

## Titanian Hydroxyl-Clinohumite: Formation and Breakdown in Antigorite Rocks (Malenco, Italy)

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**Abstract.** Petrographic evidence is presented for the breakdown of titanian hydroxyl-clinohumite to olivine + magnesian ilmenite (or geikielite) ± magnetite in the outermost zone of the Bergell aureole in the Malenco Serpentinite, Prov. Sondrio, Italy. The breakdown coincides in the field with the isograd reaction: antigorite + diopside = olivine + tremolite + H<sub>2</sub>O. It is therefore concluded that this variety of clinohumite is unstable above approximately 520° C at a pressure of 3 kbars. Elsewhere in the Malenco Serpentinite, titanian hydroxyl-clinohumite may be found to have reacted with CO<sub>2</sub> to produce antigorite, magnesian ilmenite and magnesite. Titanian hydroxyl-chondrodite was detected in one sample. Under crustal pressures, the stability field of *F*-free clinohumite is entirely contained inside that of antigorite. The stable occurrence of titanian clinohumite in high-grade metamorphic ultrabasic rocks may be attributed to the substitution of *F* for OH.

### I. Introduction

Titanian hydroxyl-clinohumite, hereafter abbreviated to Ti-Cl, can be represented by the formula  $M_8Si_4O_{16}M_{1-x}Ti_x(OH)_{2-2x}O_{2x}$ , where *M* is Mg, Fe<sup>2+</sup>, Mn and Ni, and *x* has values up to 0.5 (Jones et al. 1969; Fujino and Takeuchi 1978; Ribbe 1979). The mineral has been known for many decades as a vein and accessory rock-forming mineral in antigorite serpentinites of the Pennine Nappes in the Western, Central and Eastern Alps (Damour 1879; Brugnattelli 1904; Carpanese 1933; de Quervain 1938; Bearth 1967; Möckel 1969). The large serpentinite mass of Val Malenco (Fig. 1) in particular has provided some of the finest Ti-Cl for museums and mineralogical studies. In the vicinity of the Bergell Tonalite, the Malenco Serpentinite has undergone progressive contact metamorphism and been converted to a sequence of assemblages involving olivine, tremolite, talc, anthophyllite, cummingtonite, and enstatite (Trommsdorff and Evans 1972). Although not

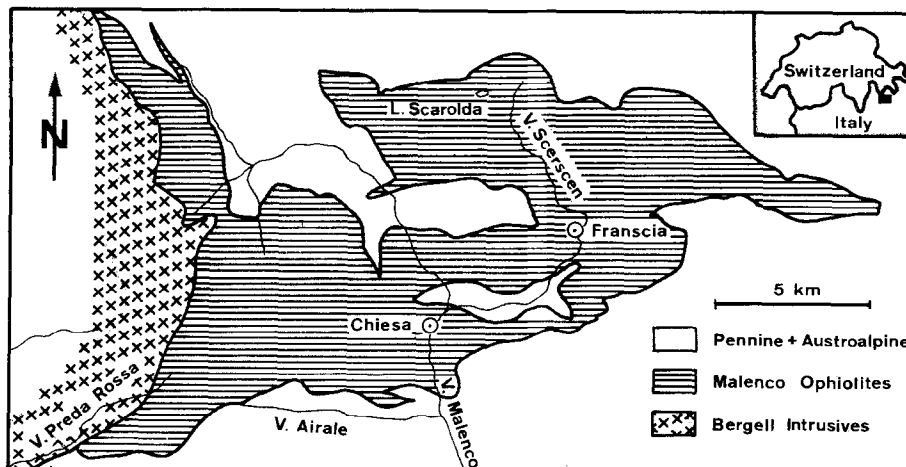


Fig. 1. Outline map of geology of Val Malenco

reported explicitly in the 1972 paper, it was noticed at that time that the easily identified megascopic red Ti-Cl appeared not to persist into the aureole. More recent, detailed mapping has confirmed this observation (Engi 1973; Mercolli 1973; Schumacher 1975; Riklin 1977). Close examination of the aureole rocks in 1977 revealed the presence of distinctive breakdown products of Ti-Cl (Evans and Trommsdorff 1978). In this paper, we explain the non-occurrence of Ti-Cl in the Bergell aureole as due to its breakdown to olivine, magnesian ilmenite and H<sub>2</sub>O, under conditions slightly cooler than those of antigorite breakdown on its own composition. Petrographic evidence for additional Ti-Cl breakdown reactions is also presented, and the probable relations among some of them in the  $T$ - $X_{\text{CO}_2}$  plane are figured.

The conclusions with regard to the stability of titanian hydroxyl-clinohumite are then reviewed in the context of occurrences of titanian clinohumite in high-grade regionally metamorphosed ultrabasic rocks and in ultrabasic xenoliths in kimberlites.

## II. Significance of Titanian Hydroxyl-Clinohumite

Humite minerals occur most typically in metamorphosed silica-poor limestones and dolomites. Another important mode of occurrence is in ultrabasic rocks, where clinohumite, characteristically titaniferous and frequently free of fluorine, is easily the commonest of the humite minerals.

Until recently, no great significance was attached to the occurrence of Ti-Cl in ultrabasic rocks. In 1970, McGetchin and Silver, and McGetchin et al. (1970) reported on an inclusion of titanian hydroxyl-clinohumite in a pyrope-rich garnet occurring as a fragment in the kimberlitic diatreme of Moses Rock on the Colorado Plateau. This mode of occurrence was interpreted as implying the formation of clinohumite along with the minerals of garnet lherzolite under  $P$ - $T$  conditions corresponding to depths of 50 to 150 km in the upper mantle. Despite its apparent rarity in kimberlite diatremes, clinohumite possesses significance by virtue of its potential role as a source of H<sub>2</sub>O for promoting partial melting in the mantle (McGetchin et al. 1970).

Titanian hydroxyl-clinohumite is now known from three localities on the Colorado Plateau: Buell Park (Allen and Balk 1954; Aoki et al. 1976), Moses Rock (McGetchin and Silver 1970), and Green Knobs (Smith and Levy 1976; Smith 1979). At Buell Park, it has been found along with titanian hydroxyl-chondrodite (Aoki et al. 1976). Ti-Cl is also known from Siberian kimberlite (Shchelkova and Brovkin 1969).

The significance of clinohumite as a mantle phase,

possibly forming in a downgoing lithospheric slab (Ringwood 1976), has been emphasized by recent high pressure experiments in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O (Yamamoto and Akimoto 1977). Yamamoto and Akimoto outlined a synthesis field for hydroxyl-clinohumite in the region 800°-1100° C from 29 to 77 kbars. In reconnaissance experiments on natural titanian clinohumite, Merrill et al. (1972) found breakdown temperatures of 1,100° C to 1,200° C between 10 and 30 kbars. They were unable to reverse the reaction however, and had difficulty in fully identifying the breakdown products and hence the specific reaction involved. As starting material, they used a clinohumite containing 2.37 wt.%  $F$ .

Many of the above observations would appear to be in serious conflict with our conclusion based on field study that natural Ti-Cl reaches its limit of stability close to the breakdown temperature of antigorite (Evans and Trommsdorff 1978). Aside from questions of experimental procedure, it is reasonable to suppose that the substitutions of  $F$  for OH, Ti for H<sub>2</sub>Mg, and Fe for Mg in clinohumite contribute significantly to the discrepancies. These are the subject of some recent experimental work (Duffy and Greenwood 1979; Engi and Lindsley 1979). In this paper we review the field and petrographic evidence that constrain the limits of stability of titanian hydroxyl-clinohumite in the crust.

## III. Clinohumite in the Malenco Serpentinite

The Malenco Serpentinite is a schistose antigorite-rich rock that equilibrated under high Greenschist Facies conditions (Trommsdorff and Evans 1972; Beltrami et al. 1975). Its overall chemistry is lherzolitic. Most of the metamorphic minerals in the serpentinite occur in more than one generation. The generations are distinctive in terms of grain size, growth in relation to deformation, and mineral orientation. The Greenschist Facies assemblage of minerals occurs as megacrysts in synkinematic veins as well as in the generally medium-grained serpentinite.

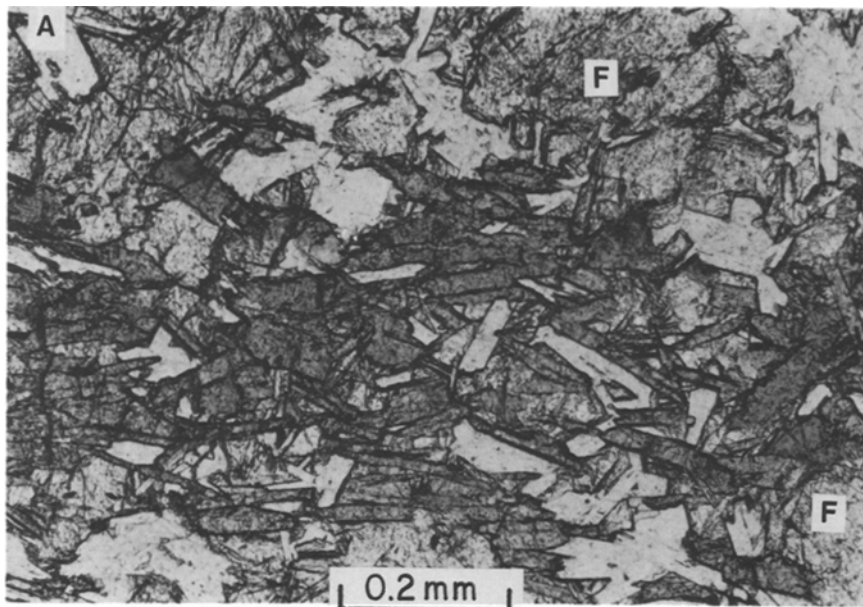
Although primary lithological layering is locally well preserved (for example, in Val Airale and Val Preda Rossa, Fig. 1), the only pre-metamorphic mineral relic is a dusty clinopyroxene that locally still contains appreciable Al and Na (Peters 1968). The main-stage regional metamorphic minerals are antigorite, olivine, diopside, chlorite, magnetite, Ti-Cl, and pentlandite. In more SiO<sub>2</sub>-rich parts of the Serpentinite, tremolite or talc occur as mainstage minerals, in the absence of olivine and diopside + olivine respectively. There is no evidence to indicate that either olivine or Ti-Cl are anything but metamorphic in origin. The earliest generations of metamorphic minerals are megacrystic

and chemically indistinguishable from later ones. Olivine megacrysts possess mild undulatory extinction and only rarely exhibit kink banding; olivine and Ti–Cl megacrysts both overgrow deformed metamorphic diopside prisms.

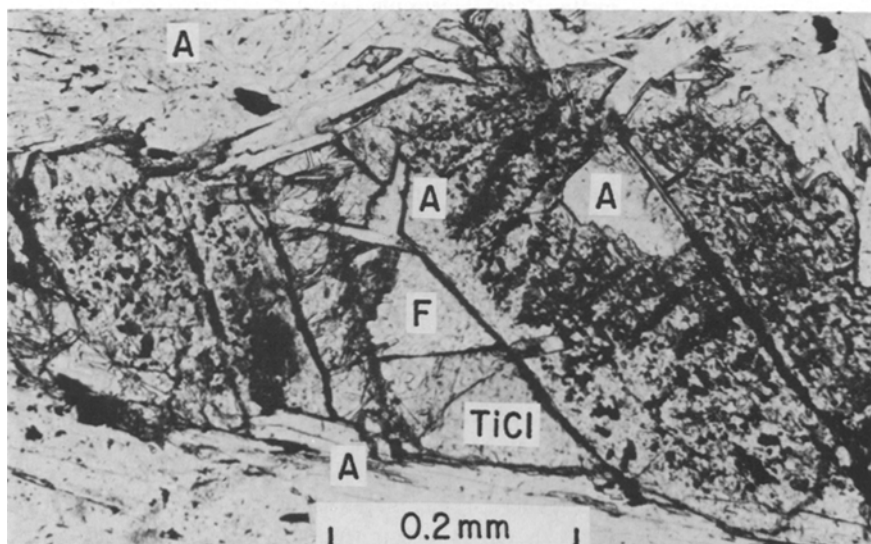
Antigorite, olivine, Ti–Cl, diopside, chlorite, and magnetite all occur in at least two metamorphic generations, one pre-dating and the other post-dating the main deformation. The early generation not uncommonly occurs as augen in pre- to synkinematic veins (e.g., de Quervain 1938; Fig. 1). Ti–Cl is most conspicuous in these veins, as patchily distributed reddish-brown crystals up to 10 cm in length. The younger generation of these minerals forms a clean schistose mosaic fabric, with platy antigorite, prismatic

or needle-shaped diopside, granular olivine, and idiomorphic (Fig. 2) or granular Ti–Cl. These minerals and chlorite also occupy the extension cracks in old pulled-apart clinopyroxenes (Fig. 3), or pressure shadows in microfold hinges. Diopside needles grew homoaxially on pre-existing clinopyroxene (Trommsdorff and Evans 1974; Plate IA) and along a secondary axial plane schistosity. Additional minerals occurring less frequently are carbonates (Trommsdorff and Evans 1977) and hydroxyl-apatite<sup>1</sup> (in mosaic-textured aggregates associated with Ti–Cl veins). Of generally late formation are brucite and perovskite

<sup>1</sup> Microprobe analysis, wt.%, SiO<sub>2</sub> 0.15, CaO 55.2, P<sub>2</sub>O<sub>5</sub> 42.1, F ≤ 0.05, Cl ≤ 0.01, H<sub>2</sub>O calculated 1.8, total 99.25



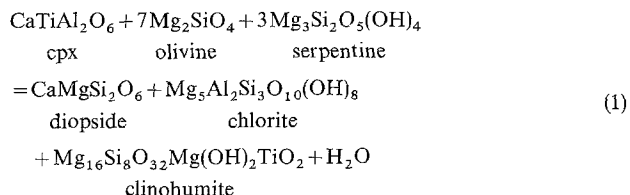
**Fig. 2.** Photomicrograph (PPL) of Malenco Serpentinite, Sample 178, showing idioblastic Ti–Cl, antigorite (*A*), olivine (*F*), and chlorite (idioblastic flakes)



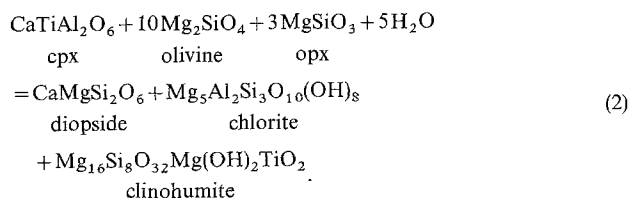
**Fig. 3.** Photomicrograph (PPL) of Malenco Serpentinite, Sample 56, showing growth of Ti–Cl and olivine (*F*) in pressure shadow of micro-boudinaged clinopyroxene crystal. Matrix of antigorite (*A*)

(in rock and veins), awaruite (de Quervain 1945, 1963), chrysotile and andradite (in veins, e.g., Amthauer et al. 1974).

Thus, Ti–Cl is unquestionably a member of the metamorphic paragenesis: antigorite + olivine + diopside + chlorite + magnetite. Its formation in the Malenco Serpentinite can be related to the breakdown of the pre-metamorphic, compositionally complex clinopyroxene. For example, Ti–Cl always occurs in rocks containing metamorphic diopside and chlorite, the typical breakdown products of the old clinopyroxene. It seems best developed in fact in association with folded mats of monomineralic acicular diopside (as also in the Zermatt Serpentinite, Bearth 1967), which no doubt represent former pyroxenite layers. It may also be observed to have grown around the edges (or within extension cracks) of former clinopyroxene crystals. These observations suggest that Ti–Cl probably formed at the expense of the  $\text{CaTiAl}_2\text{O}_6$  component of the original clinopyroxene. This can be described by the metastable dehydration reaction:



or by the metastable hydration reaction:



It is not known if the Ti–Cl formed at the expense of serpentine (1) by prograde metamorphism or from a lherzolite assemblage (2) by retrograde metamorphism.

Reactions (1) and (2) clearly do not represent stable relationships. Within the Malenco body, however, there is evidence for at least two probably stable reactions that limit the occurrence of Ti–Cl in the presence of  $\text{H}_2\text{O}-\text{CO}_2$  fluid. These reactions take place within the stability field of the serpentinite paragenesis: antigorite + diopside + chlorite + magnetite. The best documented reaction is the one limiting the stability field of Ti–Cl with increasing temperature. It takes place at the edge of the Bergell Tonalite contact aureole.

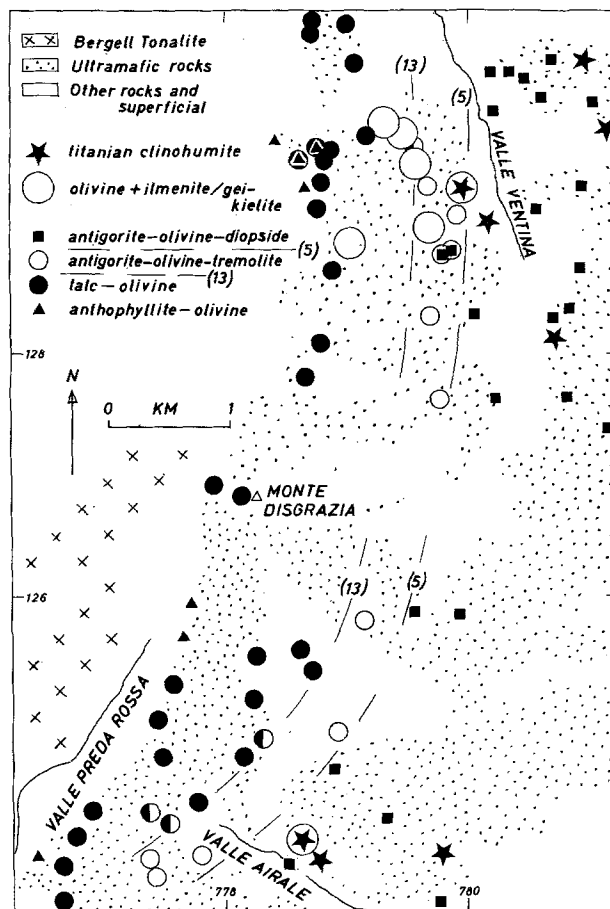
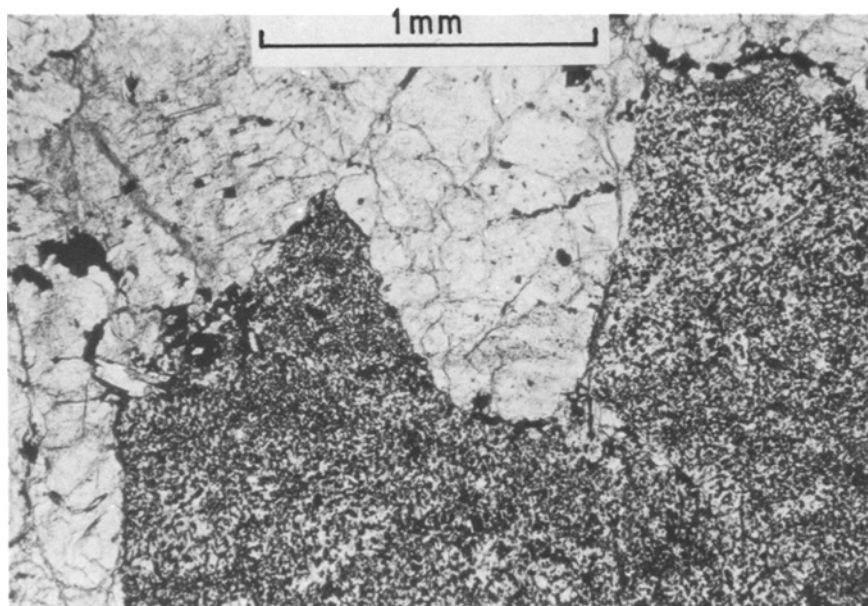


Fig. 4. Contact aureole of Bergell Tonalite in Malenco Serpentinite. Shows distribution of Ti–Cl and olivine + magnesian ilmenite pseudomorphs in relation to critical ultrabasic parageneses and isograds: (5) represents the first occurrence of tremolite + olivine, (13) the first occurrence of talc + olivine

#### IV. Breakdown of Titanian Hydroxyl-Clinohumite in the Bergell Aureole

Within the aureole of the Bergell Tonalite, the older regional metamorphic serpentinite assemblages are successively replaced by new contact metamorphic minerals (Trommsdorff and Evans 1972). The index assemblages of the different zones approaching the intrusive (Fig. 4) are: (a) tremolite + antigorite + olivine, (b) tremolite + talc + olivine, (c) tremolite + anthophyllite + olivine, and (d) tremolite + enstatite + olivine. Already within the outermost zone of the aureole [(a) above], the Ti–Cl megacrysts are found to have been nearly completely replaced by black-weathering pseudomorphs of olivine. This black olivine occurs alongside the normal brown-weathering olivine megacrysts, which survive in the aureole. The cause of the black color is seen in thin section to be a dense precipitate of tiny ilmenite granules.



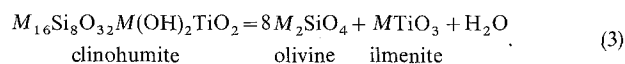
**Fig. 5.** Photomicrograph (PPL) of sample 294B from Bergell aureole showing clear olivine in knife-sharp contact with Ti-Cl pseudomorph (olivine + opaque magnesian ilmenite)

The fibrous regional metamorphic diopside characteristic of the Ti-Cl veins has given way to tremolite in these rocks. 'Two-olivine' rocks can then be observed in upgraded veins throughout the inner aureole.

In such rocks, clear olivine grains occur among olivines choked with 10  $\mu\text{m}$  granular inclusions of magnesian ilmenite. In many instances, clear and dusty olivines are in perfect optical continuity, the boundary between them knife-sharp (Fig. 5). This is a reflection no doubt of the previous oriented intergrowth of olivine and clinohumite (Brugnatelli 1904; Carpanese 1933; Tilley 1951). Small shapeless relics of pleochroic brown Ti-Cl within the dusty olivine leave no room for doubt that the inclusion-filled olivines are pseudomorphs after Ti-Cl. Although generally shapeless, the ilmenite grains are consistently oriented with their basal plane parallel to (100) of the host olivine. In this orientation, a plane of close-packed oxygens is shared. Thus both olivine and ilmenite grew topotactically at the expense of Ti-Cl. Similar pseudomorphs in the garnet lherzolite of Arami were figured by Möckel (1969).

The chemical composition of Malenco Ti-Cl is given approximately by the formula  $M_{16}\text{Si}_8\text{O}_{32}M(\text{OH})_2\text{TiO}_2$ , where  $M$  includes Mg, Fe, Mn and Ni (Brugnatelli 1904; de Quervain 1938; Jones et al. 1969; Table 1, this paper). Titanium tends to fall short of 1 atom per 26 total cations, a feature which seems to become accentuated in the more Mg-rich samples (Fig. 6). Fluorine has so far not been detected by microprobe (i.e., <0.05 wt.%) in Malenco Ti-Cl, indicating that the decline in Ti is not accompanied

by an increase in  $F$ , as it is in some clinohumites (Rice 1972). A first approximation of the thermal breakdown of Ti-Cl in the Bergell aureole may therefore be represented by:



This equation corresponds to a system of three components. The minerals are coplanar in the anhydrous system  $\text{MgO}-\text{FeO}-\text{TiO}_2-\text{SiO}_2$  only when the Ti-Cl has the Ti: $M$  ratio given.

If the mass balance (3) is a true representation of the Ti-Cl breakdown reaction, then certain volumetric and chemical relations among the two breakdown products, the original Ti-Cl, and the coexisting (clear) olivine should hold.

For example, the relative volumes of magnesian ilmenite and olivine in a typical pseudomorph should be 8.2% and 91.8% respectively. Careful measurements with a Cambridge automated image analyzer on a 18  $\times$  24 cm reflected light enlargement of a pseudomorph from 294 B (Table 2) gave: ilmenite 7.3%, olivine 92.7% ( $\sigma=0.7\%$ ).

The actual compositions of ilmenite and pseudomorph olivine, when combined in stoichiometric proportions, should produce a reasonable Ti-Cl formula. This has been tested for specimen 294B, from the antigorite+tremolite+olivine zone in the Bergell aureole, and the result compares favorably with a Malenco Ti-Cl analysis taken from the literature (Table 2). This specimen did not contain any residual Ti-Cl.

**Table 1.** Analyses of Malenco titanian clinohumites

Wt. %	1	2	3	4	5	6	7	8	9	10	11
SiO <sub>2</sub>	36.86	36.24	35.9	35.8	35.4	36.3	35.7	36.0	37.0	36.8	37.1
TiO <sub>2</sub>	4.78	5.20	5.59	5.27	5.25	4.95	5.23	5.36	4.24	4.82	4.89
Al <sub>2</sub> O <sub>3</sub>		0.37									
FeO <sup>1</sup>	11.02	10.42	11.21	14.1	14.6	10.8	12.0	11.9	7.13	8.6	7.23
MgO	45.50	46.05	44.2	42.6	42.6	46.5	44.5	44.7	49.2	46.7	48.2
MnO	tr	0.30	0.50	0.67	0.62	0.37	0.34	0.57	0.60	0.52	0.53
NiO										0.15	0.14
H <sub>2</sub> O <sup>2</sup>	1.63	1.55	1.41	1.48	1.48	1.62	1.51	1.49	1.81	1.63	1.65
	99.79	100.13	98.82	99.92	99.95	100.54	99.28	100.02	99.98	99.22	99.74

Formulae based on Si + Ti + M cations = 13

Si	4.078	3.986	4.030	4.025	3.982	3.977	3.991	3.997	4.009	4.058	4.045
Ti	0.398	0.430	0.472	0.446	0.444	0.407	0.439	0.447	0.345	0.400	0.401
Al		0.048									
Fe	1.020	0.958	1.053	1.326	1.373	0.989	1.123	1.105	0.646	0.794	0.659
Mg	7.504	7.550	7.396	7.139	7.142	7.593	7.415	7.397	7.945	7.686	7.834
Mn		0.028	0.048	0.064	0.059	0.034	0.032	0.053	0.055	0.049	0.049
Ni										0.013	0.012
H	1.204	1.140	1.056	1.108	1.112	1.186	1.122	1.106	1.310	1.200	1.198

<sup>1</sup> Total iron<sup>2</sup> Calculated from H=2-2Ti cations1: Chiesa (Brugnatelli 1904), FeO=10.05, Fe<sub>2</sub>O<sub>3</sub>=1.08  
H<sub>2</sub>O=1.572: Alpe Canciano, Poschiavo (de Quervain 1938), FeO=6.20,  
Fe<sub>2</sub>O<sub>3</sub>=4.69, H<sub>2</sub>O=1.233: Franschia (Jones et al. 1969), Jones' sample 10  
(=Smithsonian 94997); total includes 0.01% CaO

4: Chiesa, megacryst Ti-Cl, U.C. Berkeley Coll. 884.28A

5: Chiesa, rock Ti-Cl, U.C. Berkeley Coll. 884-28B

6: 47C, S of Franschia, Swiss Coords. 790.55/129.2

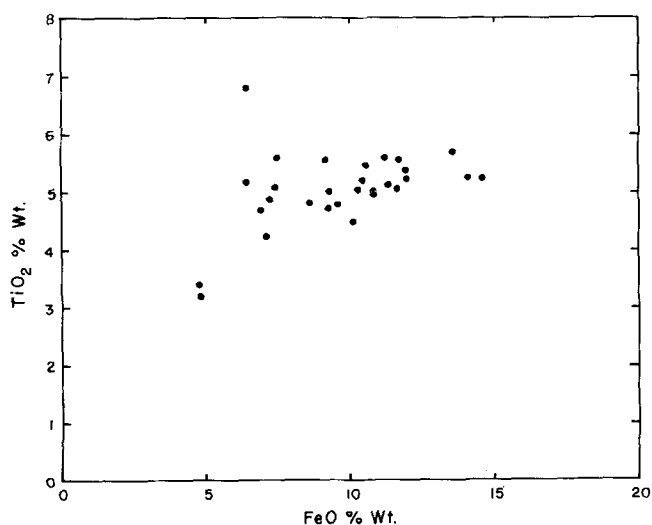
7: 46B, Lanzada, 789.35/128.55

8: 56, Val Poschiavina, 794.0/132.8, see also Fig. 3

9: 295B, Val Ventina, 780.2/129.2, see also Table 3

10: 308F, Val Airale, 778.65/123.85, see also Table 4

11: 308F, Val Airale, 778.65/123.85, partially reacted crystal



**Fig. 6.** TiO<sub>2</sub> relative to FeO in analyzed titanian hydroxyl-clinohumites. Data from this study and Brugnatelli (1904), de Quervain (1938), Jones et al. (1969), McGetchin et al. (1970), Aoki et al. (1976), Fujino and Takeuchi (1978), and Smith (1979). Point at 6.8% TiO<sub>2</sub> (inclusion in pyrope) may be in error since normal Ti limit (0.5 Ti per 13 cations) is exceeded

A mass balance was also attempted on two specimens of diopside-antigorite-olivine rocks containing relict Ti-Cl and breakdown products (Tables 3 and 4). The results were not entirely satisfactory because, for reasons that may not be purely coincidental, TiO<sub>2</sub> was low (and Mg/Fe high) in both Ti-Cl as compared to typical Malenco Ti-Cl. In specimen 308F, it was noticed that unreacted Ti-Cl crystals possessed higher Fe/Mg than the partially reacted Ti-Cl, and that the former gave a much better mass balance for Fe and Mg than the latter (Table 4). This suggests that the breakdown reaction is accompanied by progressive enrichment in Mg/Fe of the reactant phase, and presumably also of the product phases. The Mg/Fe ratio of ilmenite in the pseudomorphs was found to be variable from grain to grain but homogeneous within grains. The presence of 1 to 2 vol.% magnetite in the pseudomorphs may be the explanation for the poor mass balance for Ti. Unfortunately, the inclusion of magnetite in the mass balance worsens the otherwise excellent Mg and Fe balance (Table 4), and possibly adds a dependency on  $f_{O_2}$  for reaction (3). No fluorine, at the 0.05%

**Table 2.** Comparison of pseudomorph (sample 294B) with literature analysis of Malenco Ti-Cl

Wt. %	Clear olivine	Pseudomorph olivine	Ilmenite	4 olivine + 1/2 ilmenite	TiCl <sup>1</sup>	Magnetite
SiO <sub>2</sub>	40.9	41.2			35.9	
TiO <sub>2</sub>			52.2		5.59	0.37
Cr <sub>2</sub> O <sub>3</sub>			0.00			0.04
Fe <sub>2</sub> O <sub>3</sub> calc			4.94			68.0
FeO <sup>2</sup>	9.93	7.84	29.53		11.21	30.6
MgO	48.9	50.6	8.45		44.2	0.83
NiO	0.24	0.17	0.06			0.38
MnO	0.49	0.34	2.40		0.5	0.05
CaO	0.02	0.01			0.01	
H <sub>2</sub> O calc					1.41	
	100.48	100.16	97.58		98.82	100.27
Cation normalized						
Si		3.997	0.000	3.997	4.033	
Ti		0.000	0.476	0.476	0.472	
Fe		0.636	0.346	0.982	1.053	
Mg		7.327	0.153	7.480	7.394	
Ni		0.012	0.000	0.012	0.000	
Mn		0.028	0.025	0.053	0.047	
Ca		0.000	0.000	0.000	0.001	
		12.000	1.000	13.000	13.000	

Sample 294B: Pizzo Ventina, Val Malenco, Swiss Coords. 779.2/129.35

<sup>1</sup> Sample No. 10, Franschia, Val Malenco (Jones et al. 1969)<sup>2</sup> Total Fe for olivine and Ti-Cl**Table 3.** Attempted mass balance in Ti-Cl breakdown (sample 295B)

Wt. %	Pseudomorph olivine	Ilmenite	4 olivine + 1/2 ilmenite	Ti-Cl	Magnetite
SiO <sub>2</sub>	41.7			37.1	
TiO <sub>2</sub>		56.0		4.36	0.2
Cr <sub>2</sub> O <sub>3</sub>		0.00			0.10
Fe <sub>2</sub> O <sub>3</sub> calc		6.26			69.4
FeO	5.94	18.16		6.88	28.4
MgO	52.1	16.4		49.2	1.75
NiO	0.09	0.00		0.07	0.07
MnO	0.42	2.95		0.59	0.08
CaO	0.01				
H <sub>2</sub> O calc				1.79	
	100.26	99.77		99.99	100.00
Cation normalized					
Si	4.009		4.009	4.017	
Ti		0.473	0.473	0.355	
Fe	0.476	0.224	0.700	0.623	
Mg	7.471	0.275	7.746	7.945	
Ni	0.008	0.000	0.008	0.006	
Mn	0.036	0.028	0.064	0.054	
	12.000	1.000	13.000	13.000	

Sample 295B: Val Ventina, Val Malenco, Swiss Coords. 780.2/129.2. Analyses on single crystal of Ti-Cl, pseudomorphed on one side

**Table 4.** Attempted mass balance in Ti–Cl breakdown (sample 308 F)

	Pseudomorph olivine	Pseudomorph ilmenite	Pseudomorph magnetite	4 olivine + 1/2 ilmenite	4 olivine +0.45 ilmenite +0.033 magnetite	Ti–Cl (1)	Ti–Cl (2)
SiO <sub>2</sub>	41.7					36.76	37.1
TiO <sub>2</sub>	<sup>a</sup>	54.9	0.57			4.82	4.89
Fe <sub>2</sub> O <sub>3</sub> calc		4.86	68.30				
FeO	6.4	25.83	28.15			8.60	7.23
MgO	51.5	11.1	1.8			46.7	48.2
MnO	0.50	3.66	0.18			0.52	0.53
NiO	0.11	0.07	0.22			0.15	0.14
CaO	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>			<sup>a</sup>	<sup>a</sup>
H <sub>2</sub> O calc						1.63	1.65
	100.21	100.42	99.22			99.18	99.74
Cation normalized							
Si	4.023	0.000	0.0000	4.023	4.023	4.058	4.045
Ti	0.000	0.478	0.0005	0.478	0.432	0.400	0.401
Fe	0.517	0.293	0.0956	0.810	0.876	0.794	0.659
Mg	7.410	0.192	0.0034	7.602	7.586	7.686	7.834
Mn	0.041	0.036	0.0002	0.077	0.074	0.049	0.049
Ni	0.009	0.001	0.0002	0.010	0.010	0.013	0.012
	12.000	1.000	0.1000	13.000	13.000	13.000	13.000

(1) Non-reacted Ti–Cl adjacent to (2); (2) Ti–Cl crystal partially decomposed to olivine + ilmenite + magnetite

<sup>a</sup> Below microprobe detection limit. Sample 308 F: Swiss Coords. 778.65/123.85

level, was detected in the partially reacted clinohumites.

Most samples from the Bergell aureole contained no relict Ti–Cl. The pseudomorph olivines in these rocks should have predictable compositional differences (unless obliterated by subsequent homogenization) from the clear olivines that were formerly in exchange equilibrium with Ti–Cl. Ordinarily, Ti–Cl in exchange equilibrium with olivine has comparable Mn, virtually identical Fe/Mg (Fig. 7), and less Ni. In the products of reaction, Fe and Mn will fractionate strongly into ilmenite and Ni into olivine. Observed compositions agree entirely with these predictions; pseudomorph olivine is typically 2% more forsteritic than clear olivine (Fig. 8), and lower in Ni and Mn (Table 2). Reequilibration has evidently not taken place between these olivines, even where they form parts of one continuous crystal.

The detailed petrographic and geochemical evidence therefore supports our simple model for the breakdown of titanian clinohumite on its own composition. Small amounts of magnetite generally accompany the ilmenite precipitate, and, whereas some magnetite is usually present as inclusions in Ti–Cl before it breaks down, a portion of the magnetite should probably be included among the products of reaction (3). Whether oxygen is added or conserved

in this reaction is not known; sufficient Fe<sup>3+</sup> may be present in the clinohumite. Classical analyses of Ti–Cl (Brugnatelli 1904; Allen and Balk 1954) suggest that typically 10% of the Fe is ferric iron. As long as the ratio Ti:M in the ilmenite is the same as that ratio in the 'brucite' part of the clinohumite formula, and trace magnetite represents the additional component Fe<sup>3+</sup>, reaction (3) will be divariant in the system MgO–FeO–TiO<sub>2</sub>–SiO<sub>2</sub>–H<sub>2</sub>O. Since, in exchange equilibrium, Mg/Fe in clinohumite = Mg/Fe in olivine > Mg/Fe in ilmenite, all phases may be expected to become more Mg-rich during the reaction, and the more Fe-rich clinohumites will break down at lower temperatures. The occurrence of Ti–Cl or its breakdown products at the edge of the aureole is too sporadic to be sensitive to this effect, however.

## V. Occurrence of Magnesian Ilmenite (Geikielite)

The ratio Mg/(Mg+Fe) in Malenco Ti–Cl varies at least over the range 0.93 to 0.83 (Table 1). Despite its strong preference for Fe, the ilmenite that forms through Ti–Cl breakdown is a magnesian variety which extends well into the geikielite range (Mg/Fe > 1), for example, up to 70% Gk in sample 295 B



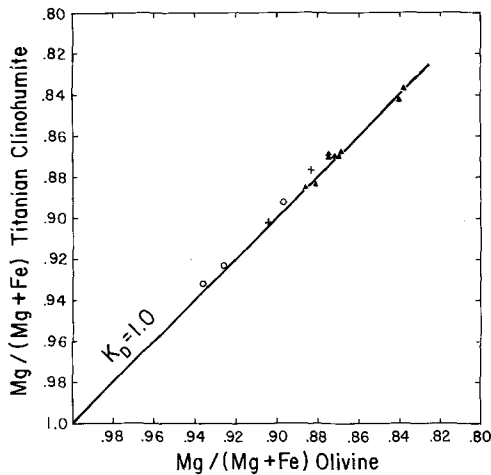


Fig. 7. Partitioning of total iron and Mg between coexisting Ti-Cl and olivine. Circles: McGetchin et al. (1970); crosses: Smith (1979); triangles: Val Malenco, this study

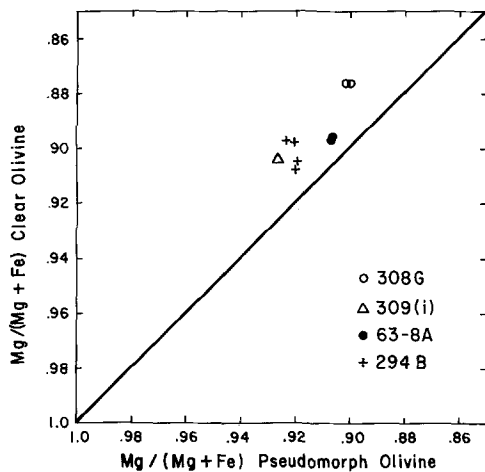
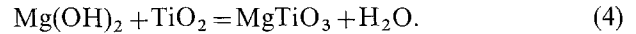


Fig. 8. Comparison of Mg/(Mg + Fe) ratio between clear and adjacent pseudomorph olivines in samples from the Bergell aureole

(Table 3). Geikielite also occurs in kimberlites (Mitchell 1977; Meyer 1977), marbles (Wise 1959; Cook 1974) and carbonatites (Mitchell 1978). All these rocks possess high Mg/Fe ratios and are free of quartz; these factors, rather than any unusual pressures or temperatures, appear adequate to account for the occurrence of geikielite.

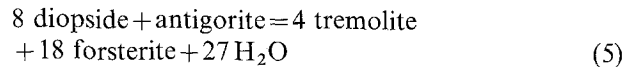
According to data in Robie et al. (1978), geikielite is more stable than periclase + rutile under crustal PT conditions. On the other hand, geikielite + quartz is less stable than both clinoenstatite + rutile and forsterite + rutile. In the presence of an H<sub>2</sub>O-bearing fluid, geikielite will possess a lower temperature limit of stability due to the reaction:



Tabulated data (Robie et al., 1978) indicate the stability of geikielite + H<sub>2</sub>O above 90° C at 1 bar, above 140° C at 5 kbar, and above 203° C at 10 kbar. Obviously, natural iron-bearing geikielite will be relatively more stable. Thus, the occurrence of geikielite in antigoritic rocks is entirely in accord with thermochemical data. Our microprobe data suggest that geikielite (Mg > Fe), as opposed to ilmenite (Fe > Mg) will form from Ti-Cl breakdown when Mg/(Mg + Fe) in the Ti-Cl is greater than about 91%, or when the product olivine has Mg/(Mg + Fe) greater than 93%.

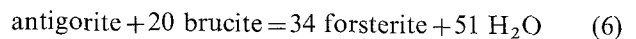
## VI. Stability of Titanian Hydroxyl-Clinohumite

Our observations on the serpentinites of Val Malenco and of the Eastern and Western Alps show that titanian hydroxyl-clinohumite appears to be restricted to rocks showing the paragenesis: diopside + antigorite + olivine (or brucite). The upper temperature limit of Ti-Cl has been located close to the isograd defined by the reaction:



which marks the outer edge of the Bergell aureole (Fig. 4). Conditions estimated for this isograd based on independent phase equilibrium and geochronologic evidence are  $T = 520 \pm 20^\circ \text{C}$  and  $P \approx 3 \text{ kbar}$  (Trommsdorff and Evans 1977) and depth =  $7500 \pm 700 \text{ m}$  (Miller et al. 1979). We can therefore refine our earlier statement slightly (Evans and Trommsdorff 1978) and conclude that Ti-Cl is less stable than olivine + magnesian ilmenite + H<sub>2</sub>O at temperatures in excess of 520° C at approximately 3 kbar. The upper limit of antigorite is only a few tens of degrees higher (Evans et al. 1976; Hemley et al. 1977). The corresponding antigorite-out isograd occurs 400 m closer to the intrusive contact than the isograd based on (5). As with all isograds, reaction (3) went only one way in the field, and the estimate of  $T$  is not based on a bracket around reversals. We should therefore not totally exclude the possibility that, at 3 kilobars, Ti-Cl is even less stable than claimed here.

Coupling the Ti-Cl breakdown reaction (3) with the equilibrium



yields a possible lower temperature limit for Ti-Cl in the presence of water, viz.

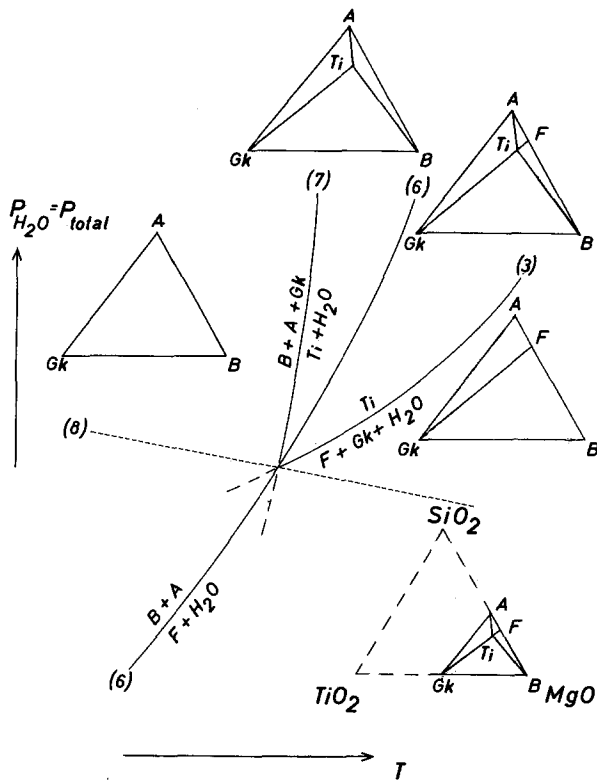
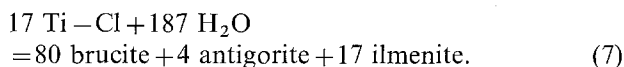
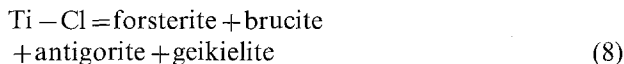


Fig. 9. Schematic  $P$ - $T$  grid of reactions among Ti-Cl, forsterite ( $F$ ), brucite ( $B$ ), geikielite ( $Gk$ ), serpentine ( $A$ ) and  $H_2O$  around a possible invariant point. The  $H_2O$ -absent reaction (8) is: Ti-Cl = forsterite + brucite + antigorite + geikielite



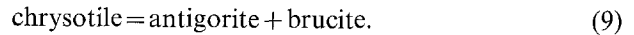
A possible array of all reactions resulting from the coupling of reaction (3) with (6) is shown in Fig. 9. Curve ( $H_2O$ ) for the reaction:



which is metastable in the  $P_{H_2O} = P_{total}$  section, is believed to have positive  $\Delta V$ , by analogy with the Ti-free reaction (Duffy 1977), hence the orientation given in Fig. 9, and our preference for this diagram as opposed to the enantiomorphic version. The diagram is also oriented such that  $H_2O$  fluid is liberated on the high  $T$  side of every reaction. The opening up of the stability field of Ti-Cl with pressure is in accord with the typical occurrence of the mineral in high pressure Greenschist and Blueschist Facies serpentinites. There is no evidence, however, that the invariant point really exists under possible geological conditions.

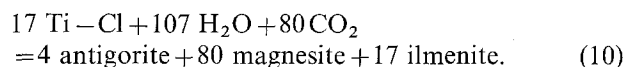
The prograde sequence of (6) and (3) is in excellent

agreement with geological observations. Reaction (7) would therefore be expected in the field at lower grade than (6), the first occurrence of olivine. Because Ti-Cl has never been observed in chrysotile-lizardite serpentinites, curve (7) is expected to lie above the reaction:



At 3 kbars, reaction (7) may therefore be expected to lie between about 290° C and 410° C (Evans et al. 1976; Hemley et al. 1977). A temperature of 380° C and 3 kbars is, in fact, obtained for (7) if 490° C and 3 kbars is adopted for Ti-Cl breakdown (3) (Engi and Lindsley 1979) and data for (6) taken from Evans et al. (1976).

We have no certain evidence of (7) having taken place in the Malenco area. Although we find the breakdown of Ti-Cl to antigorite + ilmenite, we have not found directly associated brucite and hence the complete product assemblage. Instead, we find magnesite accompanying the antigorite and ilmenite, for example, at Lago Scarolda (Fig. 1), and in the serpentinite at Zermatt (Bodengletscher). In these samples, Ti-Cl is typically fringed by a radiating intergrowth of elongate ilmenite and antigorite (Fig. 10), with magnesite occurring spottily within the fringe but more abundantly outside. Thus, instead of reaction (7) representing the low  $T$  breakdown of Ti-Cl, we are seeing its instability in a  $CO_2$ -bearing fluid, according to the reaction:



This reaction exists (Fig. 11) as a result of the intersection in the  $T$ - $X_{CO_2}$  plane of reaction (3) with the reaction:

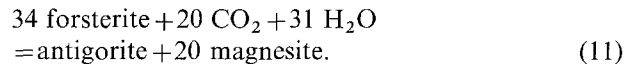


Figure 11 contains three of the reactions from Fig. 9 plus some stable reactions that result from adding  $CO_2$  to the system.

Figure 11 clearly shows the limited stability field of Ti-Cl in the presence of  $CO_2$ - $H_2O$  fluid. Its limits are entirely inside those of antigorite. If the metamorphic fluid contains more than a trace of  $CO_2$ , reaction (10) is effectively the lower temperature limit in nature of this variety of clinohumite. It may take place over a range of some 100° C or more. Because the join geikielite-antigorite is stable over the whole field of antigorite, the assemblage talc + Ti-Cl is not stable, and hence not found in the field.

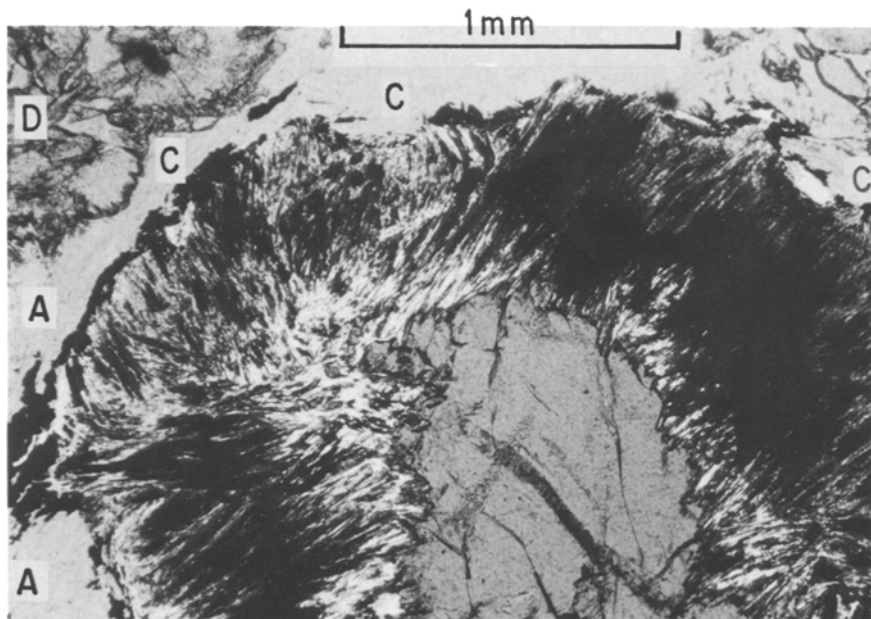


Fig. 10. Photomicrograph (PPL) of radiating intergrowth of magnesian ilmenite and antigorite (A), replacing Ti-Cl (Sample 298, Zermatt Serpentinite). C, Chlorite; D, diopside

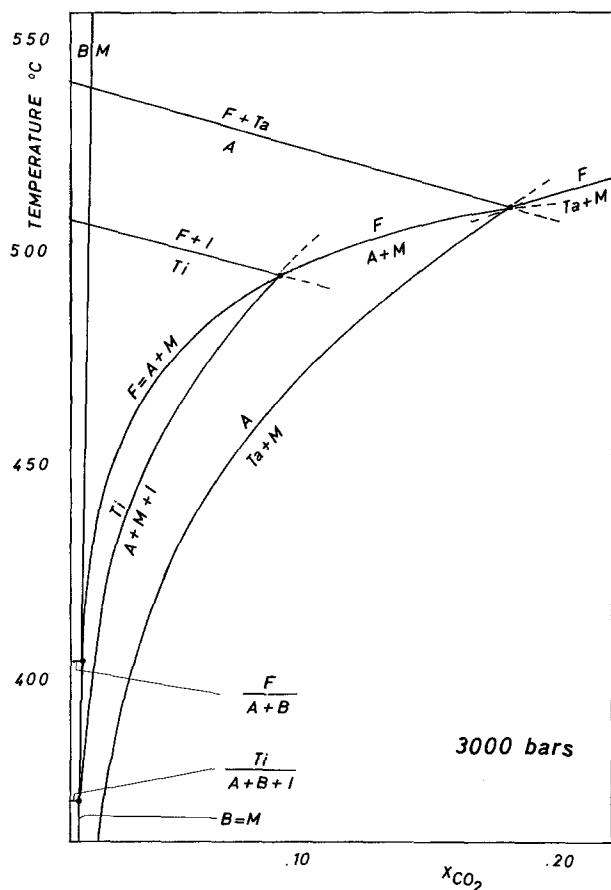
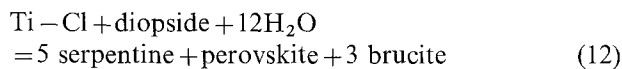


Fig. 11. Approximate locations of Ti-Cl breakdown reactions in  $T-X_{CO_2}$  section at a  $H_2O+CO_2$  pressure of 3 kilobars. F, olivine; Ta, talc; A, antigorite, Ti, Ti-Cl; M, magnesite; B, brucite; I, ilmenite

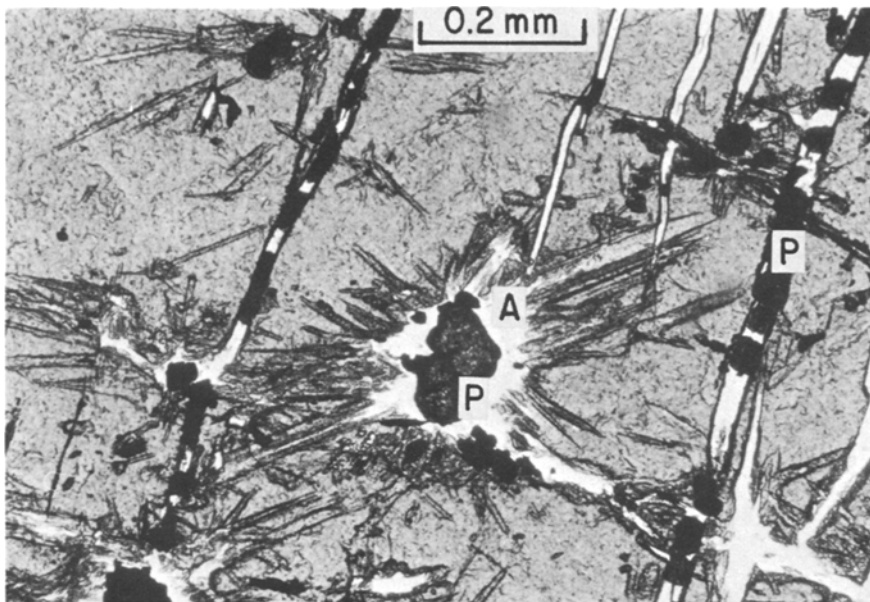
### VII. Other Reactions

Additional reactions leading to the decomposition of Ti-Cl apparently take place in the presence of Ca, since perovskite is observed among the products. For example, in the lowest grade part of the Malenco Serpentinite (Val Scerscen), Ti-Cl may be found having broken down at its margins to perovskite and antigorite (Fig. 12); olivine was not produced. Since diopside is the only mineral in the Malenco Serpentinite capable of supplying the Ca, the reaction was possibly:

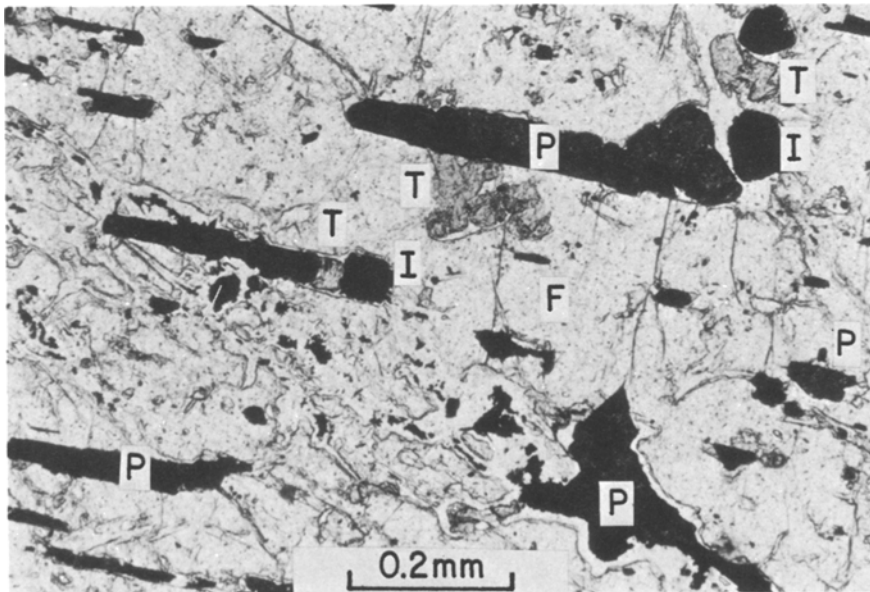


or an analogous reaction consuming  $CO_2$  and producing magnesite rather than brucite.

A sample from the slate quarries of Chiesa (Fig. 1) shows a chessboard intergrowth (Fig. 13) of Ti-Cl relics, olivine, magnesian ilmenite, perovskite, and tiny amounts of titanian chondrodite (only detectable by microprobe). Antigorite and diopside are abundant in this rock. Since perovskite occurs in part as pseudomorphs after the ilmenite, it may in this case be incorrect to regard it as a direct product of the breakdown of Ti-Cl, but rather a product of reaction among ilmenite, olivine, diopside and  $H_2O$ . This is the only rock yet found in the Malenco Serpentinite to contain titanian chondrodite, and the reason for its occurrence is not understood. Titanian hydroxyl-chondrodite has been found accompanying Ti-Cl in kimberlitic rock (Aoki et al. 1976) and serpentinite (Becker 1976).



**Fig. 12.** Photomicrograph (PPL) of Malenco Serpentine, Sample 228, showing partial breakdown of Ti-Cl (host) to perovskite (*P*) and antigorite (*A*)



**Fig. 13.** Photomicrograph (PPL) of Malenco Serpentine, Sample GM 216, showing olivine (*F*) + magnesian ilmenite (*I*) pseudomorph after Ti-Cl (three gray relics, labelled *T*). Oriented ilmenite has in turn partially altered to perovskite (*P*)

### VIII. Conclusions

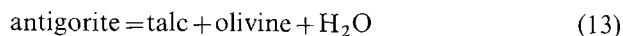
Study of natural mineral reactions in an antigorite serpentinite has shown that the stability field of titanian hydroxyl-clinohumite in the  $P-T$  and  $T-X_{\text{CO}_2}$  planes is enclosed inside that of antigorite. The occurrence of Ti-Cl corresponds fairly closely to that of the paragenesis diopside + antigorite. We estimate an upper limit for Ti-Cl at 3 kbars of  $\leq 520^\circ\text{C}$  and a lower limit of approximately  $380^\circ\text{C}$ . Higher-grade antigorite serpentinites (tremolite + olivine stable) of appropriate composition carry olivine and magne-

sian ilmenite instead of Ti-Cl (e.g., Bianchi 1914; Keusen 1972). Lower-grade serpentinites show serpentine + magnesian ilmenite + brucite (or magnesite) (e.g., Peters 1963; Dietrich 1972).

Titanian clinohumites occurring as a stable member of higher-grade (cummingtonite + olivine, or enstatite + olivine zones) metamorphic ultramafics, e.g., Val Verzasca, Ticino, Switzerland (Stäubli 1978), Ruby Range, Montana (Heinrich 1963; Desmarais 1978) contain fluorine (Jones et al. 1969). Fluorine contents found so far for Verzasca Ti-Cl are up to 2.7% *F*, and in these samples *F* correlates inversely

with  $\text{TiO}_2$  (Evans and Trommsdorff unpublished). As is the case with micas and amphiboles, fluorine clearly stabilizes titanian clinohumite in ultramafic rocks to much higher metamorphic grades. The total absence of *F* in Malenco Ti–Cl precludes a fractional breakdown in the Bergell aureole to olivine + ilmenite + more *F*-rich Ti–Cl.

The field observations presented in this paper refer to rocks crystallized under crustal pressures – in the case of the Bergell aureole, about 3 kbars. Engi and Lindsley (1979) have not only experimentally confirmed our estimate of the breakdown conditions of Ti–Cl, but have also reversed reaction (3) at 5, 15 and 20 kbars. Whether Ti–Cl remains contained inside the stability field of antigorite above 20 kbars, however, is uncertain. Delany and Helgeson (1978) calculate a negative slope for the reaction.



above 20 kbars. Thus, the coexistence at very high pressures of Ti–Cl and a dehydrated ultrabasic paragenesis, such as garnet lherzolite, cannot yet be ruled out. It is significant, however, that since the description of a Ti–Cl inclusion in pyropic garnet by McGetchin and Silver (1968, 1970), Smith (1977, 1979) has described a number of hydrated assemblages, including antigorite and Ti–Cl, in peridotite inclusions from Colorado Plateau diatremes. It is also worthy of note that, despite frequent descriptions of ilmenite-silicate intergrowths in kimberlites, there are none of olivine + ilmenite resembling the Ti–Cl pseudomorphs in the Malenco Serpentinite in the Bergell aureole. There seems little likelihood that Ti–Cl can have crystallized from kimberlite magma at  $\sim 100$  km and  $1,000^\circ\text{C}$  (Aoki et al. 1976).

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