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Stable isotope systematics of the Ventina Ophicarbonatite Zone, Bergell contact aureole

by Diego Pozzorini^{1,2} and Gretchen L. Früh-Green¹

Abstract

This study documents systematic oxygen, hydrogen and carbon isotope variations in the Ventina Ophicarbonatite Zone (VOZ), a discrete sheet of ophicarbonatite rocks located in the NW part of the Malenco ultramafic body and exposed across the contact aureole of the Oligocene Bergell pluton. The Ventina ophicarbonatites are brecciated rocks consisting of fragments of schistose serpentinite embedded in a matrix of predominantly calcite composition. Towards the Bergell pluton, the mesoscale brecciated textures are preserved, but the regional Alpine mineral assemblages and metamorphic microfabrics become progressively overprinted by contact metamorphism.

Relatively constant carbon isotope compositions of the carbonate matrix in the Ventina ophicarbonatites are comparable to marine carbonate signatures. Together with field observations, the carbon isotope ratios provide evidence that these rocks formed through faulting and brecciation during emplacement of the Adria subcontinental mantle on the seafloor. In contrast, the oxygen and hydrogen isotope signatures in the VOZ ophicarbonatites are highly variable and reflect processes of fluid-rock interaction during regional and contact metamorphism. Within the contact aureole, systematic shifts in isotopic ratios are observed towards the lithological boundaries to the surrounding massive serpentinites in profiles sampled subparallel to the contact metamorphic isograds. These variations provide strong evidence for infiltration and exchange with external, water-rich fluids, probably derived from dehydration reactions in the surrounding serpentinites during contact metamorphism. A lack of isotopic homogenization even on a hand specimen scale reflects varying degrees of overprinting and isotopic disequilibrium. As a consequence, field-based geothermometric estimates from oxygen isotope fractionations between calcite and silicate phases along the VOZ were not possible within the Bergell contact aureole. The observed isotopic patterns can be explained by kinetically controlled mineral-fluid exchange during fluid-rock interaction.

Keywords: ophicarbonatite, stable isotopes, isotopic disequilibrium, fluid-rock interaction, Alpine metamorphism, Bergell contact metamorphism, Val Malenco (N. Italy).

1. Introduction

Stable isotopes have been widely used to monitor fluid-rock interaction in metamorphic and magmatic petrology. In particular, stable isotope geochemistry provides important constraints on the thermal history and the evolution of fluids and mass transfer associated with, or produced by, the emplacement of a magmatic body. Infiltration processes of magmatic fluids or those derived from devolatilization reactions in country rocks may play an important role in driving the prograde T-X_{CO₂} path of progressive metamorphism (e.g. MOORE and KERRICK, 1976; NABELEK et al., 1984; COOK and BOWMAN, 1994). Alternatively,

fluid compositions in closed systems are buffered by the solid phases (GREENWOOD, 1975). Thus, fluid infiltration competes with the buffering capacity of the metamorphic reactions for control of fluid composition (RICE and FERRY, 1982; FERRY, 1988, 1995; COOK and BOWMAN, 1994).

Several studies of contact aureoles, where decarbonation reactions play a dominant role in controlling isotopic fractionation, have documented a correlation between isotopic composition and low-variance assemblages (e.g. LATTANZI et al., 1980; RUMBLE et al., 1982; NABELEK et al., 1984). In particular, these studies have shown that carbon and oxygen isotope ratios of carbonates from low variance assemblages become progressively lower

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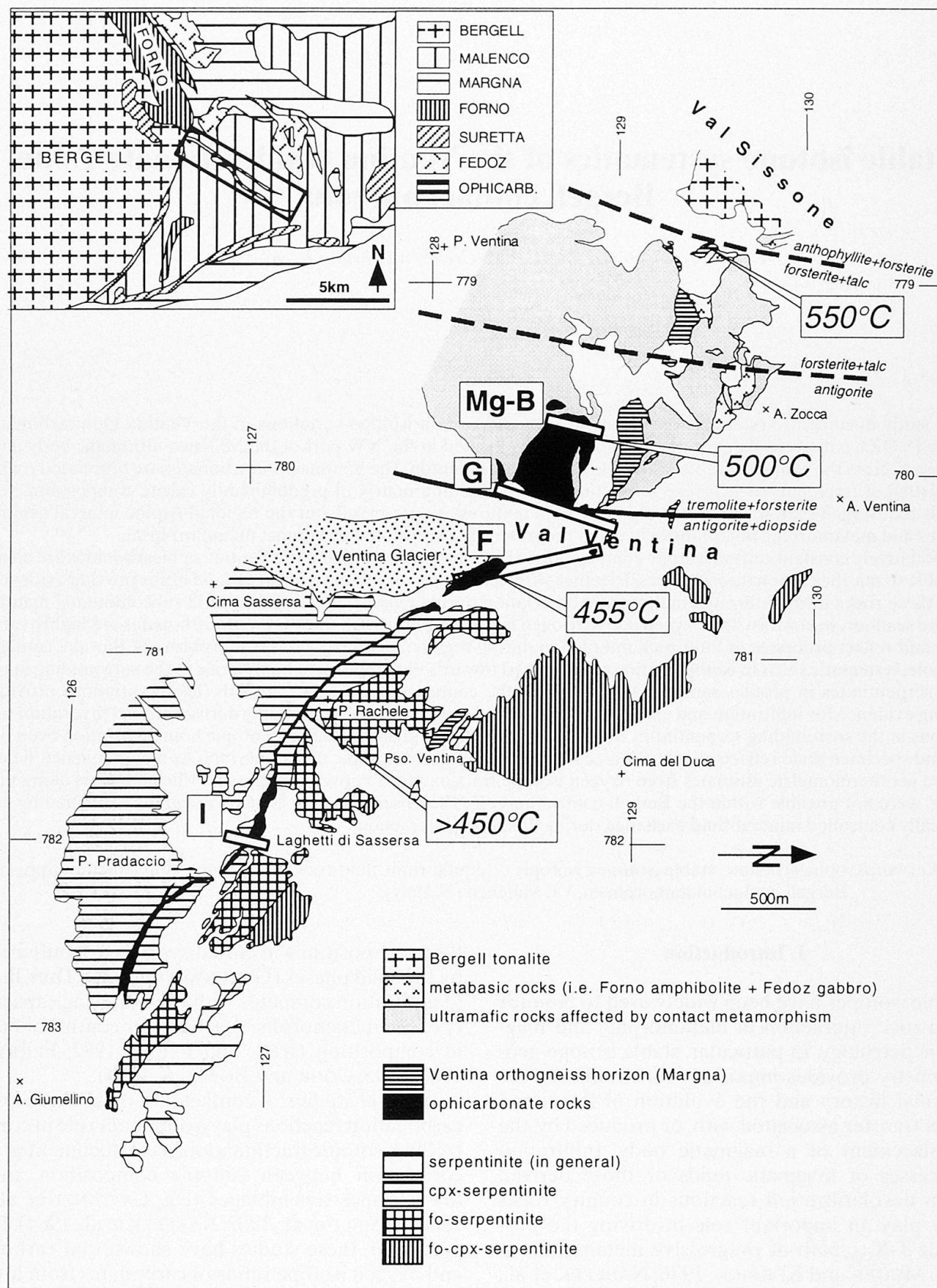


Fig. 1 Geological map of the Ventina ophicarbonate zone (VOZ), in part with data from SCHUMACHER (1975, unpubl.); TROMMSDORFF and EVANS (1977 a, b); HONEGGER (1977, unpubl.). Isograds in carbonate-free ultramafic rocks are from TROMMSDORFF and EVANS (1972); temperature estimates are from TROMMSDORFF and EVANS (1977 a, b) and TROMMSDORFF and CONNOLLY (1990). Thin white rectangular boxes labelled I, F, G, Mg-B indicate locations of isotopic profiles across the VOZ (see text).

with increasing metamorphic grade. Significant isotopic shifts occur at univariant and invariant conditions where large amounts of volatiles are produced by devolatilization reactions.

In the present study, detailed analyses of carbon, oxygen and hydrogen isotope ratios of coexisting mineral phases in ophicarbonate rocks exposed across the contact aureole of the Oligocene Bergell pluton are presented. We show that distinct isotopic trends within the Bergell contact aureole can be ascribed to fluid-rock interaction associated with the emplacement of the tonalite and that such signatures can be distinguished from the Alpine regional metamorphic signatures outside the contact aureole. These data are used to constrain the origin and scales of fluid advection during contact metamorphism. We also show that isotopic disequilibrium prevailed during fluid-rock interaction so that field-based geothermometric estimates from oxygen isotope fractionations between mineral pairs were not possible in the Bergell contact aureole.

2. Petrography of the Ventina Ophicarbonate Zone

The Ventina Ophicarbonate Zone (VOZ) consists of a 10 to 400 m wide ophicarbonate sheet that strikes NW–SE and is exposed over a distance of approximately 6 km within the Malenco ultramafic body. Towards the NW, the ophicarbonate sheet is crosscut by the Bergell intrusion, whose contact aureole developed sub-perpendicularly to the strike of the ophicarbonates (Fig. 1). The Bergell contact aureole is defined by a prograde sequence of mineral assemblages in the carbonate-free ultramafic rocks (TROMMSDORFF and EVANS, 1972).

The Ventina ophicarbonates are characteristically inhomogeneous metamorphic rocks and exhibit a prevalently brecciated texture consisting of mm- to m-sized fragments of serpentinite embedded in a fine- to medium-grained white matrix of predominantly calcite composition. The macroscopic fabrics of these rocks are variable, ranging from veined and fractured serpentinite-supported metabreccias to matrix-dominated metabreccias. Internally veined, large serpentinite fragments with calcite and rarely dolomite fillings occur within fragment-supported domains (Figs 2a and 2b). Ophicalcites and ophidolomites, depending on the nature of the carbonate species within the rock, are observed. Ophicalcites, however, make up more than 95% of the entire ophicarbonate rock volume. Magnesite veins occur within the massive ultramafic rocks in domains closer to the Bergell intrusive (SCHUMACHER, 1975; TROMMSDORFF and EVANS, 1977 a, b).

2.1. ROCK FRAGMENTS

Serpentinite fragments are the *sole* rock fragments observed within the VOZ (Figs 2a and 2b). They are predominately schistose and frequently folded, fractured and sheared. Less commonly, the fragments are massive and undeformed. Contacts between fragments and calcite matrix are prevalently sharp, with a tendency of the fragment to break up parallel to its foliation. Outside the Bergell contact aureole, the fragments consist of clinopyroxene-serpentinite and antigorite-serpentinite. Microscopic observations indicate that multiple generations of the constituent minerals developed during the pre-Alpine to Alpine metamorphic evolution. Alpine foliated antigorite is commonly accompanied by fine-grained magnetite and interlayered chlorite. Unoriented magnetite-free recrystallized antigorite may partly or completely replace schistose fragments of antigorite-serpentinite. In clinopyroxene-serpentinite fragments with a preserved, mm to dm thick magmatic layering, mineral relics record a re-equilibration stage under pre-Alpine granulite-facies conditions (POZZORINI, 1996). Coarse-grained clinopyroxenes are distinguished from finer-grained re-equilibrated clinopyroxenes. Both the coarse-grained and the re-equilibrated clinopyroxenes are rimmed by an almost pure Alpine diopside.

Towards the Bergell pluton, the rock fragments of the VOZ become increasingly overprinted by the Bergell contact metamorphism. In thin section, idiomorphic tremolite overgrowths on foliated antigorite, and tremolite rimming and gradually replacing clinopyroxene relics are observed. Domains with recrystallization of calcite and antigorite become more frequent. The recrystallized unoriented antigorites are coarser-grained than similar occurrences of unoriented antigorite in rock fragments outside the contact aureole. In Val Sissone, closest to the Bergell intrusion (Fig. 1), a 4–5 m wide outcrop of ophicarbonate rocks is preserved between tremolite-talc-forsterite-fels and tonalite. The pre-existing serpentinite clasts occur as massive fragments that are completely replaced by forsterite, tremolite, chlorite and talc. The brecciated texture of the rock, however, is still preserved.

2.2. MATRIX CARBONATE

The fabrics of the matrix carbonate vary from calcite polygonal equilibrium textures to mylonitic textures (Figs 2c and 2d). A wide variety of grain sizes and grain shapes (isometric, tabular, pris-

matic) is observed, with single coarse-grained calcite crystals surrounded by very fine grained mylonitic calcite bands. Fibrous calcites occur in fracture-filled veins of various width (μm to mm) within serpentinite fragments in fragment-supported domains. Polygonal equilibrium textures are prevalent in less deformed matrix-supported domains and are characterized by medium- to coarser-grained monomineralic calcite aggregates with an increase in grain size towards the aggregate centre. These domains locally contain single unoriented fine-grained antigorite blades resulting in calcite-antigorite annealed textures or poikiloblastic textures. Fine-grained mylonitic textures are common and are concentrated along discrete shear zones. In some cases, aggregates of coarser grained calcite in veins crosscut pre-existing calcite veinlets within fragments or may occur at the interface between a serpentinite fragment and the calcite matrix. Crosscutting relationships between different sets of veins observed on a thin section scale in general indicate not more than two calcite generations.

2.3. CONTACT METAMORPHISM OF OPHICARBONATE ROCKS

Outside the Bergell contact aureole, between Val Ventina, Laghetti di Sassera and Alp Giumellino (Fig. 1), the Alpine regional metamorphic minerals within the VOZ comprise calcite, antigorite, tremolite, diopside, magnetite, chlorite, dolomite, forsterite and titanian clinohumite. Thermal constraints for Alpine regional metamorphism in the ophicarbonate rocks are given by calcite-dolomite thermometry. Temperatures of $430 \pm 30^\circ\text{C}$ have been estimated by TROMMSDORFF and EVANS (1977a) in the VOZ outside the contact aureole. These temperatures represent minimum peak-temperatures of Alpine regional metamorphism in the Malenco ultramafic body (MELLINI et al., 1987).

Towards the Bergell pluton, a sequence of prograde isobarically univariant equilibria occurs in the ophicarbonates (TROMMSDORFF and EVANS, 1977 a, b; TROMMSDORFF and CONNOLLY, 1990; TROMMSDORFF and CONNOLLY, 1996). These univariant equilibria are separated by invariant assemblages, which have been mapped in the field

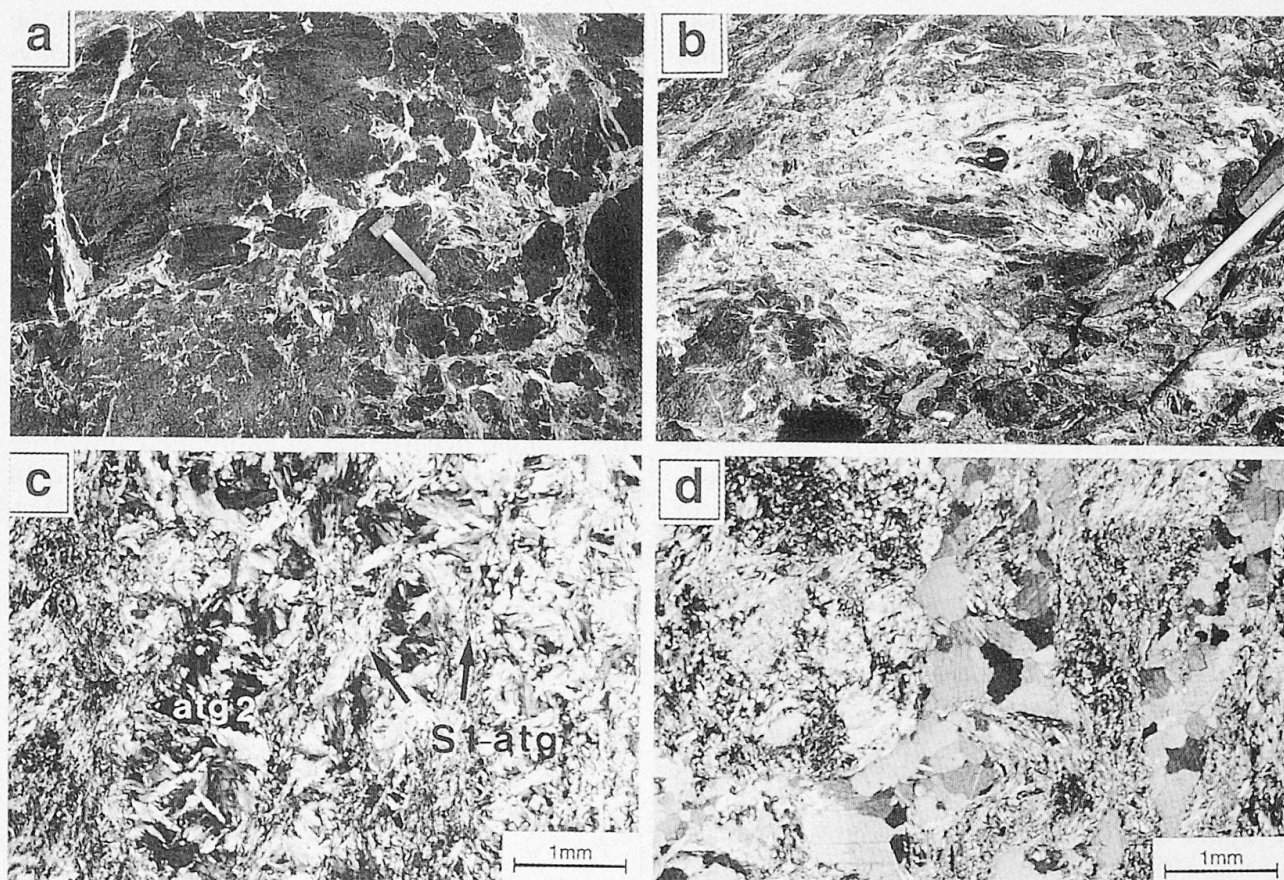


Fig. 2 Typical textures of the Ventina ophicarbonates. (a) Brecciated, fragment-supported domains. (b) Matrix-supported domains. (c) Microphotograph showing Alpine regional metamorphic antigorite (S1-atg) of serpentinite clasts and small recrystallized serpentinite fragments (atg2). (d) Microphotograph showing polygonal equilibrium calcite textures between folded serpentinite clasts.

Tab. 1 Locations and range of isotope ratios of samples from the VOZ (for locations see also Fig. 1). Numbers in brackets refer to numbers of analyses.

Sample	Swiss map coordinates	Distance from tonalite contact (km)	$\delta^{13}\text{C}$ calcite (‰ VPDB)	$\delta^{18}\text{O}$ calcite (‰ VSMOW)	$\delta^{18}\text{O}$ antigorite (‰ VSMOW)	δD antigorite (‰ VSMOW)
<i>Alp Giumellino</i>						
93R	783'400–126'200	6.25	1.8–2.4 (4)	11.5–12.2 (4)	7.5–9.5 (3)	–74 to –80 (2)
<i>Laghetti di Sassersa</i>						
92P	782'200–126'775	4.40	1.1–1.4 (2)	11.0–11.7 (2)		
90I2–7	782'125–126'850	4.30	1.0–1.8 (16)	11.3–12.7 (16)	7.2–8.6 (7)	–104 to –83 (4)
90I10–13	782'020–126'980	4.20	1.0–1.4 (11)	12.8–13.4 (11)	8.3 (1)	–84 (1)
91L4–7	781'675–127'100	3.80	1.3–1.9 (6) 1.1–1.5 (4) ¹	10.2–11.4 (6) 10.9–11.2 (4) ¹		
<i>Val Ventina</i>						
90H5	780'750–127'975	2.54	1.4–1.5 (2)	11.8–12.0 (2)		
90H9	780'750–127'975	2.54	1.4–1.5 (10)	12.1–12.5 (10)	8.2–8.7 (2)	–87 (1)
92F1	780'610–128'050	2.42	1.5–3.0 (18)	8.3–10.1 (18)	5.6–6.2 (6)	–109 to –80 (5)
93F	780'610–128'050	2.40	1.3–1.4 (2)	8.7–8.9 (2)		
91F1–AM	780'610–128'050	2.40			5.8–6.0 (6)	–89 (1)
91F1	780'610–128'050	2.39	1.5–2.2 (7) ¹	9.3–10.8 (7) ¹	6.7–7.4 (11)	–88 to –66 (8)
92F2	780'600–128'125	2.38	0.9–1.2 (7)	10.3–12.1 (7)	7.0–7.5 (3)	–84 (1)
91F3	780'600–128'175	2.36	1.6 (1) 1.0–1.6 (2) ¹	11.8 (1) 11.6 (1) ¹	8.4–8.5 (4)	–79 to –75 (2)
90F1–7	780'575–128'150	2.35	1.1–1.2 (7)	10.7–12.5 (7)	7.7–9.0 (4)	–87 to –63 (3)
91F2	780'575–128'150	2.35	0.9–1.2 (20)	11.5–12.2 (20)	7.8–8.1 (2)	
91F4	780'600–128'200	2.31	1.6–2.5 (11)	10.7–12.2 (11)	7.6 (2)	
91F5	780'500–128'775	2.25	1.2–1.8 (10) 1.4 (3) ¹	11.5–13.2 (10) 12.3 (3) ¹	8.3–8.4 (2)	–70 (1)
92G1	780'425–128'825	1.83	1.2–2.3 (8)	11.0–11.4 (8)	7.6–7.7 (3)	–69 (1)
93G	780'050–128'275	1.83			5.3–5.5 (4)	–63 to –50 (2)
90G7–15	780'050–128'375	1.8	0.7–2.0 (9)	9.3–12.7 (9)	6.6–7.5 (5)	–59 to –48 (3)
90G16–19	780'175–128'575	1.8	1.0–1.3 (7)	12.7–14.4 (7)	8.2–10.1 (3)	–51 (1)
Mg206	779'900–128'800	1.42	0.9–2.1 (6)	10.8–13.1 (6)		
Mg201	779'730–128'620	1.42	1.1–1.9 (6)	8.3–9.9 (6)	5.9 (1)	
Mg202	779'750–128'630	1.40	0.4–0.7 (2)	9.8–10.0 (2)	4.8 (1)	
90G4–6	779'900–128'800	1.39	0.4–1.4 (11)	11.0–12.4 (11)	7.8–8.0 (4)	–58 (2)
90B	779'750–128'775	1.33	1.2–1.4 (3)	8.6–8.9 (3)	5.8–5.9 (3)	–50 (2)
93B1–7	779'750–128'775	1.33	0.6–1.9 (6)	8.8–9.6 (6)	5.3 (2)	
93B11	779'750–128'775	1.33	0.9 (1)	9.6 (1)		
Mg205	779'810–128'820	1.33	0.9 (1) –0.4 (4) ¹	11.4 (1) 11.4 (4) ¹		
90G2	779'775–128'850	1.31	1.3 (1)	10.3 (1)		
Mg204	779'760–128'800	1.31	1.9 (2)	12.3–12.5 (2)		
<i>Val Sissone</i>						
91E1B	778'800–129'450	0.17	–4.2 to –3.8 (2)	13.1–13.3 (2)	7.5 (2)	–98 (1)
91E1C	778'800–129'450	0.17	–3.3 to 0.3 (3)	10.2–12.3 (3)	7.3 (1)	–88 (1)
91E1E	778'800–129'450	0.17	1.2–1.9 (2)	12.0 (2)	9.4 (chl) (2)	–52 (chl) (1)
91E1G	778'800–129'450	0.17	1.1–1.2 (2)	10.4–10.8 (2)		

¹ dolomite samples

(TROMMSDORFF and EVANS, 1977 a, b). With increasing temperature, the field sequence of the invariant assemblages is: (1) antigorite + diopside +

forsterite + tremolite + calcite; (2) antigorite + dolomite + forsterite + tremolite + calcite; (3) antigorite + forsterite + talc + magnesite; and (4)

antigorite + dolomite + forsterite + tremolite + talc.

Temperature estimates obtained with calcite-dolomite thermometry along the VOZ indicate that the prograde contact metamorphism occurred over a temperature range of 430 to 550 °C (TROMMSDORFF and EVANS, 1977 a, b; TROMMSDORFF and CONNOLLY, 1990; FERRY, 1995). The topology delineated in a T-X_{CO₂} diagram calculated by TROMMSDORFF and CONNOLLY (1990) for a pressure of 3.5 kbar is supported by mineral assemblages observed in the field. Their calculations indicate that the evolved fluid was internally buffering by the univariant assemblages during progressive contact metamorphism of the ophi-carbonate rocks. Variations of the mineral assemblages observed on a mesoscopic scale are attributed to variations in bulk rock composition of the ophi-carbonate domains, which in turn, depend on the bulk rock compositions of the ultramafic fragments.

3. Stable isotope signatures in the Ventina Ophi-carbonate Zone

3.1. METHODS

Silicate mineral separates were prepared from small cores drilled from 1–2 cm thick slabs of fresh rock specimen and successively crushed and sieved in different fractions, depending on mineral grain-sizes and extent of mineral intergrowths. The fractions were further washed in 3M HCl to remove carbonate minerals and surface contamination, then ultrasonically cleaned and rinsed in distilled water. Antigorite in antigorite-rich fractions was separated from magnetite using a hand-magnet and successively purified by hand-picking under the binocular microscope. Mixtures of silicate phases (antigorite, diopside, tremolite, magnetite, chlorite, forsterite) were separated with standard high density liquids and hand-picking. Purity of all mineral separates was better than 97%.

Calcite samples were obtained directly from polished slabs of fresh rock specimen using a hand drill. Dolomite was prepared following the initial procedure of the silicates, then crushed in an agate mortar and successively washed in 2M acetic acid to remove calcite and surface contamination, and finally rinsed in distilled water.

Oxygen isotope analyses of antigorite and whole-rock samples were performed by conventional extraction techniques using ClF₃ to liberate oxygen in Ni-bombs at 600–650 °C for 12–15 hours (BORTHWICK and HARMON, 1982). The oxy-

gen was then converted to CO₂ by reaction with heated graphite (CLAYTON and MAYEDA, 1963). Carbon and oxygen isotope analyses of carbonates were determined on CO₂ gas liberated by reaction with 100% phosphoric acid (MCCREA, 1950) at 50 °C for calcite and 90 °C for dolomite. For hydrogen isotope analyses, mineral separates and whole-rock samples were dried at 150 °C under vacuum overnight, then heated in a vacuum to > 1200 °C to liberate H₂O and H₂, which was converted to H₂O in a copper oxide bypass. The obtained total water aliquot was converted to hydrogen by reaction with elemental zinc at 480 °C for 30 minutes.

The isotopic ratios were determined by conventional mass spectrometric analysis at the ETH-Zürich and are reported in standard δ -notation in per mil (‰) relative to the Vienna Pee Dee Belemnite (VPDB) international standard for carbon and relative to Vienna Standard Mean Ocean Water (VSMOW) for oxygen and hydrogen. Repeat measurements of individual samples yielded an overall reproducibility of ± 0.15 – 0.2 ‰ for oxygen isotope ratios and ± 1 ‰ for hydrogen

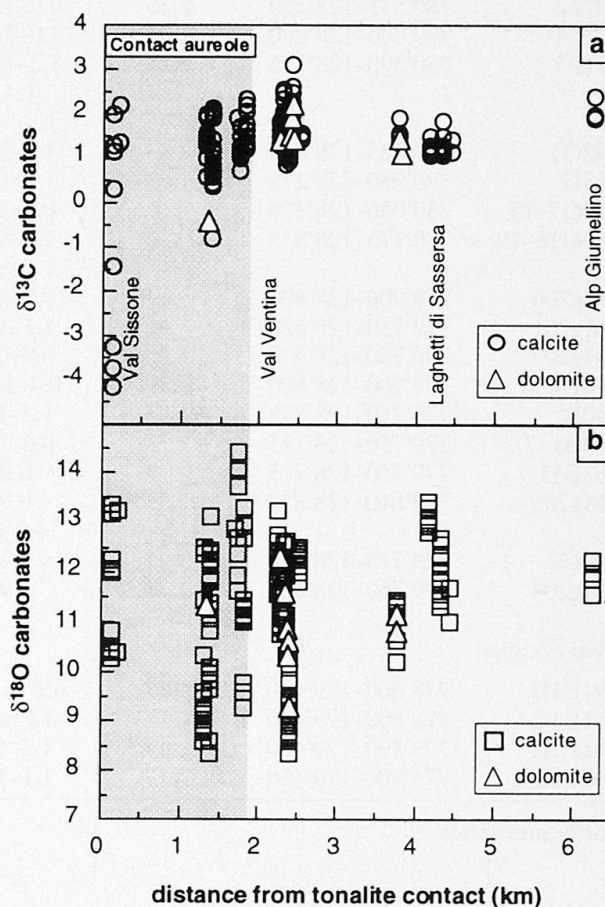
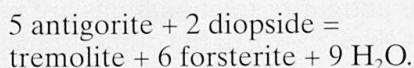


Fig. 3 Regional isotopic trends along the VOZ. Carbon and oxygen isotope compositions of carbonates plotted against the distance from the tonalite intrusion.

isotope ratios. The overall reproducibility for carbon isotope ratios was $\pm 0.1\text{‰}$.

3.2. REGIONAL ISOTOPIC TRENDS ACROSS THE CONTACT AUREOLE

The isotopic results and the locations of the samples from the VOZ are presented in table 1. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonates (mostly calcite) from the VOZ are plotted against the distance from the tonalite contact in figure 3. The extent of the Bergell contact aureole is shown as the shaded region in figure 3; the outer edge of the aureole, at approximately 1.8 km from the tonalite, corresponds to the first isograd reaction in the carbonate-free ultramafic rocks (TROMMSDORFF and EVANS, 1972):



On a regional scale, the carbon isotope ratios are relatively constant throughout the Bergell contact aureole (0.5–2.5‰ VPDB). These values are comparable to marine signatures in non-metamorphic, pelagic limestones of the Southern Alps and carbonates from ophicarbonates in lower-grade ophiolitic units in the Swiss Alps (WEISSERT and BERNOULLI, 1984; FRÜH-GREEN et al., 1990). In contrast, a number of the calcite samples directly at the contact to the tonalite in Val Sissone have significantly lower $\delta^{13}\text{C}$ values that suggest local, partial resetting during Bergell contact metamorphism (Fig. 3a).

In contrast to the carbon isotope ratios, the $\delta^{18}\text{O}$ values of the carbonates along the VOZ are highly variable and do not represent marine compositions, but clearly reflect the imprint of Alpine regional metamorphism and subsequent Bergell contact metamorphism. In the area outside of the contact aureole (Laghetti di Sassersa and Alp Giumellino), the carbonate $\delta^{18}\text{O}$ values range from 10.5 to 13.5‰ (VSMOW). Within the contact aureole, they show a larger variation from 8.3 to 14‰. Moreover, samples located at the same distance from the tonalite contact show variations of up to 5–6‰ (Fig. 3b). Calcite samples closest to the intrusive body in Val Sissone are less variable, with $\delta^{18}\text{O}$ values ranging from 10.4 to 13.5‰.

The $\delta^{18}\text{O}$ values of antigorite from the serpentinite clasts and from the calcite-antigorite matrix display a similar regional pattern (Fig. 4a), reflecting Alpine regional metamorphic signatures gradually overprinted by Bergell contact metamorphism. Away from the contact aureole, $\delta^{18}\text{O}$ values of Alpine regional antigorite in general vary from 7.0 to 9.5‰, indicative of isotopic variations prior

to Bergell contact metamorphism. The variation in $\delta^{18}\text{O}$ values is greater (4.8‰ to 10‰) towards and within the contact aureole. Again, samples located at the same distance from the tonalite contact show distinct variations in $\delta^{18}\text{O}$ (4–5‰). No systematic decrease towards the intrusion, i.e. with increasing temperature, is observed in the calcite-antigorite oxygen isotope fractionations ($\Delta_{\text{calcite-antigorite}}$) (Fig. 4b). Variations in $\Delta_{\text{calcite-antigorite}}$ as large as 2–3‰ occur on a centimetre- to metre-

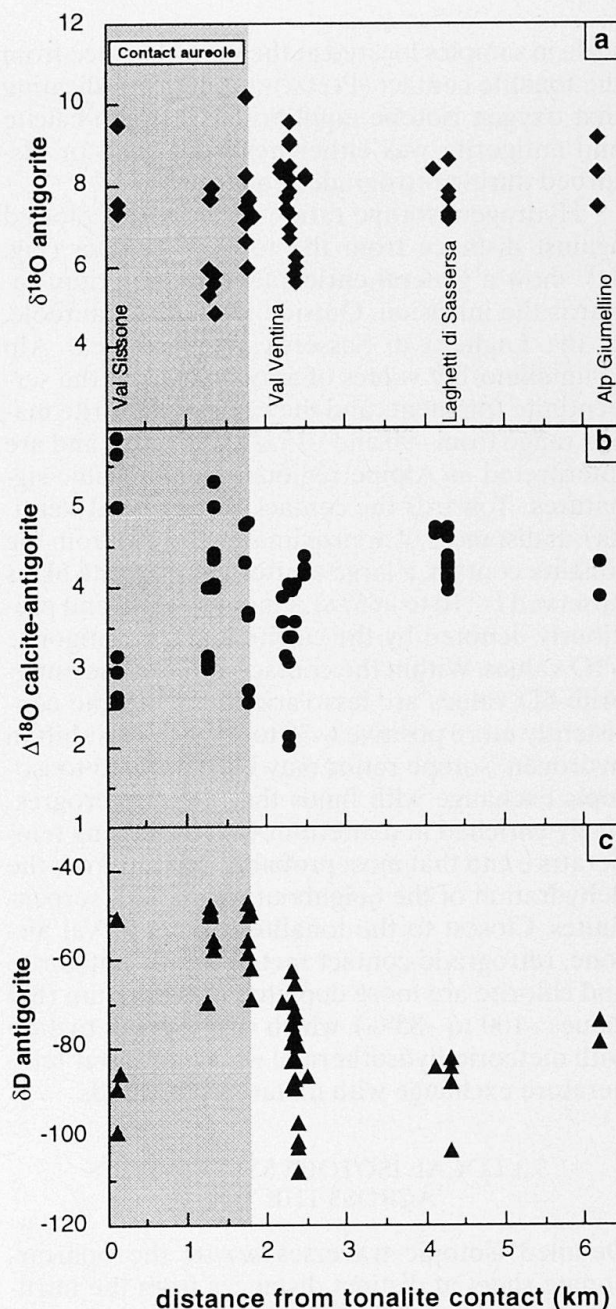


Fig. 4 Regional isotopic trends along the VOZ. (a) Oxygen isotope compositions of antigorite plotted against the distance from the tonalite intrusion. (b) Calcite-antigorite oxygen isotope fractionations. (c) Hydrogen isotope ratios of antigorite.

Tab. 2 Local isotopic variations in profiles across the VOZ and at varying distances away from the Bergell Pluton.

Profile	Distance from tonalite contact (km)	Profile length (m)	$\delta^{13}\text{C}$ range calcite (‰ VPDB)	$\delta^{18}\text{O}$ range calcite (‰ VSMOW)	$\delta^{18}\text{O}$ range antigorite (‰ VSMOW)
Profile I	4.2	10	1.0–1.8	11.0–13.2	7.0–8.5
Profile F*	2.4–1.8	800	0.9–2.6	8.3–13.2	5.6–9.5
Profile G	1.8	600	0.7–2.0	9.2–14.4	5.2–10.0
Profile Mg-B	1.3	260	0.4–2.0	8.2–12.2	4.8–5.8

* Profile F is not oriented perpendicularly to the strike of the VOZ. This is due to the fact that a significant part of the ophicarbonates sheet in Val Ventina is covered with quaternary deposits and glacier (see also Fig. 1).

scale in samples located at the same distance from the tonalite contact (POZZORINI, 1996), indicating that oxygen isotope equilibrium between calcite and antigorite was either never attained or disturbed during retrograde processes.

Hydrogen isotope ratios of antigorite, plotted against distance from the tonalite contact (Fig. 4c), show a general enrichment in deuterium towards the intrusion. Outside the contact aureole, in the Laghetti di Sassera area and near Alp Giumellino, δD values of antigorite from the serpentinite fragments and the calcite-antigorite matrix range from -90 and -75 ‰ (VSMOW) and are interpreted as Alpine regional metamorphic signatures. Towards the contact aureole (Val Ventina), at distances of approximately 2.4 km from the tonalite contact, a large scatter in antigorite δD is observed (-110 to -65 ‰), similar to the trend previously denoted by the calcite and the antigorite $\delta^{18}\text{O}$ values. Within the contact aureole, the antigorite δD values are less varied and become consistently more positive (-70 to -50 ‰). This shift in hydrogen isotope ratios may be attributed to isotopic exchange with fluids that became progressively enriched in deuterium with increasing temperature and that most probably derived from the dehydration of the neighbouring massive serpentinites. Closest to the tonalite contact in Val Sissone, retrograde contact metamorphic antigorite and chlorite are more depleted in deuterium (δD values -100 to -85 ‰), which suggests interaction with meteoric-hydrothermal waters or lower temperature exchange with metamorphic fluids.

3.3. LOCAL ISOTOPE SYSTEMATICS ACROSS THE VOZ

Detailed isotopic traverses across the ophicarbonates sheet at distinct distances from the intrusion (i.e. subparallel to the contact metamorphic isograds) help constrain the extent of the isotopic variations observed on a regional scale. Locations of the traverses are shown in figure 1; the range in isotopic composition and the distance across the

VOZ, i.e. away from the southern boundary to the massive serpentinites, for each profile are listed in table 2. In the short profile I, located outside the contact aureole in the Laghetti di Sassera area, the calcite and antigorite oxygen isotope ratios and the calcite-antigorite fractionations are relatively constant (Figs 5 a–c). In the other profiles F, G and Mg-B, the oxygen isotope compositions of calcite and antigorite become successively depleted towards the lithologic contacts to the surrounding massive serpentinites. At the same time, the $\Delta^{18}\text{O}_{\text{calcite-antigorite}}$ values change systematically towards the external portions of the ophicarbonates sheet.

In profiles F and G at the outer edge of the contact aureole, shifts in calcite and antigorite $\delta^{18}\text{O}$ values towards the lithologic boundary of the VOZ are on the order of 5 to 6‰ (calcite, Fig. 5a) and 4 to 5‰ (antigorite, Fig. 5b), respectively. Calcite-antigorite oxygen isotope fractionations decrease from 4.5–5‰ down to 2.5‰ at the southern boundary of the sheet (Fig. 5c). In the central part of the contact aureole, profile Mg-B crosscuts the VOZ at 1.3 km distance from the intrusive body. Even though no progressive change from centre to boundary is observed, the $\delta^{18}\text{O}$ values are equivalent to the most negative values observed at the southern boundaries in profiles F and G (Figs 5a and 5b). This suggests isotopic resetting from values of ≈ 14 ‰ and 10‰ for calcite and antigorite, respectively. The calcite-antigorite fractionations along profile Mg-B scatter unsystematically between 3 and 5‰ (Fig. 5c).

The $\delta^{18}\text{O}_{\text{calcite}}$ versus $\delta^{18}\text{O}_{\text{antigorite}}$ values of the data for the detailed profiles are plotted in figure 6. In this diagram, the lines denoted by $\Delta = 3$ to $\Delta = 5$ represent the range in equilibrium delta values with decreasing temperature, and provide a simple test for oxygen isotope equilibrium during metamorphism. Oxygen isotope disequilibrium in the VOZ is indicated by the fact that the $\delta^{18}\text{O}_{\text{calcite}}$ versus $\delta^{18}\text{O}_{\text{antigorite}}$ values in the profiles do not plot along a single isotherm but scatter in a δ - δ plot. This is best illustrated for profile G, where the

$\Delta^{18}\text{O}$ values range from 3 to 5‰. If changes in $\Delta^{18}\text{O}$ values were attributed to mass balance effects, a correlation between isotopic signatures and modal data would be expected. On the other hand, if changes in calcite-mineral $\Delta^{18}\text{O}$ values are attributed to temperature effects, a significant temperature increase along profiles F and G towards the southern boundary of the VOZ would be expected. Calcite-diopside oxygen isotope fractionations observed along profile F are listed

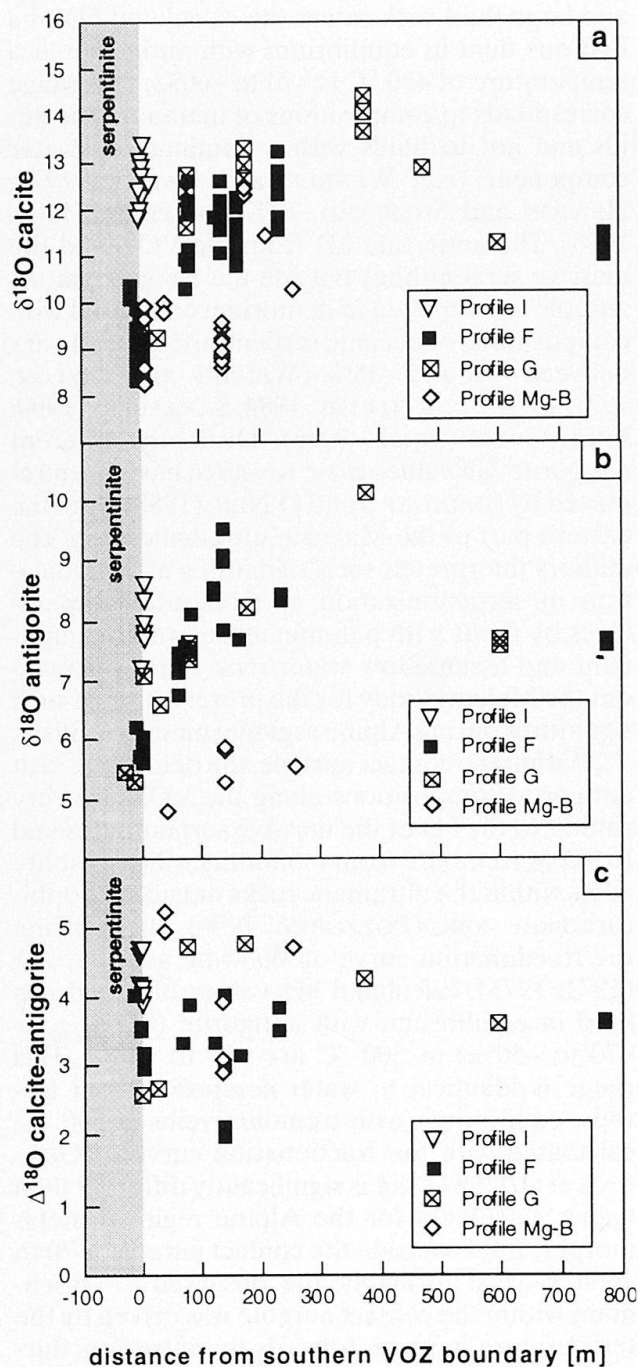


Fig. 5 Local oxygen isotope systematics of calcite and antigorite in profiles across the VOZ at distinct distances from the tonalite contact plotted against the distance from the southern boundary of the VOZ.

in table 3. The $\Delta^{18}\text{O}_{\text{calcite-diopside}}$ values are very similar to the calcite-antigorite fractionations and decrease towards the lithological boundary. Applying the calcite-diopside fractionation factors of CHIBA et al. (1989) and ZHENG (1993a), the decrease in calcite-diopside oxygen isotope fraction-

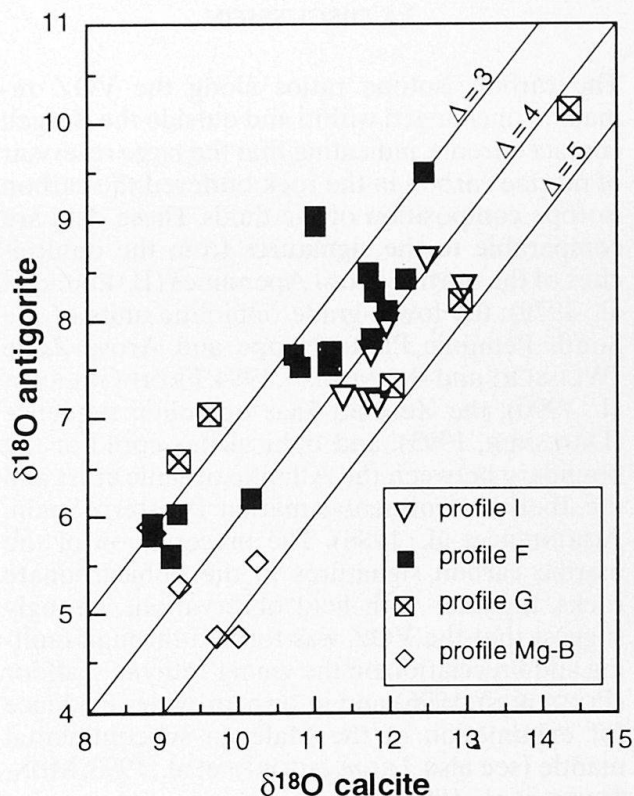


Fig. 6 $\delta^{18}\text{O}$ antigorite versus $\delta^{18}\text{O}$ calcite plot of the data from the local profiles across the VOZ. Lines denoted with Δ represent oxygen isotope equilibration at constant temperatures, with temperature decreasing from $\Delta = 3$ to $\Delta = 5$.

Tab. 3 Variations in calcite-diopside oxygen isotope fractionations ($\Delta^{18}\text{O}_{\text{cc-di}}$) and temperature estimates along profile F.

Distance from southern boundary to serpentinite (m)	$\Delta^{18}\text{O}_{\text{cc-di}}$	$T(^{\circ}\text{C})^1$	$T(^{\circ}\text{C})^2$
170	3.64	534	484
170	3.75	522	469
170	4.03	494	433
140	4.78	431	351
140	3.81	516	460
80	4.07	490	427
10	3.06	608	577
10	2.81	645	623

¹ CHIBA et al. (1989): $10^3 \ln \alpha_{\text{cc-di}} = 2.37 \times (10^6/T^2)$

² ZHENG (1993a):

$$10^3 \ln \alpha_{\text{cc-di}} = 0.1 \times (10^6/T^2) + 3.78 \times (10^3/T) - 1.53$$

ations correspond to a temperature increase on the order of 150 °C. Clearly, an increase in temperature is unlikely because the strike of profiles F and G is subparallel to the isograds of Bergell contact metamorphism. Furthermore, there is no petrographic evidence for such a temperature increase.

3.4. DISCUSSION

The carbon isotope ratios along the VOZ remained unchanged within and outside the Bergell contact aureole, indicating that the large reservoir of marine carbon in the rock buffered the carbon isotope composition of the fluids. These data are comparable to the signatures from the ophicalcites of the north-central Apennines (BARBIERI *et al.*, 1979), the lower-grade ophiolitic units of the South Penninic Platta Nappe and Arosa Zone (WEISSERT and BERNOULLI, 1984; FRÜH-GREEN *et al.*, 1990), the Zermatt-Saas ophiolitic sequence (DRIESNER, 1993), and ophicalcites cored at the boundary between the Atlantic oceanic crust and the Iberian continental margin (western Spain, AGRINIER *et al.*, 1988). The preservation of the marine carbon signatures in the ophicarbonate rocks, together with field observations, strongly suggest that the VOZ was formed through faulting and brecciation on the young Tethyan seafloor (POZZORINI, 1996) and in turn, provides evidence for exhumation of the Malenco subcontinental mantle (see also TROMMSDORFF *et al.*, 1993; MÜNTENER *et al.*, 1995).

Petrologic data provide strong evidence for water-rich fluids coexisting with the Ventina ophicarbonate rocks during Alpine regional metamorphism and Bergell contact metamorphism (TROMMSDORFF and EVANS, 1972, 1977 a, b). Mineral phase equilibria indicate that ophicarbonate rocks have a limited stability field in T - X_{CO_2} space and that fluids in equilibrium with the metamorphic assemblages are always very water-rich (TROMMSDORFF and EVANS, 1977a; TROMMSDORFF and CONNOLLY, 1990).

In hydrothermal systems, oxygen fugacity and pH of the fluids can have a strong control on the isotope systematics of carbon (OHMOTO, 1972). The relatively homogeneous $\delta^{13}\text{C}$ values observed in the profiles across the VOZ indicate that oxygen fugacity and pH of the fluids within the VOZ associated with Bergell contact metamorphism did not influence the carbon isotope pattern. A slight increase in $\delta^{13}\text{C}$ of 0.5 to 1‰ at the lithologic boundary between the VOZ and the massive serpentinites, observed along the profiles across the ophicarbonate sheet, is probably associated with a change from highly reducing conditions in

the bordering massive serpentinites to oxidising conditions within the ophicarbonate zone (POZZORINI, 1996).

Antigorite δD values from the VOZ away from the contact aureole are comparable to hydrogen isotope data of antigorite in the massive serpentinites in the Laghetti di Sassersa area (δD close to -90‰) reported by BURKHARD and O'NEIL (1988). Applying the serpentine-water fractionation curve of WENNER and TAYLOR (1971, 1973) and assuming isotopic equilibrium and large fluid-rock ratios, the calculated δD of a hydrous fluid in equilibrium with antigorite at a temperature of 430 °C is -70 to -60‰. This range corresponds to compositions of metamorphic fluids and not to fluids with a dominant seawater component (e.g. WENNER and TAYLOR, 1973; HEATON and SHEPPARD, 1977; SHEPPARD, 1980, 1986). The antigorite δD from the VOZ and the massive serpentinites outside the Bergell contact aureole are depleted in deuterium compared with compositions of oceanic serpentinites, which vary between -70 and -35‰ (WENNER and TAYLOR, 1971, 1973; BONATTI *et al.*, 1984; SAKAI *et al.*, 1990; FRÜH-GREEN *et al.*, 1996). Distinctly different antigorite δD values close to -40‰ have been reported by BURKHARD and O'NEIL (1988) from the eastern part of the Malenco ultramafic body. The authors interpreted such signatures as an indication of serpentinization at moderate temperatures by fluids with a dominant seawater component and assume low water/rock ratios throughout the Malenco body for the preservation of such signatures during Alpine regional metamorphism.

Within the contact aureole, the deuterium-rich antigorite compositions along the VOZ are very similar to the δD of the massive serpentinites and to δD of tremolite from monomineralic tremolite veins within the ultramafic rocks outside the ophicarbonate zone (POZZORINI, 1996). By applying the fractionation curve of WENNER and TAYLOR (1971, 1973), calculated δD values of a hydrous fluid in equilibrium with antigorite ($\delta\text{D}_{\text{antigorite}} = -70$ to -50 ‰) at 500 °C are -55 to -30‰. This range is identical to water compositions in isotopic equilibrium with tremolite veins at 500 °C, calculated with the fractionation curve of GRAHAM *et al.* (1984), but is significantly different than values calculated for the Alpine regional metamorphic fluids outside the contact aureole (-70 to -60‰). Most probably, the observed D-enrichment within the contact aureole was driven by the temperature increase towards the intrusion, during which metamorphic water released by dehydration of the massive serpentinites became progressively enriched in deuterium due to equilibration at increasing temperature. In contrast, meta-

morphic water released by dehydration of the serpentinite at a constant temperature would produce a progressive D-depletion in antigorite with increasing dehydration progress.

3.5. CONSEQUENCES FOR FIELD-BASED GEOTHERMOMETRIC ESTIMATES

In figure 7, the $\Delta^{18}\text{O}_{\text{calcite-antigorite}}$ values from the detailed profiles along the VOZ are plotted against the contact metamorphic temperature determined by calcite-dolomite solvus geothermometry (TROMMSDORFF and EVANS, 1977a,b; TROMMSDORFF and CONNOLLY, 1990). These data are further compared with the theoretical calcite-antigorite fractionation curve of ZHENG (1993b) determined with the increment method (curve 1) and with a composite fractionation curve (curve 2) calculated from empirical serpentine-water fractionation factors of WENNER and TAYLOR (1971) and experimentally determined calcite-water fractionation factors of O'NEIL et al. (1969). As discussed previously, the large variations of the $\Delta^{18}\text{O}_{\text{calcite-antigorite}}$ values indicate that oxygen isotope equilibrium between calcite and antigorite was in general not attained within the VOZ. Thus, it is evident from figure 7 that a field-based geothermometric calibration of calcite-antigorite

oxygen isotope fractionations across the Bergell contact aureole may not be established.

Comparison between the observed calcite-antigorite fractionations with the calcite-serpentine fractionation curves indicates that the lower $\Delta^{18}\text{O}_{\text{calcite-antigorite}}$ values plot relatively close to the theoretical curve 1 of ZHENG (1993b) and to the composite curve 2 (WENNER and TAYLOR, 1971; O'NEIL et al., 1969). In particular, a large number of the $\Delta^{18}\text{O}_{\text{calcite-antigorite}}$ values along profile F approach the two theoretical curves suggesting that the calcite-dolomite temperature estimates close to the edge of the contact aureole are in agreement with the oxygen isotope equilibrium temperatures predicted from the two theoretical curves. Along profile I, even the lowest $\Delta^{18}\text{O}_{\text{calcite-antigorite}}$ values plot above the fractionation curves 1 and 2. This may be interpreted as an effect of oxygen isotope disequilibrium prior to Bergell contact metamorphism (i.e. during Alpine regional metamorphism) or as a wrong prediction of curves 1 and 2 at lower temperatures.

The open circles in figure 7 represent calcite-antigorite and calcite-chlorite fractionations from two samples directly on the contact to the tonalite in Val Sissone, plotted relative to calcite-dolomite solvus temperatures. These temperatures are compared with calcite-diopside oxygen isotope

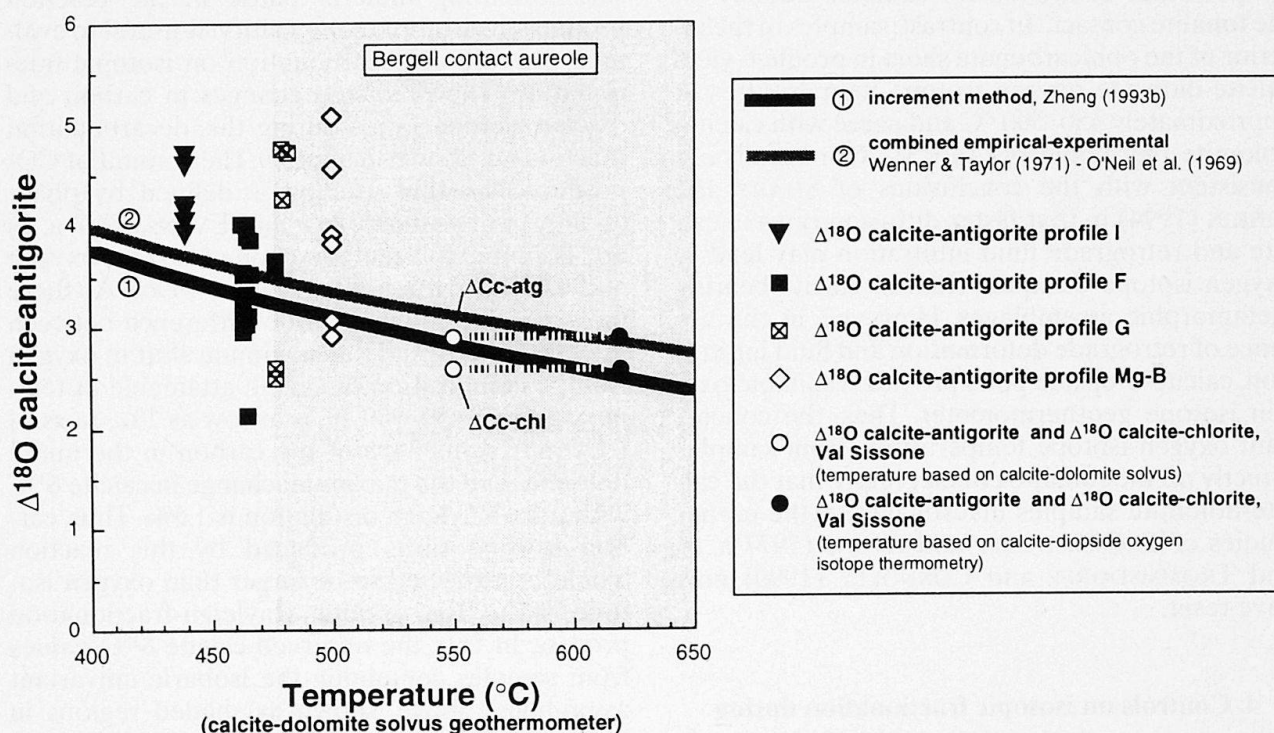


Fig. 7 Calcite-antigorite oxygen isotope fractionations observed along the VOZ, plotted against temperature determined from calcite-dolomite solvus geothermometry by TROMMSDORFF and EVANS (1977 a,b) and TROMMSDORFF and CONNOLLY (1990). Theoretical oxygen isotope calcite-serpentine fractionation curves from the literature are shown for comparison. The discrepancy between calcite-dolomite geothermometry and calcite-diopside oxygen isotope temperature estimates is illustrated by the tie lines that link the circles (see text).

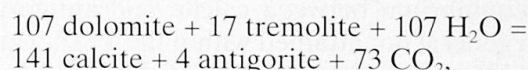
temperatures calculated from theoretical fractionation factors of ZHENG (1993a), shown as solid circles. The difference between the two temperature estimates is illustrated by the tie lines that link the solid and open circles. The discrepancy in temperature may reflect different rates of intercrystalline diffusion of Ca and Mg between calcite and dolomite and oxygen diffusion between calcite and diopside. Recent studies of SHARP and JENKIN (1994) suggest that oxygen diffusion in diopside is extremely slow, with closure temperatures above approximately 750°, even for very small grain sizes. In the samples investigated in our study, diopside is medium to fine-grained and coexists with coarse-grained calcite and minor amounts of fine-grained chlorite. As there is no textural or petrographic evidence in these samples for retrograde deformation or alteration during cooling, the calcite-diopside fractionations should reflect peak metamorphic temperature conditions (SHARP and JENKIN, 1994). In fact, on the basis of theoretical fractionation factors of ZHENG (1993 a, b), both calcite-diopside and calcite-chlorite mineral pairs yield concordant oxygen isotope temperatures of 620 °C. This is also consistent with temperature estimates of 640 °C, calculated from calcite-diopside fractionation factors of CHIBA et al. (1989) but is approximately 50–70 °C higher than the calcite-dolomite solvus temperatures estimated for samples directly on the tonalite contact. In contrast, samples in the interior of the ophicarbonate sheet in profile F yield calcite-diopside oxygen isotope temperatures of approximately 450–500 °C and agree with calcite-dolomite thermometry (Tab. 3). Our results are consistent with the conclusions of SHARP and JENKIN (1994) in that faster diffusion rates in calcite and retrograde fluid infiltration may lead to oxygen isotope disequilibrium in calcite-bearing metamorphic assemblages. However, in the absence of retrograde deformation and fluid infiltration, calcite-diopside pairs provide a reliable oxygen isotope geothermometer. Thus, the concordant oxygen isotope temperatures from samples directly on the tonalite contact imply that the calcite-dolomite samples investigated in the earlier studies of TROMMSDORFF and EVANS (1977 a, b) and TROMMSDORFF and CONNOLLY (1990) may have reset.

4. Controls on isotopic fractionation during contact metamorphism

Two end-member processes may be considered to explain the observed isotopic patterns in the VOZ: metamorphic devolatilization and interac-

tion of the ophicarbonate rocks with an external fluid. Isotopic shifts caused by metamorphic devolatilization can be approximated by two general end-member mechanisms: closed-system (batch) devolatilization and open-system fractional or Rayleigh distillation (e.g. NABELEK et al., 1984; RUMBLE, 1982; VALLEY, 1986). Evaluation of these processes require estimates of the initial isotopic compositions of the phases in the rock and knowledge of the isotopic fractionation between the volatile phases and the minerals in the rock at a given temperature. In a closed system model, the volatile phase does not immediately escape from the system, but continuously equilibrates with the rock. In contrast, the open-system Rayleigh distillation model dictates that the volatile phase continuously escapes from the system and thereby produces larger isotopic shifts as the mole fraction, F , of the element of interest decreases in the system (Fig. 8).

A common decarbonation reaction observed along the VOZ in the outer part of the contact aureole is the isobaric univariant assemblage (reaction 8c in TROMMSDORFF and EVANS, 1977 a, b):



which occurs over the temperature interval between 450 and 500 °C. Because calcite is the sole carbon-bearing mineral phase in the reaction products, its isotopic composition is useful to evaluate the role of decarbonation on isotopic fractionation. The predicted changes in carbon and oxygen isotope ratios during this decarbonation reaction are shown in figure 8. The amount of CO₂ produced by this reaction is defined by phase equilibria (TROMMSDORFF and EVANS, 1977 a, b) and is limited to a mole fraction of 0.87 for oxygen and 0.65 for carbon (POZZORINI, 1996). At these mole fractions, there is little difference between the two models, and the maximum shift in oxygen isotope composition of calcite attainable at temperatures of 450–500 °C is as low as 1‰. Loss of CO₂ represents 34% of the carbon in the initial dolomite and the maximum change in calcite $\delta^{13}\text{C}$ with pure Rayleigh distillation is 1.5‰. Thus, carbon isotope shifts produced by this reaction would be expected to be larger than oxygen isotope shifts for a pure Rayleigh-fractionation process. In fact, the observed calcite $\delta^{18}\text{O}$ values from samples containing the isobaric univariant assemblage above, shown as shaded regions in figure 8, indicate that the changes in $\delta^{18}\text{O}$ are much larger than 1‰ and the variations in $\delta^{13}\text{C}$ are not greater than 1.5‰.

Since metamorphic devolatilization alone is insufficient to explain the oxygen isotope shifts

observed along and across the VOZ, such shifts must have resulted from interaction with fluids from an external source. According to VALLEY (1986), the major factors leading to extensive isotopic exchange during fluid infiltration in contact aureoles are: (1) a high and continuous fluid supply; (2) a large difference in isotopic composition between infiltrating fluid and infiltrated rock; and (3) an enhanced rock permeability. The most probable fluid source in the Bergell contact aureole leading to fluid-rock interaction in the ophicarbonate rocks is water released by progressive dehydration of the neighbouring massive serpentinites. This is consistent with petrographic evidence, in particular, the breakdown reaction of antigorite to forsterite and talc that releases large amounts of water, and would explain the constant carbon isotope shifts along and across the VOZ. Because such a fluid would be largely depleted in ^{18}O with respect to the observed oxygen isotope composition of the minerals in the ophicarbonate rocks, pronounced isotopic shifts within the ophicarbonates resulting from fluid-rock interaction would be expected.

Rock permeability is generally high in fractured and porous rocks. However, relatively impermeable rocks may become important fluid conduits when permeability is enhanced by local,

small transient fluid over-pressures caused by devolatilization reactions. Both dehydration and decarbonation reactions can result in a positive $\Delta V_{\text{reaction}}$ during contact metamorphism. These positive volume changes create pressure gradients sufficient for fluid expulsion leading to dilatation and hydrofracturing of the rock (e.g. RUMBLE and SPEAR, 1983; NABELEK et al., 1984; VALLEY, 1986). Even very small rock porosities (i.e. < 1%) may provide sufficient permeability to segregate fluids evolved at reasonable metamorphic reaction rates (WALTHER and ORVILLE, 1982).

Interaction of the Ventina ophicarbonates with an external fluid and in particular the relatively large amounts of water that may have been introduced into the ophicarbonate sheet, do not contradict the fact that isobaric univariant and invariant assemblages are observed in the field. The low variance assemblages observed along the VOZ indeed indicate that the chemical composition of the fluid was buffered by the mineral assemblages (TROMMSDORFF and EVANS, 1977 a, b; TROMMSDORFF and CONNOLLY, 1990). However, this does not imply that the isotopic composition of the fluid is also entirely determined by the isotopic composition of the mineral phases. In the case of interaction of an externally derived, iso-

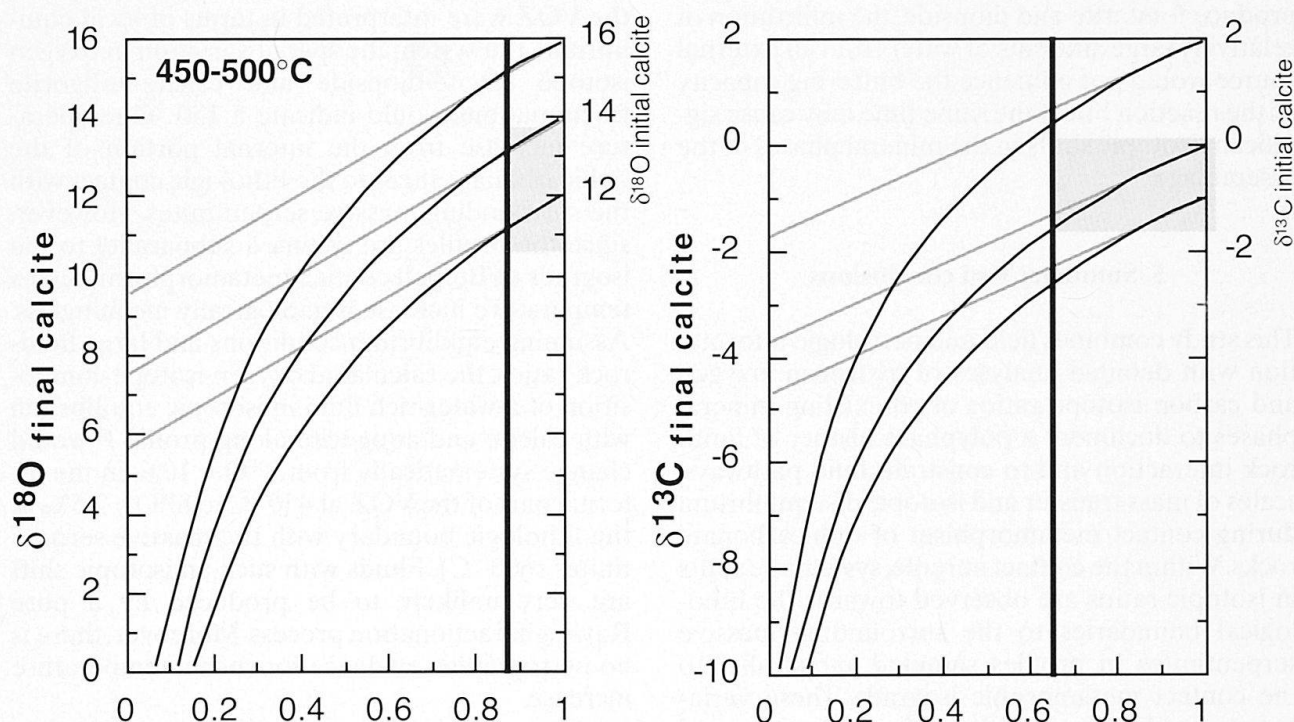
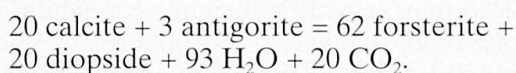


Fig. 8 Predicted changes in oxygen and carbon isotope ratios with progressive decrease in mole fraction, F , during closed system batch decarbonation (straight grey lines) and Rayleigh decarbonation (curves) calculated for the reaction: dolomite + tremolite + H_2O = calcite + antigorite + CO_2 . The vertical lines represent the limit of decarbonation as predicted by phase equilibria (TROMMSDORFF and EVANS, 1977 a, b). The shaded regions shows the range of isotopic compositions of VOZ samples with this mineral assemblage.

topically light fluid with the ophicarbonates, the buffering capacity of the mineral assemblages may be significantly larger for the chemical composition than for the isotopic composition of the fluid.

A mineral reaction that is frequently observed in the VOZ is the isobaric univariant assemblage (reaction 3c of TROMMSDORFF and EVANS, 1977 a, b):



The maximum X_{CO_2} at which this univariant assemblage is stable is given by the location of the invariant point in the T - X_{CO_2} diagram of TROMMSDORFF and CONNOLLY (1990), that is $X_{\text{CO}_2} = 0.007$. If one mole of pure water derived from the dehydrating massive serpentinites enters the VOZ the reaction above will proceed until the fluid has an equilibrium composition of $X_{\text{CO}_2} = 0.007$. This reaction has a high buffering capacity because only small amounts of minerals are consumed or produced to buffer 1 mole of pure water to a composition in equilibrium with the assemblage. Assuming modal proportions in the ophicarbonate rocks to be 45 vol.% antigorite, 38 vol.% calcite and 17 vol.% diopside, if 1 mole of antigorite is available, 1000 moles of pure water can enter the ophicarbonate rock and be chemically buffered. Hence, in an open system where calcite and antigorite may produce forsterite and diopside, the infiltration of relatively large amounts of water from an external source would not influence the buffering capacity of the reaction but at the same time may cause significant isotopic shifts in the mineral phases of the assemblage.

5. Summary and conclusions

This study combines field and petrologic information with detailed analyses of hydrogen, oxygen and carbon isotope ratios of co-existing mineral phases to document a polyphase history of fluid-rock interaction and to constrain fluid pathways, scales of mass transfer and isotopic disequilibrium during contact metamorphism of ophicarbonate rocks. Within the contact aureole, systematic shifts in isotopic ratios are observed towards the lithological boundaries to the surrounding massive serpentinites in profiles sampled subparallel to the contact metamorphic isograds. These variations provide strong evidence for infiltration and isotopic exchange with external, water-rich fluids, probably derived from dehydration reactions in the surrounding serpentinites during contact metamorphism.

Field-based geothermometric estimates from oxygen isotope fractionations between calcite and silicate phases were not possible due to large variations in $\Delta^{18}\text{O}_{\text{calcite-mineral}}$ values that occur along isothermal profiles across the VOZ, even on a cm-scale. However, in profile F at the outer edge of the contact aureole, calcite-diopside fractionations in samples located in the interior of the ophicarbonate sheet and furthest away from the contact to the massive serpentinites yield oxygen isotope temperatures that are consistent with calcite-dolomite solvus temperature estimates. In contrast, calcite-diopside and calcite-chlorite fractionations in samples directly on the contact to the tonalite intrusion yield oxygen isotope temperatures that are slightly higher than those obtained with calcite-dolomite solvus thermometry by TROMMSDORFF and EVANS (1977a,b) and TROMMSDORFF and CONNOLLY (1990). This suggests that in the near vicinity of the tonalite contact, Ca and Mg partitioning in calcite-dolomite pairs may have reset during cooling.

The isotopic variations observed along and across the VOZ are too large to be explained purely by a process of Rayleigh distillation. The lack of distinct coupled trends between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of calcite suggests that metamorphic devolatilization did not significantly influence the isotopic pattern during contact metamorphism. If the isotope signatures observed in profiles across the VOZ were interpreted in terms of local equilibrium, the systematic spatial variation in oxygen isotope calcite-diopside and calcite-antigorite fractionations would indicate a 150 °C temperature increase from the internal portion of the ophicarbonate sheet to the lithologic contact with the surrounding massive serpentinites. However, since the profiles are oriented subparallel to the isograds of Bergell contact metamorphism, such a temperature increase is geologically meaningless. Assuming equilibrium conditions and large fluid-rock ratios, the calculated oxygen isotope composition of a water-rich fluid in isotopic equilibrium with calcite and antigorite along profile F would change systematically from $\delta^{18}\text{O} \approx 10\text{‰}$ in the internal part of the VOZ at 450 °C to $\delta^{18}\text{O} \approx 7.5\text{‰}$ at the lithologic boundary with the massive serpentinites (600 °C). Fluids with such an isotopic shift are very unlikely to be produced by a pure Rayleigh fractionation process. Moreover, there is no petrographic evidence for such a temperature increase.

Alternatively, the spatial features of the isotope patterns can be explained by interaction of the ophicarbonate rocks with an externally derived, isotopically light water-rich fluid in equilibrium with the dehydrating massive serpentinites.

The spatial variations in calcite-diopside and calcite-antigorite oxygen isotope fractionations suggest that fluid-rock interaction occurred under isotopic disequilibrium and can be explained by kinetically controlled mineral-fluid isotopic exchange (SHARP and JENKIN, 1994; POZZORINI, 1996; POZZORINI et al., in prep.). The pronounced shifts in hydrogen and oxygen isotope ratios towards the massive serpentinites suggests that the lithological boundaries were sites of enhanced permeability and promoted channelling of metamorphic fluids during contact metamorphism (see also FERRY, 1995).

The introduction of large amounts of externally derived, ^{18}O -depleted water-rich fluids in the Ventina ophicarbonates would have negligible effects on the buffering capacity of the mineral assemblages in controlling the chemical composition of the pore fluid. Low variance mineral assemblages can persist even if significant amounts of water-rich fluid are introduced, however, significant shifts in the isotopic compositions of the mineral phases may occur.

This study documents the necessity for careful petrological investigations in the interpretation of stable isotope signatures in contact metamorphic aureoles. In turn, it further emphasises the importance of detailed systematic analyses of multiple isotopes in co-existing mineral phases in studying processes of fluid advection and mass transfer during regional and contact metamorphism. The systematic variations in isotopic signatures in the Ventina Ophicarbonate Zone suggests that the regional effects of dehydration reactions and fluid advection during contact metamorphism may be greater than that those defined solely on the basis of mineral assemblages. The large variations in isotope ratios observed outside of the contact aureole, defined by the breakdown of antigorite + diopside, suggest that the contact aureole around the Bergell pluton may extend to distances as great as 2.5 km from the intrusive contact. Thus, stable isotopes provide a powerful tool to define the limits of fluid-rock interaction during contact metamorphism and to trace fluid infiltration pathways in rocks where mineral assemblages have a high internal buffering capacity.

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References

- AGRINIER, P., MÉVEL, C. and GIRARDEAU, J. (1988): Hydrothermal alteration of the peridotites cored at the ocean/continent boundary of the Iberian margin; petrologic and stable isotope evidence. In: BOILLLOT, G., WINTERER, E.L. et al. (1988): Proceedings of the Ocean Drilling Program, Scientific Results, 103, 225–234.
- BARBIERI, M., MASI, U. and TOLOMEO, L. (1979): Stable isotope evidence for a marine origin of ophicalcites from the north-central Apennines (Italy). *Marine Geol.*, 30, 193–204.
- BONATTI, E., LAWRENCE, J.R. and MORANDI, N. (1984): Serpentinization of ocean-floor peridotites. *Earth Planet. Sci. Lett.*, 70, 88–94.
- BORTHWICK, J. and HARMON, R.S. (1982): A note regarding ClF_3 as an alternative to BrF_5 for oxygen isotope analysis. *Geochim. Cosmochim. Acta*, 46, 1665–1668.
- BURKHARD, D.J.M. and O'NEIL, J.R. (1988): Contrasting serpentinization processes in the eastern Central Alps. *Contrib. Mineral. Petrol.*, 99, 498–506.
- CHIBA, H., CHACKO, T., CLAYTON, R.N. and GOLDSMITH, J.R. (1989): Oxygen isotope fractionations involving diopside, forsterite, magnetite and calcite: Application to geothermometry. *Geochim. Cosmochim. Acta*, 53, 2985–2995.
- CLAYTON, R.N. and MAYEDA, R.K. (1963): The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. Cosmochim. Acta*, 27, 43–52.
- COOK, S.J. and BOWMAN, J.R. (1994): Contact metamorphism surrounding the Alta stock: Thermal constraints and evidence of advective heat transport from calcite + dolomite geothermometry. *Amer. Mineralogist*, 79, 513–525.
- DRIESNER, T. (1993): Aspects of petrographical, structural and stable isotope geochemical evolution of ophicarbonate breccias from ocean floor to subduction and uplift: an example from Chatillon, Middle Aosta Valley, Italian Alps. *Schweiz. Mineral. Petrogr. Mitt.*, 73, 69–84.
- FERRY, J.M. (1988): Infiltration-driven metamorphism in northern New England, USA. *J. Petrology*, 29, 1121–1159.
- FERRY, J.M. (1995): Fluid flow during contact metamorphism of ophicarbonate rocks in the Bergell aureole, Val Malenco, Italian Alps. *J. Petrology*, 36, 1039–1053.
- FRÜH-GREEN, G., WEISSERT, H. and BERNOULLI, D. (1990): A multiple fluid history recorded in Alpine Ophiolites. *Journal Geol. Soc. London*, 147, 959–970.
- FRÜH-GREEN, G.L., PLAS, A. and LÉCUYER, C. (1996): Petrologic and stable isotope constraints on hydrothermal alteration and serpentinization of the EPR shallow mantle at Hess Deep (ODP Site 895). Proceedings of the Ocean Drilling Program, Scientific Results, 147, 255–291.
- GRAHAM, C.M., HARMON, R.S. and SHEPPARD, S.M.F. (1984): Experimental hydrogen isotope studies: hydrogen isotope exchange between amphibole and water. *Amer. Mineralogist*, 69, 128–138.
- GREENWOOD, H.J. (1975): Buffering of pore fluids by metamorphic reactions. *Am. J. Sci.*, 275, 573–593.

- HEATON, T.H.E. and SHEPPARD, S.M.F. (1977): Hydrogen and oxygen isotope evidence for seawater hydrothermal alteration and ore deposition, Troodos complex, Cyprus. In: *Volcanic processes in ore genesis*, Geol. Soc. London, spec. paper, 7, 42–57.
- LATTANZI, P., RYE, D.M. and RICE, J.M. (1980): Behaviour of ^{13}C and ^{18}O in carbonates during contact metamorphism at Marysville, Montana: Implications for isotope systematics in impure dolomitic limestones. *Am. J. Sci.*, 280, 890–906.
- McCREA, J.M. (1950): The isotopic chemistry of carbonates and a paleotemperature scale. *Journ. Chem. Phys.*, 18, 849–857.
- MELLINI, A., TROMMSDORFF, V. and COMPAGNONI, R. (1987): Antigorite polysomatism: behaviour during prograde metamorphism. *Contrib. Mineral. Petrol.*, 97, 147–155.
- MOORE, J.N. and KERRICK, D.M., (1976): Equilibria in siliceous dolomites of the Alta aureole, UTAH. *Am. J. Sci.*, 276, 502–524.
- MÜNTENER, O., HERMANN, J. and TROMMSDORFF, V. (1995): Extensional metamorphism and exhumation of granulites, Mantle-Crust section (Malenco, central Alps). *Terra Abstract EUG-8*, Strasbourg.
- NABELEK, P.I., LABOTKA, T.C., O'NEIL, J.R. and PAPIKE, J.J. (1984): Contrasting fluid/rock interactions between the Notch Peak granitic intrusion and argillites and limestones in western Utah: evidence from stable isotopes and phase assemblages. *Contrib. Mineral. Petrol.*, 86, 25–34.
- OHMOTO, H. (1972): Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. *Econ. Geol.* 67, 551–579.
- O'NEIL, J.R., CLAYTON, R.N. and MAYEDA, T.K. (1969): Oxygen isotopic fractionation in divalent metal carbonates. *J. Chem. Phys.*, 5, 5547–5558.
- POZZORINI, D. (1996): Stable isotope investigations of ophicarbonate rocks, Bergell aureole, Valmalenco: constraints on fluid-rock interaction. Ph. D. Thesis ETH-Zürich Nr. 11436.
- RICE, J.M. and FERRY, J.M. (1982): Buffering, infiltration and control of intensive variables during metamorphism. In: FERRY, J.M. (ed.): *Characterization of metamorphism through mineral equilibria*, Reviews in Mineralogy, Mineralogical Society of America, 10, 263–326.
- RUMBLE, D. (1982): Stable isotope fractionation during metamorphic devolatilization reactions. In: FERRY, J.M. (ed.): *Characterization of metamorphism through mineral equilibria*, Reviews in Mineralogy, Mineralogical society of America, 10, 327–352.
- RUMBLE, D., FERRY, Y.M., HOERING, T.C. and BOUCOT, A.J. (1982): Fluid flow during metamorphism at the Beaver Brook fossil locality, New Hampshire. *Am. J. Sci.*, 282, 886–919.
- RUMBLE, D. and SPEAR, F.S. (1983): Oxygen-isotope equilibration and permeability enhancement during regional metamorphism. *Journal Geol. Soc., London*, 140, 619–628.
- SAKAI, R., KUSAKABE, M., NOTO, M. and ISHII, T. (1990): Origin of waters responsible for serpentinization of the Izu-Ogasawara-Mariana forearc seamounts in view of hydrogen and oxygen isotope ratios. *Earth Planet. Sci. Lett.*, 100, 291–303.
- SCHUMACHER, T. (1975): *Geologisch-petrographische Untersuchungen des Malencoserpentins und der Marnagesteine bei Chiareggio*, Diplomarbeit ETH Zürich (unpubl.).
- SHARP, Z.D. and JENKIN, G.R.T. (1994): An empirical estimate of the diffusion rate of oxygen in diopside. *J. metamorphic Geol.*, 12, 89–97.
- SHEPPARD, S.M.F. (1980): Isotopic evidence for the origins of waters during metamorphic processes in oceanic crust and ophiolite complexes. In: *Association mafiques-ultramafiques dans les orogènes*, Colloq. Int. C.N.R.S. (Cent. Natl. Rech. Sci.), Paris, 272, 135–147.
- SHEPPARD, S.M.F. (1986): Characterization and isotopic variations in natural waters. In: VALLEY, J.W., TAYLOR, H.P. Jr., O'NEIL, J.R. (eds): *Stable Isotopes in high temperature geological processes*, Reviews in Mineralogy, Mineralogical Society of America, 16, 165–181.
- TROMMSDORFF, V. and EVANS, B.W. (1972): Progressive metamorphism of antigorite schist in the Bergell tonalite aureole (Italy). *Am. J. Sci.* 272, 423–437.
- TROMMSDORFF, V. and EVANS, B.W. (1977a): Antigorite-ophicarbonates: phase relations in a portion of the system $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O-CO}_2$. *Contrib. Mineral. Petrol.* 60, 39–56.
- TROMMSDORFF, V. and EVANS, B.W. (1977b): Antigorite-ophicarbonates: contact metamorphism in Valmalenco (Italy). *Contrib. Mineral. Petrol.* 62, 301–312.
- TROMMSDORFF, V. and CONNOLLY, J.A.D. (1990): Constraints on phase diagram topology for the system $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O-CO}_2$. *Contrib. Mineral. Petrol.* 104, 1–7.
- TROMMSDORFF, V. and CONNOLLY, J.A.D. (1996): The ultramafic contact aureole about the Bregaglia (Bergell) tonalite: isograds and a thermal model. *Schweiz. Mineral. Petrogr. Mitt.* 76, 539–549.
- TROMMSDORFF, V., PICCARDO, G.B. and MONTRASIO, A. (1993): From magmatism through metamorphism to sea floor emplacement of subcontinental Adria lithosphere during pre-Alpine rifting (Malenco, Italy). *Schweiz. Mineral. Petrogr. Mitt.*, 73, 191–204.
- VALLEY, J.W. (1986): Stable isotope geochemistry of metamorphic rocks. In: VALLEY, J.W., TAYLOR, H.P. Jr., O'NEIL, J.R. (eds): *Stable Isotopes in high temperature geological processes*, Reviews in Mineralogy, Mineralogical society of America, 16, 445–490.
- WALTHER, J.V. and ORVILLE, P.M. (1982): Volatile production and transport in regional metamorphism. *Contrib. Mineral. Petrol.*, 79, 252–257.
- WEISSERT, H. and BERNOULLI, D. (1984): Oxygen isotope composition of calcite in Alpine ophicarbonates, a hydrothermal or Alpine metamorphic signal? *Eclogae geol. Helv.*, 77, 29–43.
- WENNER, D.B. and TAYLOR, H.P. Jr. (1971): Temperature of serpentinisation of ultramafic rocks based on $^{18}\text{O}/^{16}\text{O}$ fractionation between coexisting serpentine and magnetite. *Contrib. Mineral. Petrol.*, 32, 165–185.
- WENNER, D.B. and TAYLOR, H.P. Jr. (1973): Oxygen and hydrogen isotope studies of the serpentinisation of ultramafic rocks in oceanic environments and continental ophiolite complexes. *Am. J. Sci.*, 273, 207–239.
- ZHENG, Y.F. (1993a): Calculation of oxygen isotope fractionation in anhydrous silicate minerals. *Geochim Cosmochim. Acta* 57, 1079–1091.
- ZHENG, Y.F. (1993b): Calculation of oxygen isotope fractionation in hydroxyl-bearing silicates, *Earth Planet. Sci. Lett.*, 120, 247–263.

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