

Contrasting serpentinization processes in the eastern Central Alps

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Abstract. Stable isotope compositions have been determined for serpentinites from between Davos (Arosa-Platta nappe, Switzerland) and the Valmalenco (Italy). δD and $\delta^{18}O$ values (-120 to -60 and 6 – 10‰ , respectively) in the Arosa-Platta nappe indicate that serpentinization took place on the continent at relatively low temperatures in the presence of limited amounts of metamorphic fluids that contained a component of meteoric water. One sample of chrysotile has a $\delta^{18}O$ value of 13‰ providing evidence of high W/R ratios and low formation temperature of lizardite-chrysotile in this area. In contrast, relatively high δD values (-42 to -34‰) and low $\delta^{18}O$ values (4.4 – 7.4‰) for serpentine in the eastern part of the Valmalenco suggest a serpentinization process that took place at moderate temperatures in fluids that were dominated by ocean water. The antigorite in the Valmalenco is the first reported example of continental antigorite with an ocean water signature. An amphibole sample from a metasomatically overprinted contact zone to metasediments ($\delta D = -36\text{‰}$) indicates that the metasomatic event also took place in the presence of ocean water. Lower δD values (-93 to -60‰) of serpentines in the western part of the Valmalenco suggest a different alteration history possibly influenced by fluids associated with contact metamorphism. Low water/rock ratios during regional metamorphism (and metasomatism) have to be assumed for both regions.

Introduction

Ultramafic rocks are usually serpentinized. The character and extent of the serpentinization process depends on a number of factors including whether the alteration occurred at constant volume or isochemically, the source of the water, the temperature, and the fluid/rock ratio. These factors are reflected by the hydrogen and oxygen isotope compositions of the serpentine minerals. Variations in the hydrogen and oxygen isotope compositions and the serpentinizing fluids have been investigated by Barnes and O'Neill (1969), Wenner and Taylor (1969, 1971, 1973, 1974), Margaritz and Taylor (1974), Heaton and Sheppard (1977), Ikin

and Harmon (1983), and Yui and Yeh (1986). Major conclusions inferred from these data are: (1) formation of continental lizardite-chrysotile took place on the continent at relatively low temperatures (often less than 150°C and possibly as low as surface temperatures, Barnes and O'Neill 1969) in the presence of low- T alteration-fluids that contain varying proportions of meteoric water, (2) most oceanic serpentines (dredged from the ocean floor) with characteristically high δD values (-35 to -68‰) and low $\delta^{18}O$ values (0.8 – 6.7‰) formed at moderate temperatures ($350 \pm 50^\circ\text{C}$) in the presence of a fluid dominated by ocean water, and (3) ophiolitic serpentines do not bear the isotopic composition typical of oceanic serpentines and may have formed after uplift under low temperature continental conditions.

If continental serpentinization were to occur at near surface temperatures, we should expect to observe minerals with relatively high $\delta^{18}O$ values (around 12 – 15‰ or higher depending on the isotopic composition of the surface water) because the magnitude of the isotopic fractionation factors are large at low temperatures. However, values this high have only rarely been observed in a few samples from ophiolites in Troodos, Cyprus (Margaritz and Taylor 1974) and Vourinos, Greece (Wenner and Taylor 1973), a suite of serpentine-like mineraloids called deweylites (Wenner and Taylor 1974) and a single sample from the present study. The paucity of such data may reflect a sampling bias but could also mean that water/rock ratios are fairly low during most serpentinization processes on the continent and, consequently, that the oxygen isotopic composition of the serpentine is largely inherited from the precursor minerals (Barnes et al. 1978).

In this study the stable isotope geochemistry of ophiolitic serpentinites from the Arosa-Platta nappe in the eastern Central Alps are contrasted with those of serpentines from the nearby Valmalenco region. The results help to more clearly define the nature of serpentinization processes occurring in zones of continental collision.

Geology and mineralogy

Serpentinized ultramafics in the eastern Central Alps belong to the Pennine nappes and occur along a N-S section of about 60 km at the boundary to overlying Austroalpine nappes, from the Davos-Arosa region, Switzerland, to the Valmalenco, Italy (Fig. 1).

The northern occurrences of serpentine (Arosa-Platta nappe between Davos and the Engadin) are ultramafic tectonites of a dissected ophiolite remnant which include associated tholeiitic

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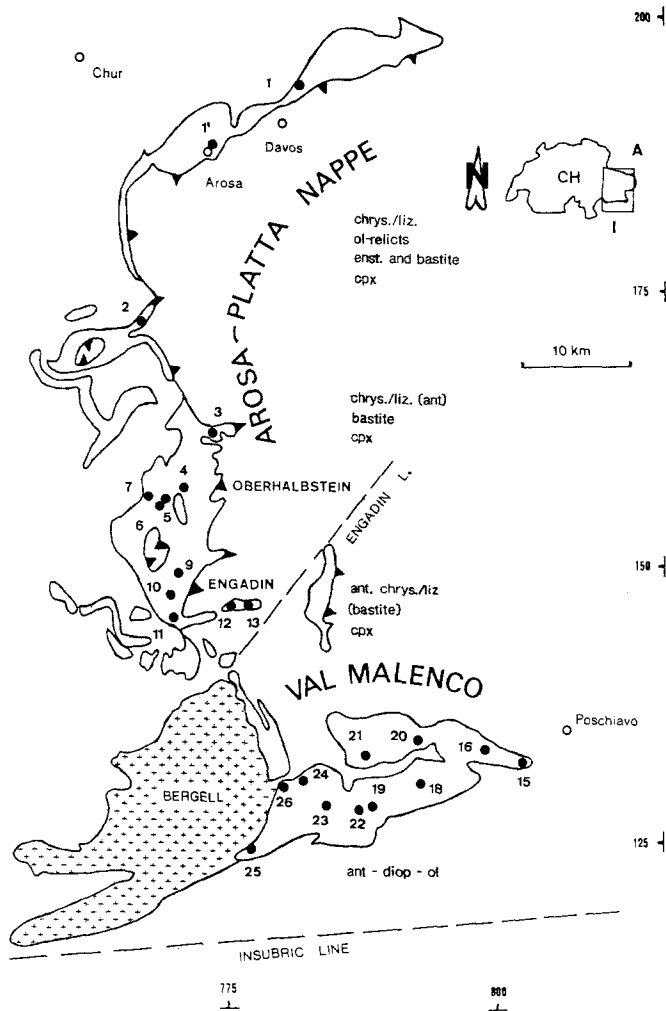


Fig. 1. Tectonic sketch map with the ophiolites of the Arosa-Platta nappe and the Val Malenco ultramafic complex and the main silicate assemblages in the serpentinites. The sampling localities for stable isotope analyses are: Arosa-Platta nappe: 1: Davos (Da); 1': Arosa; 2: Tgant Ladrung (OH1); 3: Tinzener Ochsenalp (OH4); 4: Gruba (OH5); 7: Muttans (OH11); 9: Schlucht Bivio (SchB); 10: Sur al Cant Fuorcla (SCF, OSCF); 11: Lunghin Area (Lungh); 12: Blaunca (Bl); 13: Grevasalvas (Grev); Valmalenco: 15: Selva; 16: Pass d'Ur (P. d'Ur); 18: Franscia (Fr.); 19: Chiesa; 20: Nero; 21: Alpe Senevedo (VM6); 22: above Chiesa (Prim); 23: Laghetti di Sassera (Lagh); 4: Val Ventina (Vent); 25: Val Masino, Preda Rossa (V. Mas); 26: Val Sissone, (V. Siss)

meta-basalts and meta-sediments (radiolarites, cherts etc.) of Upper Jurassic to Upper Cretaceous age (Peters 1963; Dietrich 1967, 1969, 1970, 1979). A progressive alpine (regional) metamorphism correlates with the degree of serpentinization: in the prehnite-pumpellyite facies (Davos-Arosa) chrysotile/lizardite (chrys/liz) occurs with some relict olivine. Orthopyroxene (opx) can be unaltered or serpentinized in the north. With increasing grade of metamorphism to the south, ol and opx are serpentinized. Chrys/liz predominate up to the middle of the Oberhalbstein, and antigorite is the most abundant mineral with the transition to the greenschist facies. Cpx occurs fresh or exsolved with opx lamellae throughout the entire Arosa-Platta nappe (Burkhard 1987).

The Valmalenco ultramafic rocks occupy an area of about 180 km². The typical metamorphic association is antigorite-olivine-diopside; antigorite is the only serpentine mineral, besides microscopic occurrences of chrysotile discovered by Mellini et al. (1987). Olivine is in most cases recrystallized and the pyroxene is pure diopside. Some of it contains exsolved chlorite lamellae

of a former high-Al component. Bucher and Pfeiffer (1973) suggested that the ultramafic complex may be of pre-Mesozoic age because it has a pre-alpine foliation and contains more than one generation of metamorphic minerals. During late Tertiary time the serpentinite complex was intruded by the Bergell granodiorite (Bregaglia Intrusion) in the western part of the Valmalenco which caused a contact metamorphic overprint to the amphibolite (\pm granulite) facies (Trommsdorff and Evans 1972, 1977; Gautschi and Montrasio 1978; Burkhard 1987).

Al-spinel is common in the Davos region whereas two spinels, an Al-Cr- and a Cr-spinel occur in the Oberhalbstein and the Engadin. In the east Valmalenco, the original Cr-spinel is altered and recrystallized to a Cr-bearing magnetite, whereas the Cr content of relict centers occasionally exceeds 30 wt.% in the west Valmalenco. An irregular and a high content of TiO₂ is characteristic of all Valmalenco spinels (Burkhard 1987; Burkhard and Amstutz 1988).

Small massive Fe-Cu(-Ni) sulfide deposits are generally located at the boundary to the Austroalpine nappe units in the Oberhalbstein and the Engadin (Dietrich 1972). They are in the serpentinite body and not related to tectonic elements in the Valmalenco (De Capitani et al. 1981). Detailed descriptions and discussion of these sulfide occurrences and accessory opaque phases are given in Burkhard (1987).

Analytical procedures

Only fresh and unaltered serpentine minerals were selected for stable isotope analysis and the parent rocks were normally well serpentinized. The samples were ground with a mortar and pestle, washed with HCl to remove carbonate, and the magnetite was removed with a hand magnet. The purity of the final separates was usually better than 98%.

The mineral separates were pumped in vacuum at 150° C for several hours and then heated to 1400° C to quantitatively liberate water. Any H₂ produced during this procedure was converted to H₂O by oxidation over a CuO furnace. The water was then reacted with Zn at 450° C to produce H₂ for isotopic analysis. Oxygen was liberated from the minerals by reaction with ClF₃ at 550° C and converted over a heated graphite rod to produce CO₂ for isotopic analysis. The isotopic ratios were determined on conventional isotope ratio mass spectrometers. The data are reported in the familiar δ -notation in ‰ relative to the SMOW standard. The precision of the $\delta^{18}O$ and δD values are better than ± 0.2 and $\pm 1‰$ respectively.

Results

The isotopic analyses and sample locations are given in Tables 1 and 2 and the isotopic data δD and $\delta^{18}O$ are plotted in Fig. 2. Figures 3 and 4 show the N-S and E-W distribution of $\delta^{18}O$ for the Arosa-Platta nappe and the Valmalenco, respectively, and in Fig. 5 δD values are plotted on a sketch map of the area. The data for the samples from the Arosa-Platta nappe correspond to the field observed by Wenner and Taylor (1973, 1974) for continental alpine type chrys/liz. The antigorites in the east Valmalenco region have δD and $\delta^{18}O$ values of around $-40‰$ and 4 to 7‰, respectively. Such values are typical for serpentine and amphibole which formed in fluids with a dominant component of ocean water (e.g. Wenner and Taylor 1973; Heaton and Sheppard 1977; Stakes and O'Neil 1982; Smith et al. 1984). The Valmalenco serpentines are the first reported examples of antigorites with an ocean water signature that are found on the continent. It is noteworthy that, to date, only one stable isotope analysis has been reported for antigorite collected from the ocean floor, and this is a picrolite variety (Wenner and Taylor 1973). In the west Valmalenco the

Table 1. Stable isotope compositions of serpentinites in the Arosa-Platta nappe

Sample field #	Region Arosa-Platta nappe	Swiss Coordinates	Sample description	δD	$\delta^{18}O$
Da 7	Davos, Totalpserp.	780.34/189.74	C/L, cpx, (opx)	-134	7.0
Da 8	Davos, Totalpserp.	780.38/189.82	C/L, B, cpx, massive	-119	6.7
Da 9	Davos, Totalpserp.	780.39/189.85	C/L, cpx, (opx)	-126	6.8
Da 11	Davos, Totalpserp.	780.94/189.23	C/L, cpx, (opx)	-116	6.8
Da 17	Davos, Totalpserp.	781.00/190.43	C/L	-104	9.8
DaDrus 1	Davos		C/L, B	-120	7.8
Arosa 1	Arosa	770.14/184.76	C/L, cpx, (opx)	-125	6.7
Arosa 4	Arosa	768.05/184.75	C/L	-95	10.6
OH1/4	N-Oberhalbstein	746.55/168.27	C/L, sulf	-60	10.0
OH1/9	N-Oberhalbstein	746.55/168.27	C/L, B, later veins, (carb)	-62	13.0
OH4/1	N-Oberhalbstein	771.85/159.25	C/L, B, carb massiv	-62	7.8
OH5/11	Middle Oberhalbst.	769.20/153.79	C/L cpx, massiv	-69	6.9
OH5/12	Middle Oberhalbst.	769.20/153.79	C/L ilv, massiv	-58	6.1
OH11/3	Middle Oberhalbst.	765.93/152.76	C/L, B	-97	7.0
OSSF3	S-Oberhalbstein	768.67/144.38	A, massiv	-69	6.0
OSSF4	S-Oberhalbstein	768.67/144.38	A, later vein	-103	6.4
Lungh 14	Engadin	771.00/142.42	A, cpx, filt-like (carb)	-76	6.2
LP	Engadin	771.56/142.34	A, (chl)	-50	6.9
LPP	Engadin	771.32/142.34	C/L, B, (A)	-100	7.2
Bl. 5	Engadin	774.64/143.92	A, (C/L), (cpx)	-47	9.9
Bl. 11	Engadin	774.50/143.70	A, later vein sulf.	-60	9.6
Bl. 12	Engadin	774.50/143.70	A, (C/L), sulf	-66	9.6
Grev. 1	Engadin	776.12/144.32	A, (C/L)	-62	6.5
Grev. 6	Engadin	776.20/144.23	A, L, (carb)	-70	6.2

Table 2. Stable isotope compositions of serpentinites in the Valmalenco

Sample field #	Region Valmalenco	Swiss Coordinates	Sample description	δD	$\delta^{18}O$
Selva 1	E-Valm	800.50/130.70	A-schist (diop)	-42	6.5
P. d'Ur 1	E-Valm	797.23/131.45	A, act. (carb)	-36	7.2
Fr. 1	E-Valm	790.20/129.10	A, diop (carb)	-39	7.4
Fr. 7	E-Valm	790.20/129.10	A, diop	-34	4.7
VM6/11	E-Valm	783.35/132.85	A, ol (carb)	-40	5.2
Chiesa 1r	E-Valm	785.40/128.60	A-schist	-37	4.4
Chiesa 3a	E-Valm	785.77/127.90	A, diop	-49	5.8
Prim 8	E-Valm	784.31/126.00	A, carb	-40	4.9
Lagh. 7	W-Valm	781.95/126.90	A, diop-r	-93	7.1
Lagh. 10	W-Valm	782.10/126.89	A, sulf	-90	7.7
Vent. 5	W-Valm	780.55/130.00	A, (ol, trem, chl, diop)	-61	5.7
Vent. 7	W-Valm	780.20/130.15	A, diop-r	-75	n.a.
V. Mas 4	W-Valm	773.60/122.80	trem, ol	-90	5.8
V. Mas 6	W-Valm	773.60/122.80	A, diop-r	-76	4.3
V. Siss 1	W-Valm	778.72/129.70	ol, trem, tc, (anth)	-55	5.3
V. Siss 2	W-Valm	778.72/129.70	A, tc (chl)	-52	5.1
V. Siss 5	W-Valm	778.45/130.00	trem, anth	-72	4.3

Description. C: chrysotile; L: lizardite; A: antigorite; B: bastite; cpx: clinopyroxene; diop: diopside; diop-r: diopside relicts; ol: olivine; act: actinolite; chl: chlorite; trem: tremolite; tc: talc; anth: anthophyllite; carb: carbonate; sulf: sulfide

$\delta^{18}O$ values are similar to those in the east Valmalenco but the δD values are distinctly lower.

Discussion

Water/rock ratios

Water/rock ratios (W/R) can be crudely calculated from the $\delta^{18}O$ value of the rock or dominant mineral in the rock using the equation of Taylor (1974).

$$W/R = [\delta(R_f) - \delta(R_i)] / [\Delta + \delta(W_i) - \delta(R_f)]$$

where $\Delta = \delta(R) - \delta(W)$, and R and W are the atom percents of oxygen in the rock and water, respectively, and i and f refer to the initial and final conditions. The serpentine-water fractionation of Wenner and Taylor (1971) was used in the calculation:

$$\Delta = 0.6(10^6 T^{-2}) - 5.4.$$

Many $\delta^{18}O$ values of the serpentine minerals are in the range of 6 to 8‰ and are thus not much different from those of the precursor minerals olivine and pyroxene (Taylor 1968). In these cases either the W/R ratios were small

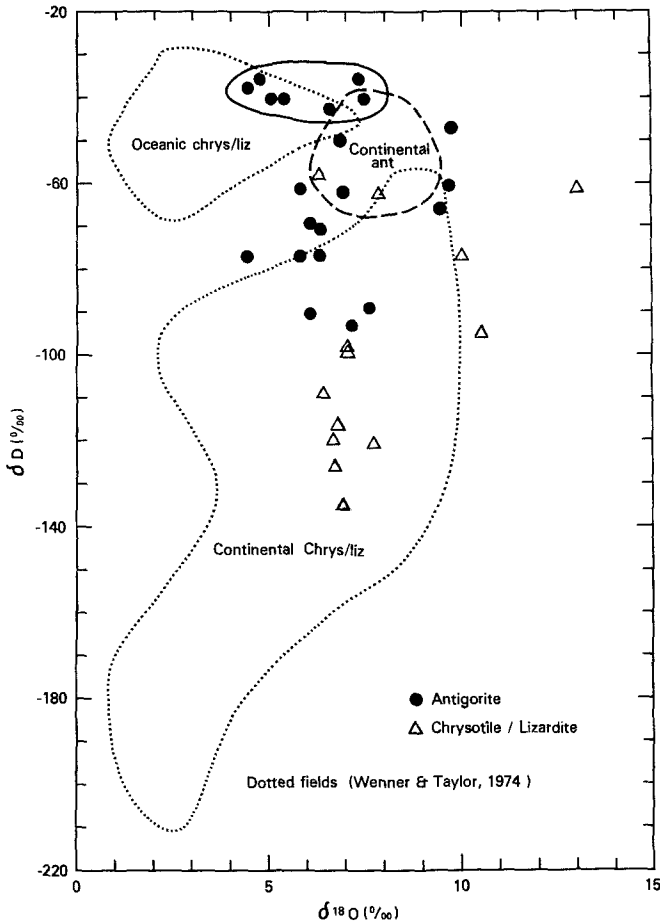


Fig. 2. $\delta^{18}O$ vs δD of serpentine from the Arosa-Platta nappe and the Valmalenco

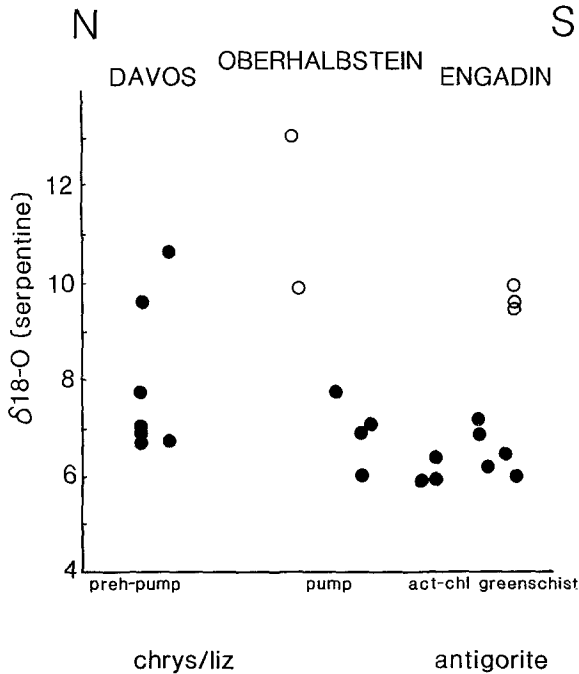


Fig. 3. $\delta^{18}O$ of serpentine from the Arosa-Platta nappe versus increasing grade of metamorphism from N to S. Open circles refer to samples from small massive sulfide deposits. For discussion, see text

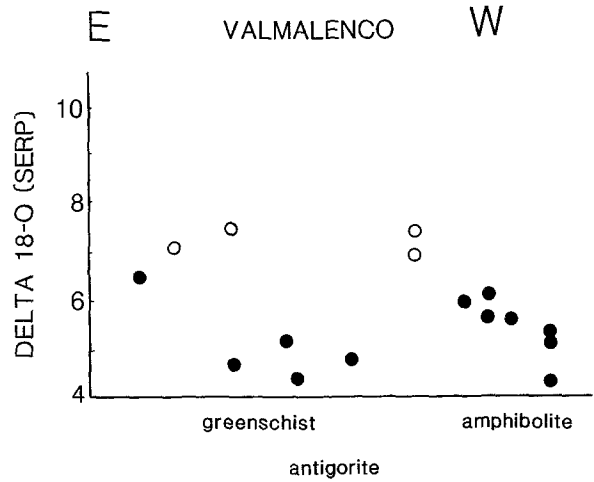


Fig. 4. $\delta^{18}O$ of antigorite from the Valmalenco area from E to W. Open circles refer to samples from small massive sulfide deposits. For discussion, see text

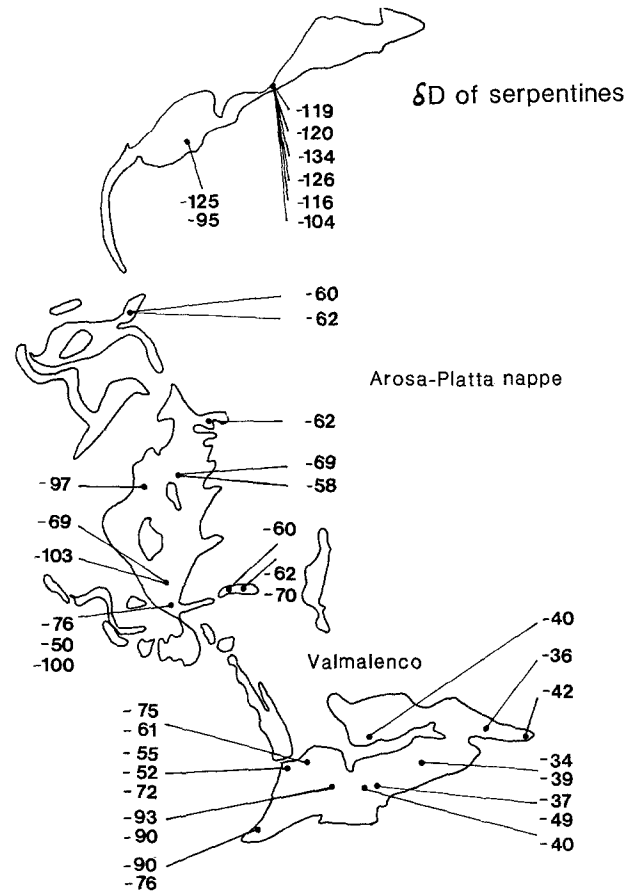


Fig. 5. δD of serpentine from the Arosa-Platta nappe and the Valmalenco serpentines

or the metamorphic fluid was already close to oxygen isotope equilibrium with serpentine at the temperature of serpentinization. In the Valmalenco, especially in the east, $\delta(R_f)$ values of around 4‰ imply high W/R ratios in the presence of fluids with a dominant component of ocean water for which $\delta(W_i) = 0$. The high δD and low $\delta^{18}O$ values of serpentines in the east Valmalenco provide evidence that this was the case. A W/R ratio is 0.2 for a temperature of 400°C which is a reasonable assumption for the Valmalenco antigorite.

In Fig. 3 the $\delta^{18}\text{O}$ values of serpentinites in the Arosa-Platta nappe are shown in relation to the geographical location of the sampling sites from N to S, the direction of increasing grade of metamorphism. The open circles refer to analyses of serpentine (chrysliz and ant) from sample localities with the small massive sulfide deposits which are usually located close to a tectonic boundary to the Austroalpine nappes. The increase in $\delta^{18}\text{O}$ from values presumably near 6.0‰ for the precursor minerals to values of about 10–13‰ suggests that either W/R ratios were high and temperatures of serpentinization were low for these samples or that the $\delta^{18}\text{O}$ values of the fluids were as high as about 10‰. Such high values are common for regional metamorphic fluids. Since most of the data are in the 6–8‰ range, samples with high $\delta^{18}\text{O}$ values are presumably very local. From the geological evidence of extensive serpentinization of these rocks and enhanced tectonization close to the nappe boundary, it would appear that W/R ratios were indeed high in these cases.

The very high $\delta^{18}\text{O}$ value of 13.0‰ for sample OH1/9 from the Oberhalbstein (chrysliz) is particularly noteworthy. Hitherto, values this high have been observed only for a few samples (deweylites) from the Troodos ophiolite, Cyprus by Margaritz and Taylor (1974) and a single sample from the Vourinos ophiolite, Greece by Wenner and Taylor (1973). The Oberhalbstein sample OH1/9 contains large bastites which Wenner and Taylor (1973) also noted are associated with higher $^{18}\text{O}/^{16}\text{O}$ ratios of samples from a given area. The relation between the presence of bastites and unusual ^{18}O enrichment is not understood. This sample also contains a minor portion of later serpentine vein material which might be responsible in part for the oxygen isotope composition. However, serpentine veins of different generations are common in metamorphosed serpentinites. Due to the extremely small size of these veins, they could not be separated for isotopic analyses.

With the exception of the samples just discussed, the $\delta^{18}\text{O}$ values of these serpentines, like those of chrysliz from most areas of the world, are near those of the precursor minerals (Wenner and Taylor 1974). There is a general trend over a spread of about 2‰ to lower $\delta^{18}\text{O}$ values with increasing grade of metamorphism. This trend is best explained by some combination of higher temperatures and lower W/R ratios for the higher grade rocks. In any event, the W/R ratios must be fairly low in the higher grade rocks for the $\delta^{18}\text{O}$ values to remain similar to those of the precursor olivine and pyroxene.

Figure 5 is a similar presentation of data in relation to geographical location of samples in the Valmalenco. In this case the sole serpentine mineral determined under the microscope is antigorite and the $\delta^{18}\text{O}$ values are presented from east (Pass d'Ur) to west (Val Ventina). Again the open circles (higher $\delta^{18}\text{O}$ values) are associated with rocks located close to a tectonic boundary, in this case to Pennine meta-sediments. Noteworthy is the uniformity of the low $\delta^{18}\text{O}$ values in the east and west Valmalenco despite remarkable variations of δD values.

The serpentinization process

A general controversy concerns the question of whether stable isotope data of serpentines, once formed, preserve their isotopic composition during later geological events or whether isotopic exchange occurs such that the original

composition is (completely) overprinted (Wenner and Taylor 1974; Sakai and Tsutsumi 1978; Sheppard 1980; Yui and Yeh 1986). Sakai and Tsutsumi (1978) and Sheppard (1980) concluded that a solution of the problem requires more experimental data on the kinetics of exchange and equilibrium factors. However, it is generally accepted that hydrogen isotope exchange reactions between minerals and water proceed with greater facility than oxygen isotope exchange reactions as shown for example by the experiments of O'Neil and Kharaka (1976). While this may not be a valid generalization, the west Valmalenco antigorites, discussed below, may provide a new example of post-formational hydrogen exchange.

The Arosa-Platta nappe. The very low δD values (to -134‰) of all serpentinites from the Davos and Arosa region indicate that meteoric water was a significant if not the dominant component of the serpentinizing fluid in this region. In the Oberhalbstein the δD values of all serpentines range from -97 to -58‰ indicating that in this region serpentinization took place in the presence of not only meteoric water, but also of metamorphic fluids. However, it cannot be decided whether meteoric water was introduced exclusively during a late serpentinization event or whether serpentinization took place in the presence of a composite fluid, although a mineralogical connection between the degree of serpentinization and the grade of regional metamorphism has been outlined. A recrystallization of serpentine, i.e., the formation of later serpentine generations, very likely occurred in the presence of predominantly meteoric water; sample OSCF4 ($\delta D = -103\text{‰}$) contains large quantities of a late serpentine generation occurring in veins. In the Oberengadin, where antigorite predominates, the δD values range between -76 and -47‰ . The value of -100‰ (sample LPP) again seems to correlate with high amounts of a young serpentine generation, in this case picrolitic varieties of chrysliz. It is particularly noteworthy that at the contact to the sediments and at the nappe boundary, where enhanced water circulation and high W/R ratios may be expected, the δD values indicate that the serpentinizing fluids were predominantly metamorphic water and that meteoric water played a subordinate role. The correlation between increasing intensity of serpentinization and the progressive metamorphism suggests an alteration process on the continent that was related to the regional metamorphism. However, because of the experimental problem mentioned above, whether or not an earlier serpentinization took place in the presence of ocean water cannot be unambiguously determined.

The Valmalenco. In contrast to serpentines in the Arosa-Platta nappe where the interpretation of the isotopic data is rather straightforward, the Valmalenco serpentines are exceptional and more difficult to interpret. Typical δD values of metamorphic minerals in the Alps are around -70‰ and some minerals that exchanged with meteoric water have δD values as low as -160‰ (Frey et al. 1976; Hoernes and Friedrichsen 1978). High δD values of up to -34‰ in the east Valmalenco together with low $\delta^{18}\text{O}$ values near 4.0‰ provide strong evidence for ocean water serpentinization if the data are interpreted in terms outlined by Wenner and Taylor (1973, 1974). In this case the possibility that serpentinization occurred in the presence of metamorphic and/or magmatic water can be excluded. The low

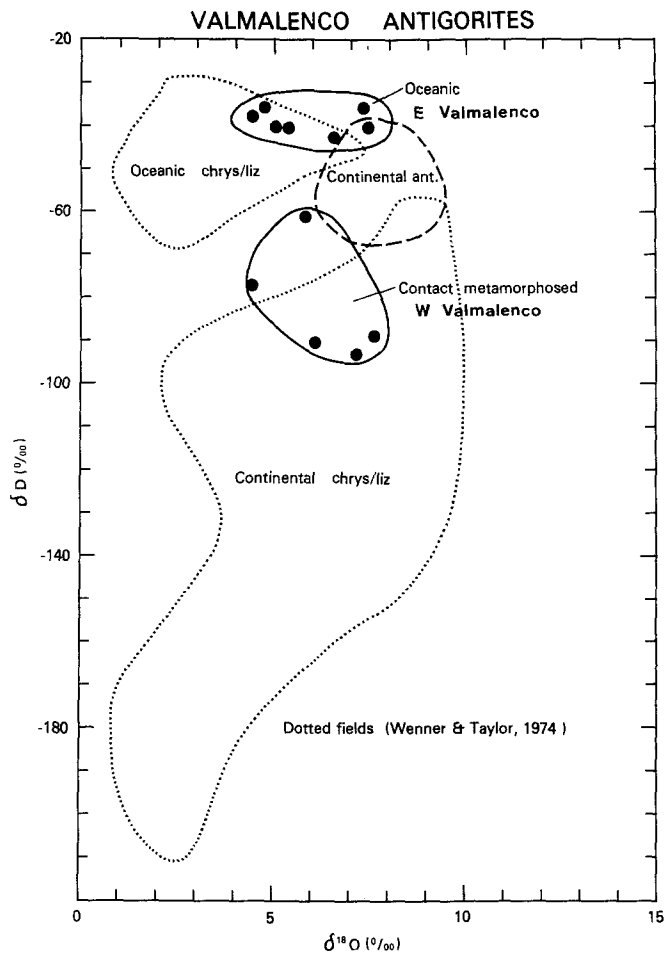


Fig. 6. Isotopic composition of the Valmalenco antigorite comparing groupings in the E and W Valmalenco

$\delta^{18}\text{O}$ values occur in both the east and west Valmalenco whereas δD values in the west Valmalenco are much lower than in the east, at -93 to -60‰ (Fig. 6). The boundary between east and west is probably NNW-SSE oriented and passes about 4 km west of Chiesa (corresponds to locality 19 in Fig. 1). If the isotopic data of the east Valmalenco are interpreted in terms of the serpentine-water fractionation of Sakai and Tsutsumi (1978), ocean water need not be necessarily the only fluid present during serpentinization but an additional minor component of meteoric water is possible. However, since these authors restricted their investigation to hydrogen isotopes, the results must be considered carefully. The presence of several antigorite generations in the Valmalenco is reflected very likely in the span of data in the east Valmalenco. Any alternative, such as a serpentinization in the presence of fluids with a dominant component of other than seawater, or a later exchange of serpentine minerals with other fluids, faces the problem that low $\delta^{18}\text{O}$ values of less than 6‰ must be explained. Because of a preserved pre-alpine foliation the main serpentinization process should have occurred pre-orogenically, and must have been accompanied by tectonization. Alpine metamorphism probably caused recrystallization and formation of younger mineral generations. A serpentinization during regional metamorphism with trapped ocean water fluids as described for example for the Monte Rosa granite (Frey et al. 1976) or for micas in the Trois Seigneurs Massif, Pyrenees, (Wickam and Taylor, 1985) is very unlikely for peri-

dotites. Two alternatives may be considered for the Valmalenco serpentinite:

(1) If the isotopic composition of serpentine minerals are retained during later geological events, serpentinization of the previous Valmalenco peridotite can be assumed to have occurred either, (a) retrograde, directly to antigorite for reasons which mainly concern the relatively high degree of mineral equilibration compared to the adjacent serpentinites of the Arosa-Platta nappe (Burkhard 1987), or, (b) prograde, from precursor chrys/liz, as suggested by Mellini et al. (1987). One may assume that the transformation to antigorite occurred pre-alpine, again because of the preserved pre-alpine foliation, and that the isotopic composition of the precursor chrys/liz were essentially retained. In case (a), the $\delta^{18}\text{O}$ - δD relation (Figs. 2 and 6) describes a new field for oceanic antigorite found on the continent; in case (b), the data field may belong to Wenner and Taylor's field for "oceanic chrys/liz".

(2) If the serpentine minerals undergo isotopic exchange with fluids during post-formational geologic events we may assume either low W/R ratios during regional metamorphism which makes this case ultimately indistinguishable from (1), or, that the antigorite data are part of an extended field for "continental antigorite" in Wenner and Taylor's presentation which means a metamorphic-magmatic isotopic signature. Major difficulties regarding an explanation of the low $\delta^{18}\text{O}$ values were mentioned above.

Sample P. d'Ur 1 from the east Valmalenco (Pass d'Ur) comes from the tectonic boundary to Pennine meta-sediments (Margna nappe). This rock has the characteristic metasomatic mineral paragenesis of this locality and contains actinolite (tremolite), carbonate, some diopside and only small amounts of antigorite. Amphibole is the dominant hydrous phase and it has a high δD value of -36‰ like the antigorite from the east Valmalenco. Thus, the metasomatic event probably also took place in the presence of ocean water. There is every reason to assume that metasomatism and serpentinization took place concurrently in the presence of the same fluid. Consequently, peridotite and sediment were already in contact very early in their history, probably before orogeny and related regional metamorphism.

There are two possible explanations for the contrast between the high δD values in the east and the low δD values in the west Valmalenco: (1) the different isotopic compositions of serpentine are primary (2) an originally uniform serpentinite composition was altered in the west to the now lower δD values by a later overprinting event related to the Bergell intrusion. Possibility (1) would separate the east from the west Valmalenco by a decisively different primary alteration history, in the east with oceanic water and in the west with metamorphic (+ meteoric) water. This also implies a severely different geologic history. It is, however, remarkable that the unusually low $\delta^{18}\text{O}$ values, characteristic of oceanic serpentine, also occur in the west. There is so much oxygen in hydrous minerals relative to hydrogen that during incomplete exchange reactions with water the hydrogen isotope composition of the mineral can change substantially while the oxygen isotope ratio is effectively buffered and remains nearly the same. So, the oxygen isotope data of the Valmalenco provide strong evidence that the entire Valmalenco serpentinite was a homogeneous body of oceanic serpentinite prior to the intrusion of the Bergell granodiorite.

Table 3. Stable isotope compositions of carbonate occurrences in serpentinites of the Arosa-Platta nappe and the Valmalenco

Sample field	Region	Swiss Coordinates	Sample description	$\delta^{13}\text{C}$ (PDB)	$\delta^{18}\text{O}$ (SMOW)
Sch. B. 1	Oberhalbstein Arosa-Platta	bolder, near Bivio	ophicarb., A, mt, sulf.	1.22	12.44
Lungh 14	Engadin Arosa-Platta	771.00/142.42	A, cpx, felt-like, (carb)	0.3	15.66
Grev. 6	Engadin Arosa-Platta	776.20/144.23	A, L, (carb)	2.59	15.60
Selva 1	East Valmalenco	800.50/130.70	A-schist, (diop), carb	2.47	15.17
P. d'Ur 1	East Valmalenco	797.23/131.45	A. act, (carb)	1.11	13.07
Fr. 1	East Valmalenco	790.20/129.10	A, diop, (carb)	2.76	14.85
Str. Fr.	East Valmalenco	789.50/128.50		3.32	12.99
Prim 8	East Valmalenco	784.31/126.00	A, carb	-2.37	11.61
Prim 9	East Valmalenco	784.31/126.00	A, carb	0.81	12.84
Prim 10	East Valmalenco	784.31/126.00	tc, carb	0.46	13.46
Lagh 4	West Valmalenco	781.80/127.00	A, diop, (carb)	1.31	13.86
V. Mas 6	West Valmalenco	773.60/122.80	A, diop-r	-2.37	10.31

Description. *Ophicarb.*: ophicarbonite; *mt*: magnetite; *L*: lizardite; *A*: antigorite; *cpx*: clinopyroxene; *diop*: diopside; *diop-r.*: diopside relicts; *ol*: olivine; *act*: actinolite; *tc*: talc; *carb*: carbonate; *sulf*: sulfide

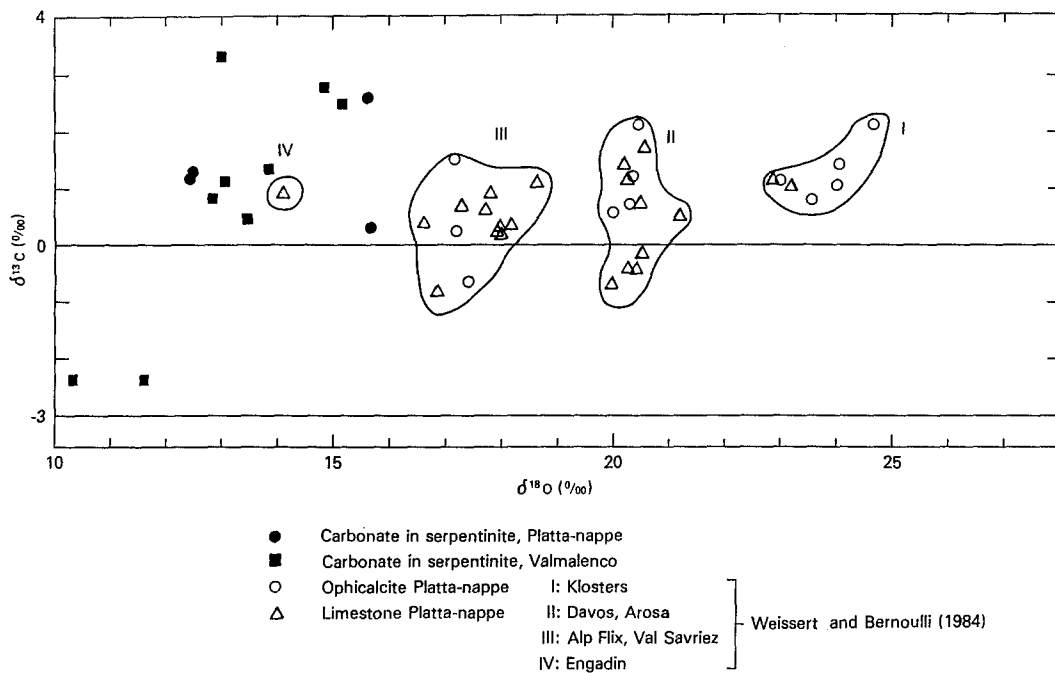


Fig. 7. $\delta^{18}\text{O}$ vs $\delta^{13}\text{C}$ of tiny amounts of carbonate in serpentinite of the Arosa-Platta nappe and the Valmalenco compared to data of opicalcite and limestone in Weissert and Bernoulli (1984)

The δD value of a single sample of the Bergell granite is -78‰ . Any water released from this crystallizing magma would have had a δD value that was higher than -78‰ because water vapor is richer in deuterium than water ($-\text{OH}$) in the melt (compare for example Taylor and Shepard, 1986). The low δD values of the intruded west Valmalenco serpentinites are very likely the result of an overprint by fluids related to the granitic intrusion and subsequent meteoric fluids. During the contact metamorphism of the west Valmalenco, water released in dehydration reactions of serpentine (antigorite + diopside = forsterite + tremolite + water, and antigorite = forsterite + talc + water, for example in Trommsdorff 1983a, b) should have been enriched in D relative to its source leaving antigorite with lowered D contents (Rumble 1982; Ikin and Harmon 1983). However, there is no obvious relation between D/H ratios and

the metamorphic mineral paragenesis, or the proximity to the Bergell intrusion.

These effects readily explain the retention of the original low $\delta^{18}\text{O}$ values and the lowering of δD values in the west Valmalenco.

Carbonates

Although serpentinites were collected only outside ophicarbonite zones in both the Arosa-Platta nappe and the Valmalenco occurrences, occasionally tiny amounts of carbonate (calcite) are observed under the microscope. In favorable cases it was possible to analyze whole rock samples for the carbon and oxygen isotope composition of the carbonate with the standard H_3PO_4 method. The results of these analyses are given in Table 3 and presented in Fig. 7.

The $\delta^{13}\text{C}$ values near zero (0.3–2.6‰ PDB for the Oberhalbstein and Oberengadin; –3.3 to –2.2‰ PDB for the Valmalenco) suggest a marine origin for all the carbon. Such carbonate was probably formed from fluids that derived CO_2 from adjacent carbonate-bearing sediments and limestone. Calcium could have been derived from clinopyroxene or brought in with the fluids. The oxygen isotope ratios of these sediments correlate well with the increasing grade of metamorphism (Weissert and Bernoulli 1984). The $\delta^{18}\text{O}$ values of the tiny amounts of carbonate in the serpentinites (12.4–15.6‰ in the Oberhalbstein and Oberengadin; 10.3–14.9‰ in the Valmalenco) unfortunately are not systematic and only roughly correlate with metamorphic grade. It was originally hoped that coexisting carbonate and serpentine could be used for oxygen isotope thermometry. Combining these results with those obtained from serpentine, one may conclude that the carbonates formed in the presence of metamorphic fluids (in the Arosa-Platta nappe) and ocean water (in the Valmalenco). This process either took place at various times, during and after the metamorphism (for example as tiny late vein fillings), or the carbonate oxygen did not completely equilibrate with the metamorphic fluid. Thus the inhomogeneous stable isotope compositions of the carbonates are not very informative.

Conclusions

Stable isotope compositions of serpentines from two adjacent serpentinitized ultramafic occurrences from the Arosa-Platta nappe and the Valmalenco are different and correlate with geologic and mineralogic differences.

In the Arosa-Platta nappe the degree of serpentinization correlates with the grade of metamorphism. The hydrogen isotope compositions of serpentine indicate that meteoric water was a dominant component of the serpentinizing fluids in the lower grade serpentinites to the north whereas metamorphic waters (and in places also meteoric water) were dominant elsewhere. Also, at nearby nappe boundaries, serpentinization is related to the regional metamorphic event as indicated by the δD values, but higher $\delta^{18}\text{O}$ values at these locations suggest that water/rock ratios were higher there.

High δD values of near –40‰ and $\delta^{18}\text{O}$ values as low as 4.0 in the east Valmalenco suggest that serpentinization of the precursor peridotite occurred predominantly in the presence of ocean water. In the west Valmalenco low $\delta^{18}\text{O}$ values are probably preserved from an original serpentinization in ocean water and the δD values were lowered by incomplete exchange reactions with fluids that exsolved from the Bergell intrusions. During the evolution of these fluids a component of meteoric water was added. In all cases the isotopic ratios suggest a limited water/rock ratio.

For the first time continental antigorite with an ocean water isotopic signature has been identified. The high $\delta^{18}\text{O}$ value of 13.0‰ measured for a sample of chrys/liz is rare and provides additional important support for the concept of low-temperature serpentinization.

Because sufficient data on the rates of isotopic exchange between serpentine and water fractionation are not available, we do not know to what extent existing isotopic compositions reflect the original serpentinization event. It is possible that, during regional metamorphism in the Arosa-Platta nappe, recrystallization of serpentine occurred at suf-

ficiently high water/rock ratios in fluids sufficiently far removed from hydrogen and/or oxygen isotope equilibrium and that the original isotopic composition was altered. We are invoking such a process to explain the isotopic relations in the west Valmalenco. However, high δD values of serpentine preserved only in the east Valmalenco have to be interpreted dominantly as an ocean water serpentinization accompanied or followed by conditions which allowed a high degree of mineral equilibration. Different generations of minerals appear to be related to regional metamorphism. One may ask why occurrences with such high δD values are not more common. In any case, the very different character of the adjacent Engadin region, mineralogically and isotopically, imply severe differences with respect to the geologic/tectonic evolution of the two areas in the alpine collision belt.

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