ‰ (V-SMOW) and are corrected to UWG-2 = 5.8‰. ²Matthews (1994) and ³Chacko et al. (1996). ⁴Average of two or three analyses with the variation about the mean given in the parenthesis.

et al. (1998) and Hoffbauer et al. (1994) yielded temperatures outside the stability field of the Qtz-Mu-Grt-Ky assemblages (cf., Spear, 1989). The oxygen-isotope data of the mineral separates and the calculated temperatures are presented in Table 4. Temperatures calculated from the bi-mineralic Qtz-Ky segregations associated with eclogite boudins yield higher temperatures than Qtz-Ky pairs from host metapelites, similar to the results of Putlitz et al. (2002).

Quartz veins/segregations in eclogites and metapelites

The Trescolmen area, as many other similar metamorphic terranes (e.g., Franz et al., 2001; Van Wyck et al., 1996; Barnicoat, 1988) contains quartz veins in eclogites and metapelites. Many quartz veins in the metapelites have a north-south orientation (approximately parallel to the D3-fold axes; see Partzsch, 1998) and occur in various sizes (length of centimeters to 10s of meters, thickness from centimeters to ~1.5 meters). Quartz

Table 4. Oxygen-isotope values¹ of quartz-kyanite pairs from Trescolmen. Included are calculated oxygen-isotope temperatures using different calibrations.

Sample	assemblage	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$	$\Delta^{18}\text{O}$	$T^\circ\text{C}$	$T^\circ\text{C}$
		‰ Qtz	‰ Ky	‰	(S) ²	(Z) ³
Tr00-EB	E1	8.90	6.69	2.21	735	620
Tr00-15b 2	E1, vein	8.90	6.75 (± 0.04) ⁴	2.15	750	635
Tr00-26	Mp1	10.33 (± 0.03)	7.74 (± 0.00)	2.59	660	535
Tr00-9a	Mp1	10.07	7.81	2.26	725	610
Tr98-52	Mp2	10.54	7.96	2.58	660	540
Tr00-2e	Mp2	10.85	8.15	2.70	640	515
Tr99-20	Mp2	10.51	8.04	2.47	680	560
Tr99-55	Mp3	12.15 (± 0.07)	9.20 (± 0.11)	2.95	600	475
Tr00-11a	Mp3	13.12	10.39	2.73	635	510
Tr00-32a	segre., Mp1	9.81	7.52	2.29	720	600
Tr00-33	segre., Mp2	10.52	8.15	2.37	700	585
Tr00-34	segre., Mp2	10.56 (± 0.04)	9.45	2.11	760	645
Tr98-25a	segre., Mp2	10.59	8.22 (± 0.06)	2.37	700	585
Tr99-10	segre., Mp3	11.96	9.68	2.28	720	605

¹ All analyses are given in ‰ (V-SMOW) and are corrected to UWG-2 = 5.8‰. ² Sharp (1995); ³ Zheng (1993). ⁴ Average of two analyses with the variation about the mean given in parenthesis.

Table 5. Oxygen-isotope ratios¹ of vein quartz and quartz segregations from Trescolmen.

Sample	$\delta^{18}\text{O}$ Qtz	comments
Tr99-7	10.71	Quartz vein, 15m × 1m
Tr99-18	10.90	Quartz vein, 10m × 0.5m
Tr99-59	10.32	Quartz seg., 4m × 4m
Tr99-9	9.98	Quartz seg., boudin neck
Tr99-46	10.06	Quartz seg., boudin neck
Tr99-54	10.16	Quartz seg., boudin neck
Tr99-57	10.79 (± 0.15) ²	Quartz vein, 70m × 1m
Tr99-40	9.53 (± 0.15)	Quartz vein in eclogite, 1.5cm × 0.5m
Tr00-18b	9.54	Quartz vein in eclogite, 1cm × 10cm
Tr00-15b2	8.90	Quartz vein in eclogite, 2cm × 5cm

¹ All analyses are given in ‰ (V-SMOW) and are corrected to UWG-2 = 5.8‰. ² Average of two analyses with the variation about the mean given in parenthesis.

veins in eclogites can be seen to crosscut foliation and banding. The size of these veins ranges from a few millimeters to several centimeters in widths and up a meter in length (cf., Heinrich, 1986). In addition, many eclogites have quartz segregations at boudin necks and in pressure shadows adjacent to metapelites.

Results of quartz separates from veins and segregations are listed in Table 5. The average composition of quartz from veins in the main metapelitic zone (Mp2) is $\sim 10.70\%$ (± 0.25), whereas quartz veins in eclogites (E1 and E2) have values $\sim 9.21\%$ (± 0.45). Quartz segregations associated with eclogite boudins have average values $\sim 10.10\%$ (± 0.10). These oxygen-isotope values of quartz are within range observed in similar metamorphic terranes (e.g., compilation of Sharp et al., 1993).

DISCUSSION

The results shown above demonstrate four main points: 1) pervasive infiltration of an exotic fluid on a large scale (i.e., area of Trescolmen, about 1 km²) did not take place, rather, the observed oxygen-isotope gradients point to local redistribution (on the scale of meters) during the Alpine orogeny; 2) oxygen-isotope fractionation among coexisting minerals in both eclogites approach similar values, indicating that both lithologies experienced the last equilibration event together; 3) the oxygen-isotope exchange between eclogite boudins and adjacent metapelites may have taken place by means of fluid flow or by diffusion in a static grain-boundary fluid; and 4) the isotopic composition of minerals may have been altered or produced during Alpine metamorphism, or alternately, the isotopic gradients are of pre-metamorphic (i.e., pre-Alpine) origin. Below, we evaluate these different possibilities and put the oxygen-isotope systematics of the Trescolmen area in a

regional perspective.

Pre-metamorphic variations

The Penninic nappe stack, including the Adula nappe, consists mainly of metagranitoid gneisses and schists of pre-Mesozoic basement with Mesozoic rocks typically separating the different nappes (Heinrich, 1986). Oxygen-isotope compositions of minerals from these basement rocks, in contrast to minerals from Mesozoic rocks, show a relatively uniform composition (i.e., $\delta^{18}\text{O}_{\text{Qtz}}$ about 10.5‰, Hoernes and Friedrichsen, 1980). This led Hoernes and Friedrichsen (1980) to conclude that there was no major fluid infiltration of the basement rocks during the Alpine orogeny. In addition, the uniform $\delta^{18}\text{O}$ values may indicate extensive interaction with a magmatic fluid previous to the Alpine orogeny. Hoernes and Friedrichsen (1980) noted that the pre-Mesozoic, gneissic rocks in the Aare massif (~40 km northwest of the Adula nappe) had the same $\delta^{18}\text{O}$ values as the high-amphibolite grade metamorphosed gneisses from the core of the Penninic nappes. They considered this as evidence that oxygen-isotope compositions of minerals, despite recrystallization, were not changed during Alpine metamorphism. They reached similar conclusion for polymetamorphic basement rocks in the eastern Alps (Hoernes and Friedrichsen, 1978).

Oxygen-isotope composition of quartz from the main metapelitic zone at Trescolmen exhibits an average value of about 10.6‰ (Fig. 7). This is indistinguishable from the average value (10.5‰) reported by Hoernes and Friedrichsen (1980) for quartz from the pre-Mesozoic rocks (ortho- and paragneisses) from the lower Penninic nappes. This suggests that $\delta^{18}\text{O}$ values of quartz at Trescolmen were not significantly altered during the Alpine orogeny. There was no major fluid influx (with $\delta^{18}\text{O}$ out of equilibrium) into these

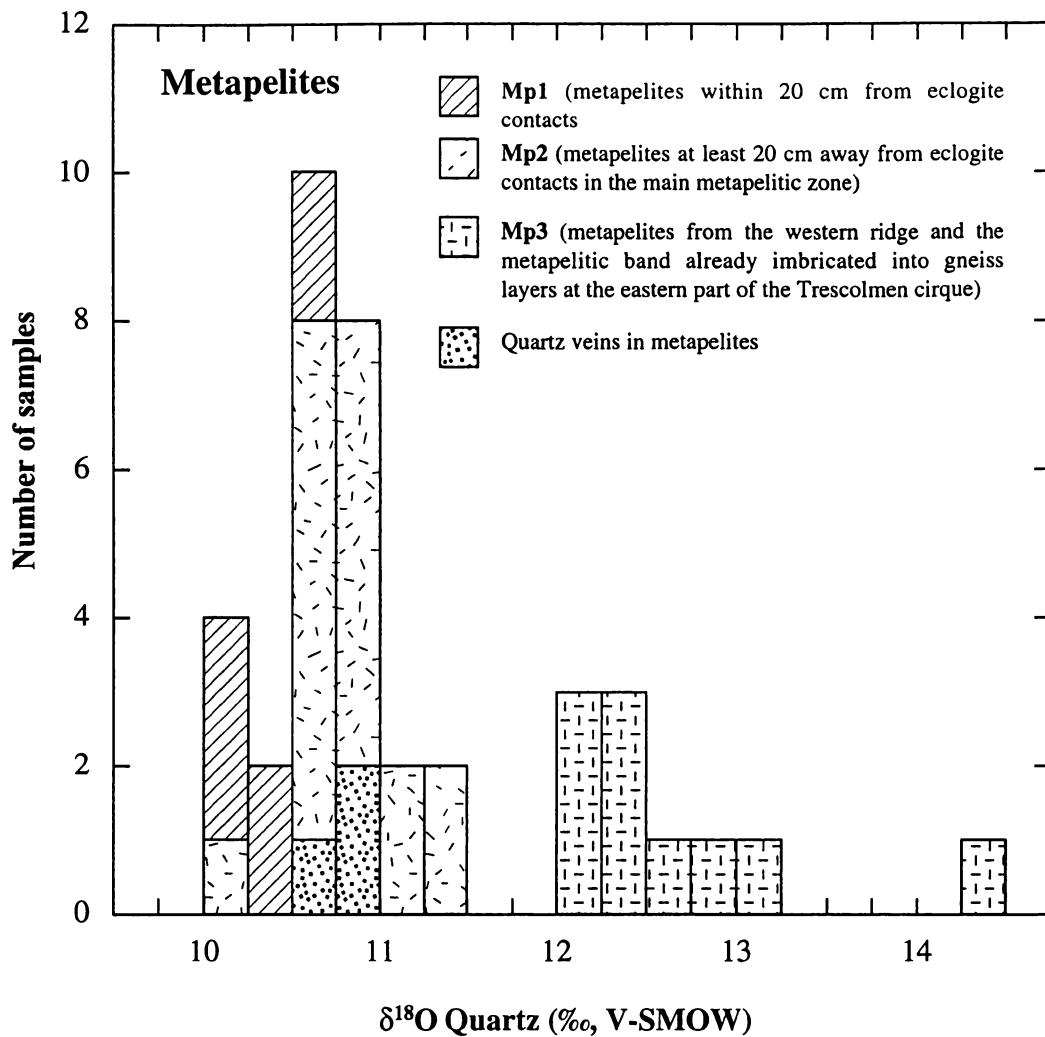


Figure 7. Histogram of quartz $\delta^{18}\text{O}$ values in metapelites and metapelite-hosted quartz veins at Trescolmen. Notice the bimodal distribution with peaks at about 10.6‰ and 12.5‰.

rocks during the two Alpine metamorphic episodes.

Although oxygen isotopes in smaller eclogite boudins, as well as rims of larger boudins, were probably modified during the Early Alpine eclogite-facies metamorphism, interior parts of larger boudins most likely retained their oxygen-isotope values from the protolith. Whole-rock $\delta^{18}\text{O}$ values of about 6 to 7‰ (calculated from modal abundances and $\delta^{18}\text{O}$ values of minerals) are indicative of MORB that has been exposed to seafloor and / or low temperature hydrothermal alteration in the upper part of the oceanic crust (e.g., Muehlenbachs, 1986). Oxygen-isotope studies of eclogitic gabbros in the western Alps have shown that pre-subduction signatures have remained undisturbed, even though the rocks subsequently experienced Alpine metamorphism (Miller and Cartwright, 2000; Putlitz et al., 2000). Thus, $\delta^{18}\text{O}$ values from large eclogite boudins at Trescolmen were probably not substantially modified during the Alpine orogeny. There is, however, evidence that the $\delta^{18}\text{O}$ values of minerals in smaller boudins and rims of larger eclogite boudins were modified (to higher $\delta^{18}\text{O}$ values) during Alpine metamorphism by local processes. Values of $\delta^{18}\text{O}_{\text{Qtz}}$ in eclogites in conjunction with structural position are given in Figure 8. The overlap of $\delta^{18}\text{O}$ values of quartz in Mp1 samples (see Figure 7) and E2 samples (see Figure 8) suggests that both crystallized in equilibrium with a similar fluid.

Oxygen-isotope fractionation and metamorphic temperatures

Oxygen-isotope thermometry can provide an independent estimate of crystallization temperatures, versus thermometry using phase equilibria. Reported temperatures from thermometry using phase equilibria and cation exchange for the Trescolmen area are in the range of 650 °C at 2.4 GPa for the eclogite-facies event (Trescolmen phase) and 650 °C at 0.65 to 1.4 GPa for the amphibolite-facies overprint (Zapport phase) (Heinrich,

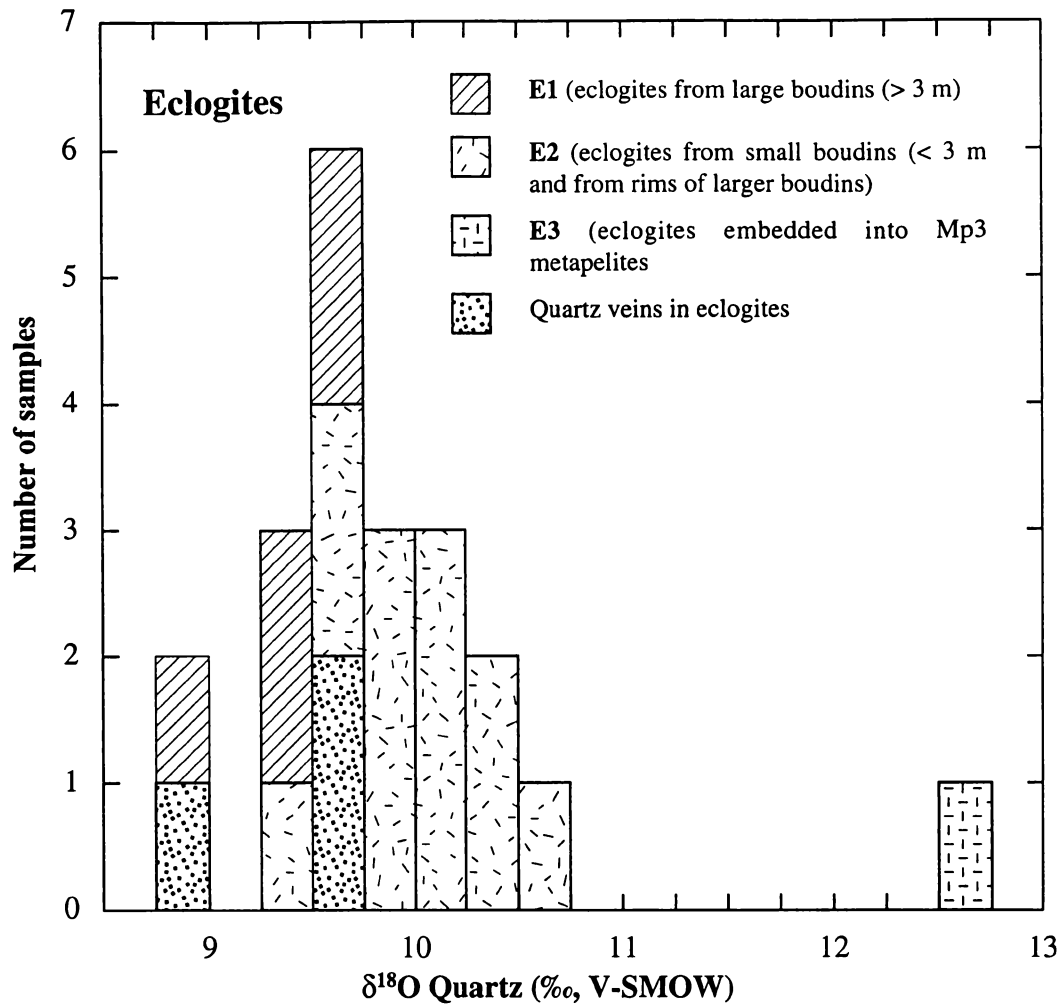


Figure 8. Histogram of quartz $\delta^{18}\text{O}$ values in eclogites and eclogite-hosted quartz veins at Trescolmen. The average is close to 9.75‰.

1986; Meyre et al., 1997; Partzsch, 1998; Meyre et al., 1999). The current investigation of metamorphic-peak temperatures at Trescolmen using oxygen-isotope fractionation among coexisting phases yielded temperatures in accord with estimates obtained from phase equilibria, cited above. However, oxygen-isotope thermometry can be complicated by polymetamorphism and various mechanisms of post-crystallization exchange during exhumation (Valley, 2001).

An assessment is warranted of the effect of polymetamorphism on oxygen-isotope fractionation for the rocks at Trescolmen. These rocks have experienced at least two metamorphic events: an early Tertiary eclogite-facies event followed by an amphibolite-facies overprint (e.g., Heinrich, 1986). Some eclogitic and metapelitic samples contain evidence suggesting an earlier (Variscan ?) metamorphic episode. If true, these rocks were already dehydrated at least once before the onset of the Alpine orogeny with the consequence that metamorphism during the Alpine events was relatively dry, which helped in the preservation of oxygen-isotope values in minerals. This preservation of oxygen-isotope values depends on several factors, such as peak-metamorphic temperatures, possible recrystallization, mineral assemblages and mode, and open or closed system movement of fluids during the different metamorphic events (Valley, 2001). Our investigation utilizes $\delta^{18}\text{O}$ values for garnet, kyanite, rutile, and quartz. Considering the low diffusivity of oxygen in garnet, rutile, and kyanite (Coghlan, 1990; Moore et al., 1998; Ghent and Valley, 1998), these minerals should preserve their initial oxygen-isotope values during subsequent metamorphic events.

The use of zoned minerals for oxygen-isotope thermometry can introduce errors into the temperature estimates. Theoretical models (Kohn, 1993) predict a zonation of \leq

0.5‰ for the encountered bulk compositions. Possible zonation of $\delta^{18}\text{O}$ in garnet, rutile, and kyanite has been assessed by microsampling, using the thin-saw-blade technique of Kohn et al. (1993). These results reveal a maximum zonation of $\sim 0.5\%$ for some garnets (cf., Wiesli et al., 2001), less than 0.1‰ for kyanite, and 0.2‰ for rutile. Compositional zonation of major elements in these garnets have been assessed by performing electron-microprobe traverses across garnet porphyroblasts, as well as by back-scattered electron images and elemental maps (see Wiesli et al., 2001). Knowledge of the compositional range in garnet is important because cation substitution can exert considerable influence on the fractionation behavior of oxygen in this mineral (Kohn and Valley, 1998).

An evaluation of open-versus closed-system behavior of fluids in metapelites and eclogites can be made using δ - δ plots. Although strictly true only for biminerally assemblages, the plots are still a good tool to assess open-closed behavior for multi-mineralic assemblages (Gregory and Criss, 1986). Isotopic compositions of coexisting Qtz-Grt, Qtz-Ky, and Qtz-Rt pairs from eclogites and metapelites are shown in Figures 9, 10, and 11. Although many samples appear to have approached isotopic equilibrium, the observed scatter, particularly for Qtz-Grt pairs, indicates a significant deviation which will be evaluated below. Oxygen-isotope ratios of minerals as a whole from both eclogites and metapelites align along calculated isotherms. This indicates that both rock types experienced the same general equilibration temperatures. Fractionation was independent of $\delta^{18}\text{O}_{\text{WR}}$ and occurred in a relatively closed system (Gregory and Criss, 1986). Furthermore, the alignment of arrays along isotherms implies that if any fluid-rock interaction took place, it must have been prior to the Alpine metamorphism.

Resetting of oxygen-isotope values of minerals due to inter- and intra-mineral dif-

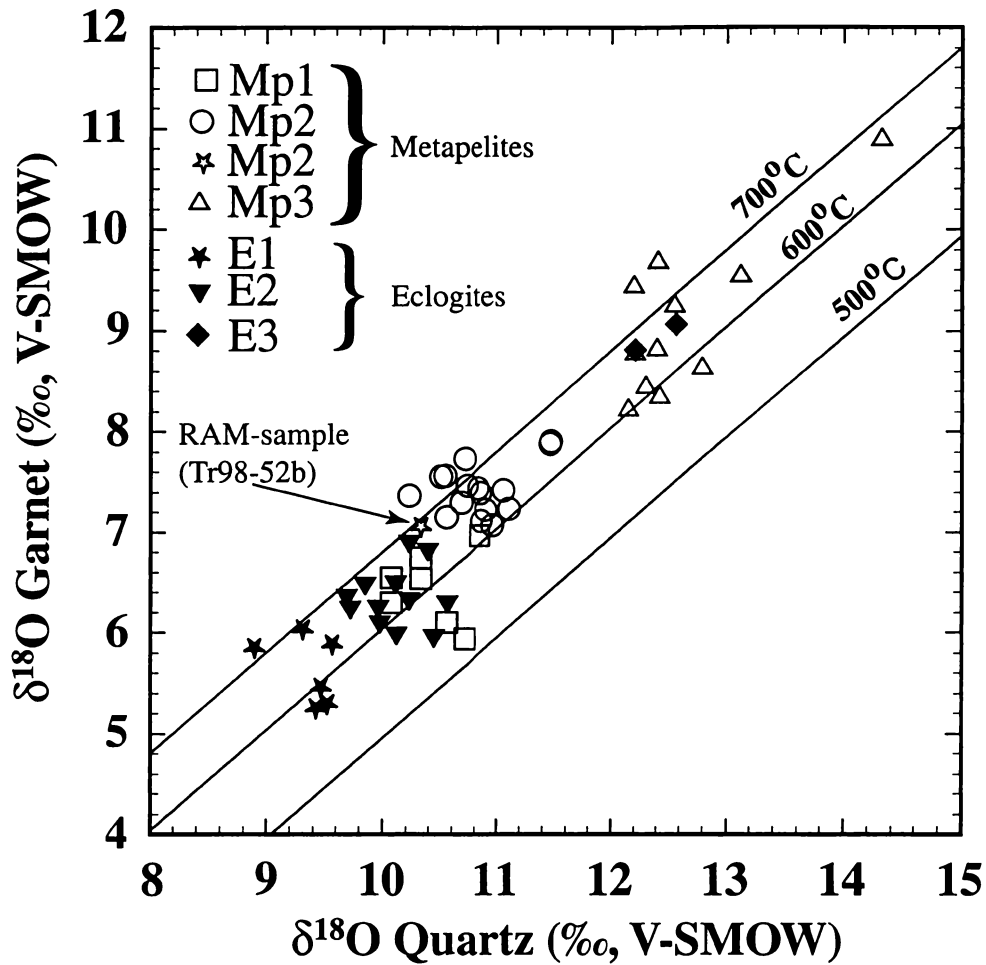


Figure 9. δ - δ plot of oxygen-isotope composition of quartz versus garnet from eclogites and metapelites from Trescolmen. The solid diagonal lines are the isotherms for temperatures of 500, 600, and 700 °C, using the relationship $\Delta(\text{Qtz-Grt}) = A \times 10^6/T^2$. The A parameter (3.03) is from Matthews (1994). Analytical uncertainty (1sd) in δ values are less than the size of the symbols used. This plot includes all the Qtz-Grt pairs from Wiesli et al. (2001). RAM = Refractory Accessory Mineral, as defined by Valley (2001).

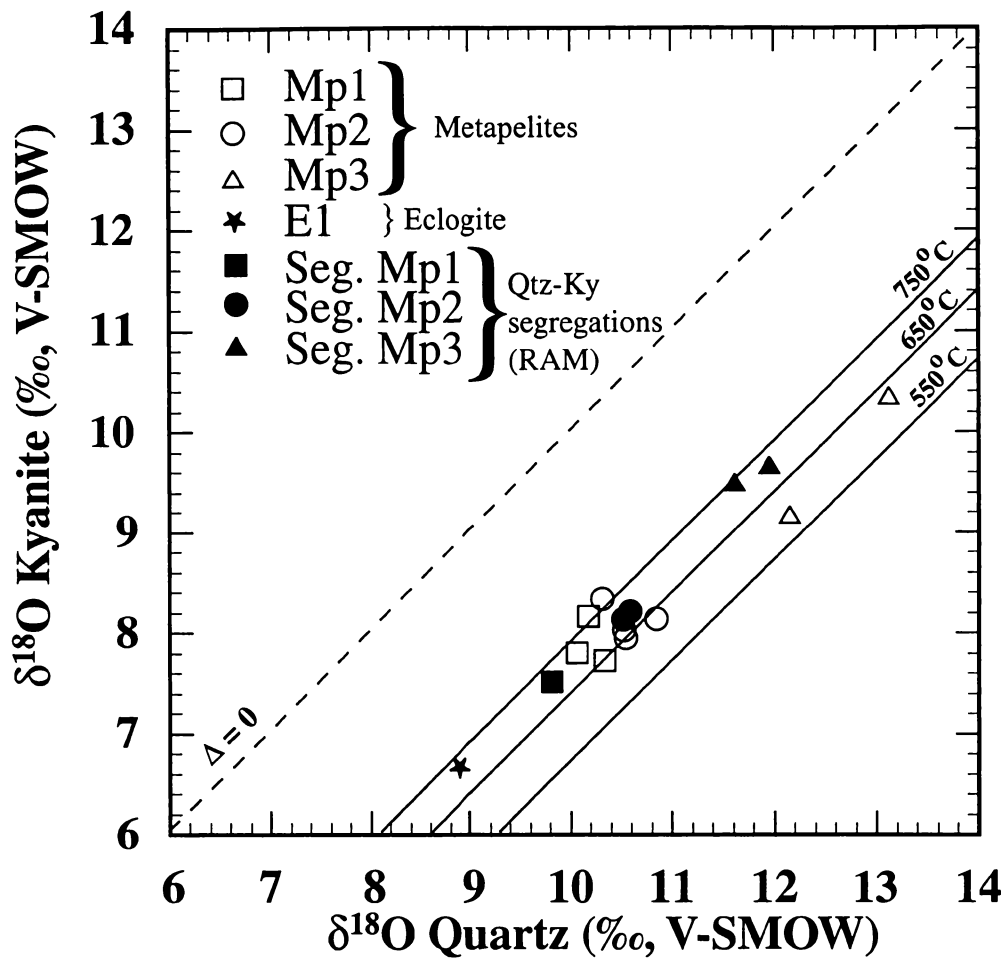


Figure 10. δ - δ plot of oxygen-isotope composition of quartz versus kyanite from eclogites, metapelites, and quartz segregations that occur with eclogite-boudin necks. The solid diagonal lines are for temperatures of 550, 650, 750°C, using the relationship $\Delta(\text{Qtz-Ky}) = A \times 10^6/T^2$. The A parameter (2.25) is from Sharp (1995). The dashed diagonal line indicates $\Delta = 0$. Analytical uncertainty (1sd) in δ values are less than the size of the symbols used. RAM = Refractory Accessory Mineral, as defined by Valley (2001).

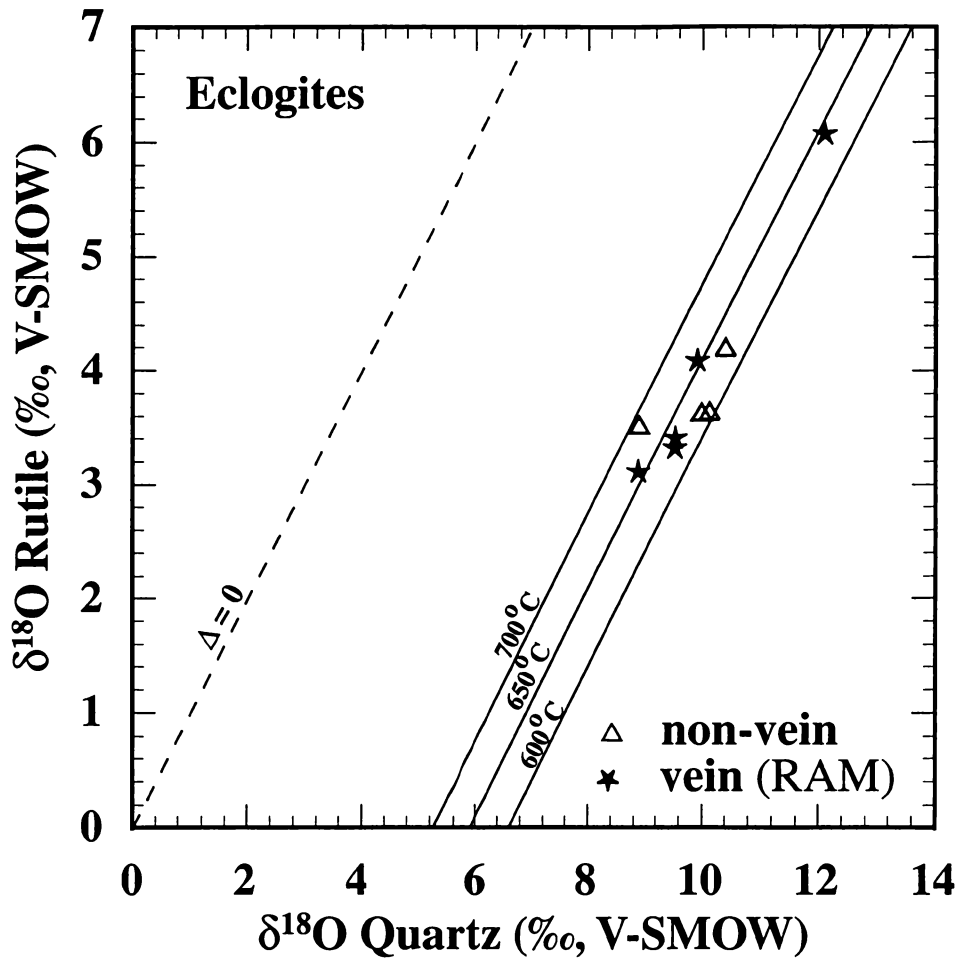


Figure 11. δ - δ plot of oxygen-isotope composition of quartz versus rutile from eclogites and eclogite-hosted quartz veins at Trescolmen. The solid diagonal lines are for temperatures of 600, 650, and 700 °C, using the relationship $\Delta(\text{Qtz-Rt}) = A \times 10^6/T^2$. The A parameter (5.02) is from Matthews (1994). The dashed diagonal line indicates $\Delta = 0$ fractionation. Analytical uncertainty (1sd) in δ values are less than the size of the symbols used. RAM = Refractory Accessory Mineral, as defined by Valley (2001).

fusion in a closed system may be evaluated by applying the Fast Grain Boundary (FGB) diffusion model of Eiler et al. (1992, 1993). This model predicts that peak metamorphic temperatures in a closed system can be preserved in bi-mineralic assemblages, especially with a modally dominant, fast-diffusing mineral (Ghent and Valley, 1998). Hence, quartz-kyanite segregations and quartz-rutile pairs from quartz veins in eclogites should be ideal candidates for the preservation of metamorphic-peak temperatures. Indeed, applying the FGB model to these bi-mineralic assemblages from Trescolmen confirms negligible resetting of $\delta^{18}\text{O}$ values during cooling, as observed in similar studies (e.g., Ghent and Valley; Moecher and Sharp, 1999; Putlitz et al., 2002).

Different calibrations of oxygen-isotope fractionation factors for the same mineral pairs yield a wide range in temperatures. The quartz-kyanite fractionation is a case in point (Ghent and Valley, 1998). Temperatures that are closest to phase equilibria restrictions are obtained by applying the empirical calibration of Sharp (1995). This calibration yields temperatures for the Qtz-Ky segregations from Trescolmen of 700-720 °C. Quartz-kyanite pairs from host rocks yield lower temperatures, ~650 °C. These lower temperatures may be the result of resetting of $\delta^{18}\text{O}_{\text{Qtz}}$ during cooling, as predicted by FGB modeling. The high temperatures obtained from the quartz-kyanite segregations could result from disequilibrium, however, no $\delta^{18}\text{O}$ zonation could be detected in the kyanite grains. Alternatively, disequilibrium could be due to early growth of low $\delta^{18}\text{O}$ quartz, as suggested by Ghent and Valley (1998). However, calculation of diffusion distances (distance $\approx (D \times t)^{1/2}$ in quartz at a temperature of 650 °C using oxygen-diffusion data (hydrothermal conditions) of Dennis (1984), and a time of 20 Ma, yields a distance of ~1.4 cm, suggesting homogenization of quartz during metamorphism on a centimeter scale. Furthermore,

$\delta^{18}\text{O}$ values of quartz from the segregations do not differ significantly ($\sim 0.3\text{‰}$) from quartz in metapelites nearby, thereby suggesting a common, local origin and equilibration event.

Thermometry of quartz-rutile pairs in eclogites shows no significant distinction for veins versus host rocks, indicating similar equilibration temperatures. Indeed, petrographic evidence suggests that the veins are in equilibrium with the host rocks. Closure temperatures for oxygen diffusion in rutile for the observed grain sizes ($> 0.3\text{ mm}$), including a cooling rate of 25 °C/Ma and $P(\text{H}_2\text{O}) = 100\text{ MPa}$, are in excess of 650 °C (Moore et al., 1998). Coupled with this is the initial fast-cooling rate from amphibolite-facies metamorphism ($> 100\text{ °C Ma}^{-1}$), as reported for the southern Adula nappe (Vance and O’Nions, 1992). Sharp (1995) noted apparent retrograde diffusional exchange in Qtz-Rt pairs, which he attributed to high-diffusion rates in rutile. We have utilized the new diffusion coefficients from Moore et al. (1998) to model possible resetting of Qtz-Rt pairs. The results indicate practically no diffusional resetting for the bimineralic vein assemblages. This implies that the obtained Qtz-Rt temperatures may indicate true crystallization temperatures of eclogite-hosted quartz veins.

Theoretically, quartz-garnet pairs, if quartz is modally dominant, i.e., not in metapelites or eclogites, should yield peak temperatures as predicted by the FGB diffusion model. However, in most cases in Trescolmen metapelites, there are additional fast-diffusing species present (i.e., white mica and plagioclase) that can explain a possible resetting. In contrast, eclogites are modally dominated by omphacite and garnet, quartz being only a minor phase. Hence, quartz-garnet pairs should be good indicators of open-system behavior of eclogites. Indeed, coarse-grained eclogites with garnet porphyro-

blasts (> 3 mm in diameter) have $\Delta_{\text{Qtz-Grt}}$ in excess of 4.00‰. X-ray maps of major-element zoning in these garnets indicates a possible pre-Alpine origin (Wiesli et al., 2001). Due to its refractory nature, garnet apparently preserved its $\delta^{18}\text{O}$ during Alpine reworking, whereas the $\delta^{18}\text{O}$ composition of quartz was modified during Alpine metamorphism.

A possible explanation for the Qtz-Grt disequilibrium is an ingress of high $\delta^{18}\text{O}$ fluids, derived from dehydrating metapelites during recrystallization of the quartz. Symplectite rims along omphacite grain boundaries are a common feature in eclogites from Trescolmen and give evidence for the presence of a late-stage fluid phase not in equilibrium with the omphacite. In two metapelitic samples (Tr98-56 and Tr99-48) adjacent to small eclogite boudins (1m size), disequilibrium between quartz and garnet was observed. The fractionation of $\Delta_{\text{Qtz-Grt}}$ of 4.44 and 4.77‰ are above the average fractionation of about 3.60‰ for quartz-garnet pairs encountered at Trescolmen. This is a clear indication that fluid exchange occurred that altered the $\delta^{18}\text{O}$ value of quartz, but left the garnet unchanged due to its refractory nature.

The unique eclogite sample Tr00-EB shows far higher calculated temperatures than any other sample of Trescolmen (Tables 2-4). The temperatures calculated for this sample are consistent for different mineral pairs, i.e., Qtz-Grt, Qtz-Rt, and Qtz-Ky. All three pairs yield temperatures between 695 and 725 °C. Application of the garnet-clinopyroxene Fe²⁺-Mg cation exchange thermometer using the calibration of Krogh Ravna (2000) to garnet-omphacite pairs in this sample (assuming a pressure of 2 GPa) yields estimates of 740-770 °C.

Furthermore, calculations, using phase equilibria among components, were performed with the reactions $6 \text{ zo} = 4 \text{ grs} + 5 \text{ ky} + \text{qtz} + 3 \text{ H}_2\text{O}$ and $12 \text{ zo} + 15 \text{ di} = 13 \text{ grs} +$

5 prp + 12 qtz + 6 H₂O (for compositions see Table A-2 in the appendix). These resulted in a temperature of 720 °C and a pressure of 2.5 GPa ± 0.39 [calculations performed with Thermocalc (Holland and Powell, 1998) using the garnet activity ($a_{\text{Grs}} = 0.062$; $a_{\text{Py}} = 0.092$) model of Berman (1990), an ideal activity model for zoisite ($a_{\text{Zo}} = 0.91$) and diopside ($a_{\text{Di}} = 0.55$) and with other activities = 1 and $P_{\text{litho}} = P_{\text{H}_2\text{O}}$]. These phase-equilibria-based temperatures are higher than previously reported from eclogites at Trescolmen (e.g., Meyre et al., 1997).

Fluid-rock interaction between eclogites and metapelites

The gradients in $\delta^{18}\text{O}$ of quartz and garnet, as revealed by sampling traverses across eclogite-metapelite contacts, point to some oxygen-isotope exchange between the two rock types. In addition, the contrasting higher $\delta^{18}\text{O}$ values of minerals in small eclogite boudins versus lower $\delta^{18}\text{O}$ values of minerals in large eclogite boudins suggest exchange with $\delta^{18}\text{O}$ -enriched fluids during Alpine metamorphism, assuming that both had the same $\delta^{18}\text{O}$ composition before the eclogite-facies event. Many authors of oxygen-isotope systematics in regional metamorphic terranes have invoked fluid infiltration with a different isotopic signature and/or pre-metamorphic gradients to explain the regional variations in $\delta^{18}\text{O}$ values (e.g., Valley, 1986; Matthews et al., 1996). In addition, some studies have demonstrated relatively small-scale heterogeneities, due to local exchange of oxygen isotopes by advection and diffusion (e.g., Bickle and Baker, 1990; Skelton et al., 2000). Taking into account the polymetamorphic history of the rocks at Trescolmen (Heinrich, 1982; Meyre and Puschig, 1993; Meyre et al., 1997; Meyre et al., 1999), as well as the modally dominant metapelites, we evaluate several of the listed possibilities that may have contributed to the observed $\delta^{18}\text{O}$ variations.

Oxygen-isotope gradients across eclogite-metapelite contacts. Isotopic gradients were produced when eclogites (basalts) were juxtaposed with pelites during early Alpine eclogite-facies metamorphism or during the late Alpine amphibolite-facies overprint that followed the high-pressure event. It is argued here that the exchange occurred during the eclogite-facies event for the following reasons: (1) Prograde dehydration of the protolith of the eclogite (i.e., amphibolite) can produce fluid with an isotopic composition that could lower $\delta^{18}\text{O}$ values of quartz-bearing metapelites nearby; (2) Garnet $\delta^{18}\text{O}$ values acquired during eclogite-facies recrystallization were most likely preserved during the later amphibolite-facies overprint (low rates of oxygen diffusion in garnet, Coghlan, 1990); and (3) Petrographic observations indicate that the amphibolite-facies overprint affected rocks at Trescolmen only in a minor way, e.g., epitactic overgrowth of biotite on phengite in the metapelites and alteration of eclogite rims to amphibolite (cf., Heinrich, 1982).

Mechanisms that may have produced the isotopic gradients between eclogite boudins and metapelites nearby include infiltration of a fluid and / or diffusion through a static grain-boundary fluid. A fluid phase was most likely present during dehydration reactions in both eclogites and metapelites. Both mechanisms, i.e., infiltration and diffusion, have been suggested by a number of investigators to be operative across boundary layers between different lithologies (e.g., Bickle and Baker, 1990; Cartwright and Valley, 1991; Puris and Wickham, 1994).

Dehydration of amphibolite to eclogite. The protolith of the eclogites, prior to the Alpine metamorphism, was most likely an amphibolite (Plas, 1959; Heinrich, 1983). Dehydration during prograde-Alpine metamorphism must have produced a fluid phase, albeit short lived, as evidenced by the quartz veins. Mineral assemblages (e.g., Qtz +

Omp + Ky + Rt) in some of the quartz veins indicate clearly formation under eclogite-facies condition (Heinrich, 1986). In a study of fluid-rock interaction between an eclogite boudin and the surrounding metapelitic country rocks at Cima di Gagnone (southern Adula nappe), Früh-Green (1987) noticed that $\delta^{18}\text{O}$ values of minerals in metapelites adjacent to the eclogite boudin were lower than in minerals from metapelites further away, similar to our observations at Trescolmen. Modeling the dehydration from amphibolite to eclogite using the Rayleigh distillation scheme of Rumble (1982), Früh-Green (1987) concluded that the fluid produced by dehydration could not be exclusively responsible for the depletion in $\delta^{18}\text{O}$ of minerals in metapelites adjacent to the eclogite boudin. In any case, the influence of dehydration on the $\delta^{18}\text{O}$ of a rock will be smaller than 1 ‰ (Valley, 1986).

Diffusion between eclogites and metapelites in an interconnected fluid. The $\delta^{18}\text{O}$ gradients observed in the two metapelite-eclogite traverses (Figs. 3 and 5) point to limited isotopic exchange over a distance of less than 1 meter. In addition, the gradients seem to be correlated with the size of the boudins, i.e., the boundary layer is wider in the vicinity of larger boudins. Unlike oxygen diffusion in quartz which is relatively fast (as demonstrated above), oxygen diffusion within garnet is slow, even over geologic time scales (e.g., the distance for O diffusion is only $\sim 10\ \mu\text{m}$ for garnet at $650\ ^\circ\text{C}$ annealed for 50 Ma, using diffusion coefficients of Coghlan, 1990). This restricted diffusion implies that garnet $\delta^{18}\text{O}$ values must have been acquired during garnet growth or recrystallization. Petrographic evidence and oxygen-isotope fractionation between quartz and garnet, particularly in coarse-grained eclogites, indicate disequilibrium, possibly due to the lack of garnet recrystallization. In contrast, fine-grained eclogites (in boudins $< 1\text{m}$) appear to have recrystallized during the Alpine orogeny. As a consequence, Qtz-Grt oxygen-iso-

tope fractionation in fine grained eclogites exhibits less scatter and probably attained equilibrium.

Oxygen transport, at the observed scale, occurred mainly by fluid infiltration or by diffusion through an interconnected fluid. Dehydration reactions during the transition from amphibolite to eclogite can not produce enough fluid to significantly lower $\delta^{18}\text{O}$ values in the adjacent metapelites (see Fröh-Green, 1987). Furthermore, there is no indication of partial melting in the metapelites at Trescolmen that might also have facilitated oxygen transport. Transport of oxygen most likely occurred through diffusion in a static, probably H_2O -rich fluid phase. Quartz veins in eclogites at Trescolmen are abundant, indicating the presence of a fluid phase during the eclogite-facies event (Heinrich, 1983, 1986). Fluid inclusions observed in quartz veins from eclogites are small, $\sim 15\ \mu\text{m}$, usually with small gas bubbles. In some of the inclusions, cubic NaCl crystals have been observed. Most of the fluid inclusions occur along healed micro fractures, indicating a secondary origin. The presence of oxygen isotope gradients in the boundary layers surrounding the eclogites, however, suggests that at least some of the fluids must have escaped pervasively along grain boundaries and micro fractures.

Many studies have shown that deformation and recrystallization enhance the rate of isotopic exchange by many orders of magnitude (e.g., Cole and Ohmoto, 1986; Yund and Tullis, 1991; Cole and Chakraborty, 2001). Given that $\delta^{18}\text{O}$ fractionation between quartz and garnet, particularly in the metapelitic part, remains relatively constant in the traverse for the large eclogite boudin (Fig. 5), recrystallization and deformation during decompression from eclogite-facies metamorphism may have been the principal mechanisms for the minerals to isotopically equilibrate with a changing fluid composition. This

conclusion is also supported by the petrographic observation that most garnets from the metapelitic part of the traverse occur as clusters of small garnets that have recrystallized from originally larger garnets.

The formation of an isotopic profile depends critically on porosity and the distribution of any fluid along grain boundaries. The connectivity of the fluid in the pore space depends on the kind of fluid, e.g., H₂O or CO₂, and on the dihedral angle, θ , formed between two intersecting fluid-mineral interfaces (e.g., Watson and Brenan, 1987). For $\theta < 60^\circ$ and a volume fraction of the fluid $\leq 1\%$, an interconnected fluid may exist, whereas for $\theta > 60^\circ$, fluids may occur isolated along grain boundaries or triple junctions (Watson and Brenan, 1987). Experimentally determined oxygen bulk-diffusion rates in natural ultra-mylonite samples (Farver and Yund, 1999) suggest a strong influence of layer silicates on the rate of geochemical transport and exchange. According to Farver and Yund (1999), oxygen transport (through bulk diffusion) in metapelites containing micas is several orders of magnitudes faster than in lithologies consisting mainly of quartz or calcite. This supports the presence of at least a transient, interconnected grain-boundary fluid in metapelites adjacent to eclogites at Trescolmen. In addition to this pervasive, grain-scale transport, field evidence also supports a more channeled flow, as evidenced by quartz veins in and around eclogite boudins.

Regional perspective of oxygen-isotope variations

Eclogites in the Trescolmen area reveal limited oxygen-isotope exchange with their host metapelites. The width of the boundary layer in the metapelites (and eclogites) seems to correlate with the size of the boudin. The larger the size, the bigger the boundary layer. On a different scale, minerals in smaller eclogite boudins (< 1 m in diameter)

exhibit higher $\delta^{18}\text{O}$ values than minerals from larger boudins. These values were most likely acquired during eclogite-facies metamorphism or early exhumation. A sampling traverse through an amphibolite rim into fresh eclogite revealed no differences in $\delta^{18}\text{O}$ values of the minerals (see Fig. 6). Heinrich (1982) suggested that fluids from dehydrating metapelites during decompression were responsible for the (partial) overprint of eclogite boudins to amphibolites. The conclusion from our oxygen-isotope data is equivocal. The fluid/rock ratios must have been low so as not to affect the $\delta^{18}\text{O}$ compositions of minerals.

Oxygen-isotope values of minerals from a few eclogite boudins on the western ridge and the metapelitic zone imbricated in the gneiss layers are significantly higher than from eclogite boudins from the main metapelitic zone. However, fractionation temperatures are similar to minerals from the main metapelitic zone, implying that both lithologies experienced the last equilibration event together. Furthermore, the $\delta^{18}\text{O}$ values of garnet and quartz from the disparate lithologies are almost identical, indicating an enrichment for the eclogite from a protolith with a presumed $\delta^{18}\text{O}$ of pristine MORB of $\sim 5.7\text{‰}$ (Harmon and Hoefs, 1995). Two scenarios can be envisaged: homogenization of the two lithologies via a fluid phase prior to the equilibration event; alternatively, the protolith of the eclogite did not have an isotopic composition of pristine mantle-derived basalt, but may have obtained an elevated $\delta^{18}\text{O}$ signature during seafloor weathering and/or low-temperature hydrothermal alteration in the upper part of the oceanic crust (e.g., Gregory and Taylor, 1981). This latter possibility is probably more likely as several studies have shown that eclogites retained their pre-metamorphic isotopic compositions despite being subducted to eclogite-facies conditions (e.g., Barnicoat and Cartwright, 1997; Snyder et al., 1997; Taylor and Neal, 1989; Putlitz et al., 2000). This suggests that eclogites at

Trescolmen may have been derived from different sections of oceanic crust.

We have also analyzed minerals from other eclogite-bearing outcrops north and south of the Trescolmen area. Measured $\delta^{18}\text{O}$ values of garnets from Alp de Confin (about 10 km north of Trescolmen) are 5.98‰ (± 0.22) which is similar to values from Trescolmen eclogites. Further north, at the locality Alt Wahli (cf., Heinrich, 1983), garnets yield $\delta^{18}\text{O}$ values of 3.79‰ (± 0.01). Similar values of garnets have been measured from eclogites in the southern part of the Adula nappe at Cima di Gagnone and Alpe Arami (cf., Heinrich, 1983) (3.57‰ (± 0.00) and 3.90‰ (± 0.10), respectively). Calculated whole-rock values of these samples (using modal abundances and mineral $\delta^{18}\text{O}$ values) are between 3.60 and 4.20‰. These numbers are below the accepted values for pristine MORB (5.7‰ ± 0.2 , Harmon and Hoefs, 1995). A possible mechanism to explain these low values could involve a parent magma with ^{18}O -depleted meteoric/hydrothermally altered oceanic crust (e.g., Nicholson et al., 1991), or hydrothermal alteration at elevated temperatures (Gregory and Taylor, 1981). The range of $\delta^{18}\text{O}$ values observed in garnets from eclogites in the Adula nappe substantiates a variety of basalt-type protoliths having experienced variable hydrothermal alteration. Deformation during the Alpine orogeny contributed to the juxtaposition of eclogites with different oxygen-isotope signatures.

SUMMARY

The absence of significant isotopic shifts in small and large eclogite boudins, as well as heterogeneous $\delta^{18}\text{O}$ values in the metapelites at Trescolmen, point to local redistribution of oxygen isotopes during the Alpine-metamorphic events. There was no large-scale influx of fluids and subsequent homogenization of oxygen isotopes as proposed, for

example, by Wickham and Taylor (1985) in the Trois Seigneurs Massif, France. Since the rocks at Trescolmen were most likely already dehydrated prior to the Alpine orogeny, Alpine metamorphism was relatively dry, which helped in the preservation of oxygen-isotope heterogeneities. Still, the isotopic gradients in the boundary layers between eclogites and metapelites provide evidence of pervasive centimeter- to meter-scale exchange during eclogite-facies metamorphism. The shape of the profile (Fig. 5) suggests diffusion through a static grain-boundary fluid with simultaneous recrystallization (caused by deformation) as a likely mechanism for isotopic exchange. In contrast, the quartz veins in eclogites and metapelites demonstrate the presence of an at least temporarily free-fluid phase and indicate a more channelized fluid transport over 10s of meters, perhaps enhanced by permeability decrease due to deformation (Yardley, 1986).

Overall, oxygen-isotope equilibrium was approached for many eclogites and metapelites from Trescolmen, although some samples show disequilibrium due to a possible pre-Alpine origin of refractory phases and /or fluid-rock interaction during the Alpine orogeny. Oxygen-isotope fractionation yields temperatures in the range of ~650 to 720 °C which are in good agreement with temperatures from phase equilibria.

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APPENDICES

Table A-1. Modal abundances and average grain size of minerals in representative eclogites and metapelites from Trescolmen.

Sample	Assemblage	Qtz	Grt	Omp	WM ¹	Bt	Czo/Zo/Ep	Pl	Ky	St	Ap	Cam	Rt/Ilm	Mag	Chl	Symp ²
Tr00-9a	Mp1	67 ³	9	-	13	2	<1	2	5	-	<1	-	<1	<1	<1	-
		(0.12) ⁴	(0.12)		(0.10)	(0.01)	(0.04)	(0.01)	(0.05)		(0.02)		(0.02)	(0.02)	(0.01)	
Tr98-56	Mp1	54	8	-	32	5	<1	-	<1	-	<1	-	<1	<1	<1	-
		(0.05)	(0.08)		(0.15)	(0.01)	(0.03)		(0.02)		(0.02)		(0.02)	(0.01)	(0.01)	
Tr99-26	Mp1	53	16	-	16	3	<1	5	6	-	<1	-	<1	<1	<1	-
		(0.05)	(0.06)		(0.10)	(0.01)	(0.04)	(0.02)	(0.05)		(0.02)		(0.02)	(0.01)	(0.01)	
Tr99-27	Mp2	60	9	-	13	4	<1	8	2	-	<1	-	<1	<1	1	-
		(0.05)	(0.10)		(0.15)	(0.01)	(0.01)	(0.01)	(0.10)		(0.02)		(0.01)	(0.01)	(0.02)	
Tr00-2e	Mp2	47	15	-	21	3	-	10	2	-	<1	-	<1	<1	1	-
		(0.05)	(0.40)		(0.10)	(0.01)		(0.01)	(0.05)		(0.02)		(0.01)	(0.02)	(0.03)	
Tr00-11a	Mp3	21	11	-	51	5	-	3	7	1	<1	-	<1	<1	<1	-
		(0.05)	(0.12)		(0.10)	(0.01)		(0.01)	(0.10)	(0.03)	(0.02)		(0.01)	(0.03)	(0.02)	
Tr00-36b	Mp3	18	12	-	22	12	-	32	-	-	<1	-	<1	<1	3	-
		(0.04)	(0.80)		(0.20)	(0.05)		(0.02)			(0.01)		(0.01)	(0.01)	(0.03)	
Tr00-EB	E1	5	28	54	<1	-	5	-	4	-	1	2	1	-	-	-
		(0.02)	(0.10)	(0.02)	(0.02)		(0.20)		(0.15)		(0.02)	(0.20)	(0.02)			<1
Tr00-17b	E1	<1	26	25	-	-	34	-	-	-	<1	10	1	-	-	(0.001)
		(0.02)	(0.10)	(0.01)			(0.30)				(0.05)	(0.06)	(0.02)			
Tr98-59	E2	8	40	46	<1	-	<1	-	<1	-	<1	1	2	-	-	-
		(0.01)	(0.04)	(0.01)	(0.03)		(0.01)		(0.01)		(0.01)	(0.02)	(0.01)			
Tr00-2c	E2	2	31	35	-	-	5	-	-	-	1	26	1	-	-	-
		(0.01)	(0.04)	(0.01)			(0.01)				(0.05)	(0.20)	(0.01)			
Tr00-27	E3	<1	35	30	<1	-	2	-	-	-	<1	10	3	-	-	18
		(0.02)	(0.05)	(0.01)	(0.03)		(0.01)				(0.01)	(0.03)	(0.01)			(0.01)
Tr00-36a ⁵	E3	4	30	24	5	-	2	-	2	-	<1	20	2	-	-	5
		(0.04)	(0.40)	(0.02)	(0.06)		(0.03)		(0.05)		(0.02)	(0.05)	(0.01)			((0.01)

¹ White mica (phengite-paragonite); ² Refers to intergrowth of plagioclase, clinopyroxene, and amphibole; ³ Modal abundance in vol.% (determined by point counting);

⁴ Average grain-size in centimeters; ⁵ This sample also includes ~5% ankerite.

Table A-2. Major-element compositions of selected minerals from sample Tr00-EB (eclogite).

Analysis	Garnet 2 (core)	Garnet 2 (rim)	Omphacite 2	Zoisite 1
SiO ₂	39.4	40.4	55.0	38.9
TiO ₂	0.18	0.03	0.07	0.04
Al ₂ O ₃	22.1	22.8	8.64	31.0
Cr ₂ O ₃	0.05	<0.03	0.17	0.10
Fe ₂ O ₃				2.68
MgO	8.97	13.6	10.8	0.10
CaO	10.8	6.33	16.1	24.1
MnO	0.55	0.38	n.d.	0.04
FeO	17.9	17.1	3.32	
Na ₂ O	0.04	<0.03	4.92	0.04
K ₂ O	n.d. ¹	n.d.	<0.03	n.d.
Total	99.9	100.6	99.1	97.0
Cations based on:	12 oxygens	12 oxygens	6 oxygens	12.5 oxygens
Si	2.980	2.981	1.982	3.002
Ti	0.010	0.002	0.002	0.002
Al	1.969	1.979	0.367	2.823
Cr	0.003	0.001	0.005	0.006
Mg	1.012	1.490	0.579	0.012
Ca	0.877	0.500	0.623	1.996
Mn	0.035	0.024	-	0.003
Fe ²⁺	1.135	1.051	0.100	
Fe ³⁺				0.156
Na	0.005	0.002	0.344	0.006
K	-	-	-	-
Total	8.026	8.029	4.002	8.006
X _{Grs}	0.285	0.162		
X _{Prp}	0.331	0.486		
X _{Alm}	0.371	0.343		
X _{Sps}	0.012	0.008		
X _{Hd}			0.103	
X _{Jd}			0.356	
X _{Di}			0.538	

¹ Not detected

PART 4

CONCLUSIONS

At Trescolmen, in the lower Penninic Adula nappe, numerous, well-exposed eclogite boudins are embedded in metapelitic-host rocks of presumably pre-Mesozoic age. Both rock types have enjoyed at least two metamorphic episodes: an early Alpine eclogite-facies high-P-T metamorphism followed by an amphibolite-facies overprint during uplift. The timing of superposition of the two disparate rock types remains uncertain but most likely happened before the Alpine orogeny.

A suite of samples from both eclogites and metapelites were chosen to investigate fluid-rock interaction between the two rock types. Besides characterization of the samples by petrography and EMP, we have used oxygen-isotope systematics to address the nature and extent of fluid-rock interactions at different scales at Trescolmen. In addition, we employed trace-element analyses, particularly from garnets, to determine the possibility of fluid infiltration into the eclogites. Detailed sample traverses across eclogite-metapelite contacts, using a core drill, allowed assessment of the mechanism of isotopic exchange between the two rock types. Furthermore, oxygen-isotope analysis of different refractory minerals allowed an independent estimate (from thermometry using cation partitioning) of crystallization temperatures during the Alpine orogeny.

Microsampling of individual garnet porphyroblasts from both eclogites and metapelites revealed only small $\delta^{18}\text{O}$ zonation which is consistent with closed-system growth of the garnets. This indicates that no exotic fluid (with a $\delta^{18}\text{O}$ signature out of equilibrium with the garnets) infiltrated the rocks. This, of course, does not preclude the infiltration of a fluid in equilibrium with the growing garnets.

Traverses across eclogite-metapelite contacts revealed a gradient in $\delta^{18}\text{O}$ in minerals from both rock types in the contact region. Taking into consideration that metapelites

are the dominant rock type at Trescolmen, any fluid-rock interaction of fluids expelled by dehydration of the former amphibolites will be limited to boundary layers surrounding the eclogite boudins. Dehydration of the protolith of the eclogites could produce a fluid with an isotopic composition to lower $\delta^{18}\text{O}$ values in the surrounding metapelites as has been shown by an oxygen-isotope study at Cima di Gagnone (southern Adula nappe). At Trescolmen, the shape of the $\delta^{18}\text{O}$ gradient with inflection points close to the interface between the two rock types points to diffusional exchange in an at least transient grain-boundary fluid.

Analysis of $\delta^{18}\text{O}$ of minerals in amphibolite rims of eclogite boudins suggests limited fluid-rock interaction during decompression. Fluid-rock ratios must have been low as not to affect $\delta^{18}\text{O}$ of the minerals. Fluids that caused the partial retrogression of eclogite boudins to amphibolite were most likely derived from dehydration reactions in the surrounding metapelites during decompression.

At the scale of Trescolmen, oxygen-isotope systematics suggests an overall approach to equilibrium conditions. The similarity of mineral-mineral fractionation in both eclogites and metapelites strongly implies that both rock types experienced the last equilibration event together. However, in large, coarse-grained eclogites, disequilibrium between quartz and garnet has been demonstrated in this study that is likely related to a pre-Alpine origin of some of the larger garnet porphyroblast. In contrast, due to recrystallization during the Alpine orogeny, quartz-garnet fractionation in small, fine-grained eclogites boudins have closely approached equilibrium. RAM (Refractory Accessory Minerals) thermometers applied to bimineralic assemblages, particularly quartz-kyanite segregations, yield consistent temperatures of $\sim 720^\circ\text{C}$, which is higher than temperature re-

ported from mineral cation exchange thermometers.

Average $\delta^{18}\text{O}$ composition of quartz from the main metapelitic zone at Trescolmen ($\sim 10.6\text{‰}$) is almost identical to quartz from pre-Mesozoic para- and orthogneisses from other lower Penninic nappes. This strongly suggests that there was no large scale fluid infiltration during the Alpine orogeny and that the observed gradients at Trescolmen were locally derived.

Trace-element zoning in garnet from eclogites could not be resolved unambiguously. The zoning patterns may be caused by a change in intensive parameters, a change in reactants (particularly of accessory minerals rich in REE's), possible metasomatism, and by crystal-chemical effects of the changing Ca content in garnet. The bell-shaped REE patterns of omphacite is likely caused by partitioning of LREE's into minerals such as clinozoisite and apatite, whereas the HREE's are preferentially partitioned into garnet. In any case, the REE budget of eclogites seems to be controlled to a large degree by accessory phases such as apatite and zoisite / clinozoisite.

Despite our efforts to shed light on the evolution and petrogenesis of the rocks at Trescolmen, many questions remain unanswered. Additional sampling of eclogite-metapelite contacts may give better constraints on the parameters that govern isotopic exchange. An investigation of fluid inclusions in quartz veins (and in other minerals) may help to determine the nature and the evolution of a fluid phase at Trescolmen. The interplay of deformation and permeability of the metapelites during uplift has not been dealt with in this study but might have some important implications for the kinetics of the dehydration reactions and the isotopic exchange. Fluid-rock interaction at Trescolmen may also be better explored by trace elements from in-situ analysis in minerals, as oxy-

gen-isotope determined fluid/rock ratios are not sensitive to low fluid fluxes. Another aspect which might be worthwhile pursuing is geochronology. Accessory minerals such as zircons, monazite have been observed in both eclogites and metapelites. These minerals, in addition to trying to date some of the porphyroblastic garnets, may offer time constraints for the polymetamorphic evolution of the rocks at Trescolmen.

VITA

René A. Wiesli was born in Flawil, Switzerland, on January 13, 1959. In Fall 1986, he started his studies at the University of Tennessee, Knoxville, and graduated in Spring 1989, with a Bachelor of Science Degree in Mathematics. Following some intermission in Switzerland, René began his graduate studies in August 1996 in the Department of Geological Sciences at the University of Tennessee in Knoxville, where he earned the Degree of Doctor of Philosophy with a major in Geology in August, 2002.

