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Tremolite- and Diopside-bearing Serpentine Assemblages in the CaO-MgO-SiO₂-H₂O Multisystem

By W. H. Oterdoom, Zürich*)

Abstract

In low grade metamorphic ultramafics, up to the upper pumpellyitefacies, the assemblage chrysotile + tremolite has been described (Rost, 1949; PETERS, 1963; DIETRICH and PETERS, 1971). Also the assemblage chrysotile + diopside has been observed at the same and higher grades up to the reaction of chrysotile to antigorite + brucite where at the same time pumpellyite disappears (DIETRICH and PETERS, 1971). Tremolite with serpentine occurs at low grade while the assemblage tremolite + forsterite is confined to higher metamorphic grades. From these observations the stable P-T topology can be deduced in the CaO-MgO-SiO₂-H₂O multisystem among the phases brucite, chrysotile, antigorite, talc, forsterite, diopside, tremolite and H₂O.

INTRODUCTION

This work is an extension of the serpentine-multisystem (EVANS *et al.*, 1976), in that CaO appears as new component besides MgO-SiO₂-H₂O. The phases diopside and tremolite contain this component. We consider a system with 8 phases and 4 components with a variance of minus two. The unique P-T net will be constructed to satisfy some field observations, by combining two partial nets, each with a variance of minus one. For this reason the thermodynamic data from EVANS *et al.* (1976) and TROMMSDORFF and EVANS (1977a) plus some field observations will be used.

CHEMOGRAPHY AND TOPOLOGY OF THE PARTICIPATING PHASES

The reasons that antigorite (A) and chrysotile (C, abbreviations see table 1) are not considered as polymorphic minerals, are only explained here briefly, for an exhaustive discussion see WICKS and WHITTAKER (1975). Because of

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the sinelike double half-wave structure with variable curvature, antigorite has a variable chemical composition (KUNZE, 1961). The stronger the curvature of the wave, the less MgO and H_2O has antigorite in comparison to the ideal serpentine composition $Mg_3Si_2O_5(OH)_4$. Theoretically the composition of antigorite can vary between those of chrysotile and talc and does not change the *relative* position of the phases in the chemographic projection (fig. 1). KUNZE

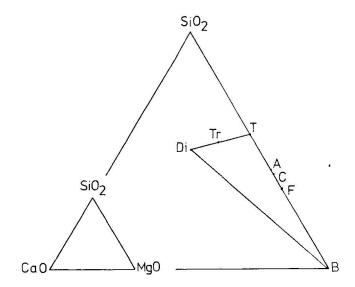


Fig. 1. Chemography of brucite B, chrysotile C, antigorite A, tale T, forsterite F, diopside Di and tremolite Tr in the system CaO-MgO-SiO₂-H₂O.

(1958, p. 316) made the connexion between the formula of the antigorite varieties and their associated layer wave-lengths (superperiods). The antigorite formula is $m \operatorname{Mg}_{3(1-1/m)}\operatorname{Si}_2\operatorname{O}_5(\operatorname{OH})_{1+3(1-2/m)}$. From X-ray studies a superperiod series of m = 17 tetrahedra per unit cell is established with $a_0 = 43.3$ Å. The antigorite formula consequently becomes $\operatorname{Mg}_{48}\operatorname{Si}_{34}\operatorname{O}_{85}(\operatorname{OH})_{62}$. The hypothesis of KUNZE (1961, p. 317) that the value of m in the superperiod series of antigorite is a function of metamorphic grade and chemical composition has not yet been investigated.

Until now no systematic derivation exists for a fully closed net of a 4 component system with 8 phases. The P-T net is constructed by means of combining two partial nets, each with a degree of freedom of minus one. We assume, that the pure phases chrysotile and forsterite can not occur together under normal geological conditions (Evans *et al.*, 1976; HEMLEY *et al.*, 1977b; DUNGAN, 1977). With this assumption it is possible to define two partial nets with forsterite or chrysotile absent. The six phases brucite, chrysotile, antigorite, talc, diopside, tremolite and the three projected components CaO-MgO-SiO₂ from H₂O form the first partial net (a pseudoternary multisystem involving only solid-solid reactions). The chemography is a triangle with all of the phases along the edges, compare with figure 9, number 49 in DAY (1972). Diopside and tremolite lie on the same site of the 4 phase colinearity along MgO-SiO₂ in projection from H₂O, implying that the invariant points [Di] and

[Tr] coincide at a different level of stability: stable to metastable (DAY, rule 4, 1972). There are 8 possible univariant reactions and 6 possible invariant points. In the absent phase notation of DAY (1972) there are 5 possible nets with maximal closure: the triangular nets ((C) (Di)), ((Tr) (B)) and ((Tr) (A)), the quadrilateral nets ((Tr) (C)) and ((Di) (A)). Only ((Tr) (A)) satisfies the assemblages observed in the field (fig. 2a). The corresponding inverse net to that shown in fig. 2a is presumed not to be correct because it cannot be constructed such that all of the appropriate reactions may be oriented with respect to the P-T axis. The nets have been constructed such, that two thermodynamic conditions are satisfied: 1) with increasing temperature at constant pressure the high-entropy side of the reaction is stabilised, 2) with increasing pressure at constant temperature the low-volume side of the reaction is stabilised. Entropy-and volume-data are summarized in table 1.

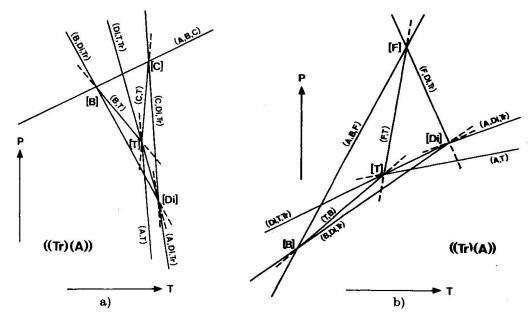


Fig. 2a and 2b. The unique P-T nets with maximum closure satisfying field data. Fig. 2a for the six phases A, B, C, T, Di, Tr and fig. 2b for A, B, F, T, Di and Tr. Mineral abbreviations, see table 1.

In the second partial system chrysotile is absent and forsterite (and H_2O) are present. The fundamental chemography is preserved (fig. 9, number 49, DAY, 1972). Also in this partial system there are 8 possible univariant reactions with 6 possible invariant points (of which, as mentioned above, [Di] and [Tr] coincide at a different level), therefore [F] and [W] coincide at the same level of stability. Of the 5 possible nets only ((Tr) (A)) satisfies the geological observations (fig. 2b). The corresponding inverse net to fig. 2b is also not possible here for the same reasons as above.

Both partial nets have three univariant reactions (Tr = Di + T, A = T + Band Di + A = Tr + B) and one invariant point, [C, F, W], in common. From this

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		V cm ³ ·gfw ⁻¹	S cal.deg. ⁻¹ gfw ⁻¹
		$\begin{array}{c} 24.63 \pm 0.07 \\ 108.5 \ \pm 0.6 \\ (102.89 \pm 0.51) \times 17^{\ 2}) \\ 136.25 \pm 0.26 \\ 43.79 \pm 0.03 \\ 66.09 \pm 0.10 \\ 272.92 \pm 0.73 \end{array}$	$\begin{array}{c} (50.6 \pm 0.4) \times 17^{2*}) \\ 62.34 \pm 0.15 \\ 22.75 \pm 0.20 \\ 34.20 \pm 0.20 \end{array}$
Fluid	absent reactions	$\Delta { m V~cm^3}$	⊿S cal.deg. ⁻¹
(BTFW) (BCAFW) (CTFW)	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrr} & -6.86 \pm & 1.25 \\ T & -73.66 \pm 18.17 \\ & -14.62 \pm 12.50 \\ Di & -19.11 \pm 12.52 \\ & 4.49 \pm & 0.80 \\ B & 2.67 \pm 21.82 \end{array}$	$\begin{array}{c} 6.17 \pm \ 9.62 \\ 1.81 \pm \ 0.83 \\ 18.43 \pm 14.02 \\ 4.36 \pm \ 9.07 \\ 3.91 \pm \ 9.09 \\ 0.45 \pm \ 0.52 \\ 26.08 \pm 16.19 \\ 2.26 \pm \ 0.96 \end{array}$

Table 1. Molar volume and entropy data (298.15 k, 1 bar)

Sources of data

Without indication: ROBIE and WALDBAUM (1968), ¹) KING et al. (1967), ²) KUNZE (1961), ^{2*}) modified from S_{298}^{o} antigorite $[Mg_3Si_2O_5(OH)_4]$ given by KING et al. (1967), as 53.2, by recomputing apparent impurities (as quartz and ice) with the Kunze-type formula (OTERDOOM, 1975).

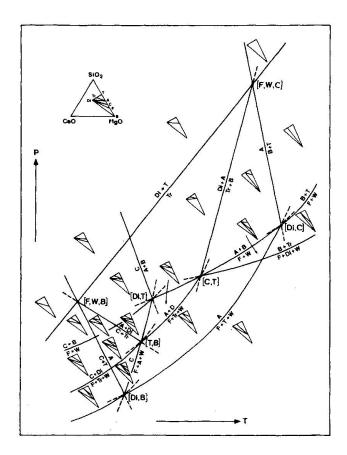
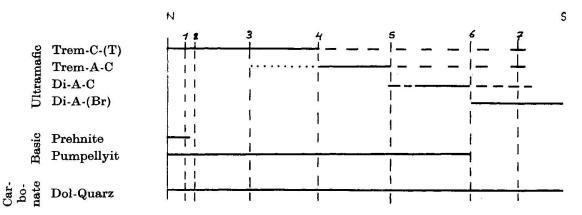


Fig. 3. Schematic temperaturepressure diagram of the stable part of the multisystem net for the system CaO-MgO-SiO₂-H₂O with the phases antigorite, chrysotile, brucite, talc, forsterite, diopside, tremolite and H₂O.

framework the whole net can be built up, remembering that in a non-degenerate system with the variance of minus two, three invariant points lie on a single univariant reaction curve (KORZHINSKII, 1959, p. 128, table 2). The stable part of the net that results in this manner has been drawn in fig. 3. The corresponding inverse net to fig. 3 is not considered possible for geological reasons (EVANS *et al.*, 1976, p. 83).

FIELD- AND PETROGRAPHIC-DATA

Chrysotile + tremolite, antigorite + diopside and forsterite + tremolite are the relevant natural serpentine assemblages, formed by the addition of CaO to the system MgO-SiO₂-H₂O. Chrysotile + tremolite are found at the lowest metamorphic grades. The assemblages antigorite + diopside and forsterite + tremolite have formed during the progressive metamorphism and are related through reaction (BCT). This reaction (BCT) takes place between the forsterite-forming reaction from antigorite + brucite and the antigorite breakdown reaction to forsterite + talc (Evans and TROMMSDORFF, 1970; TROMMSDORFF and Evans, 1972). Antigorite + diopside have formed from chrysotile + tremolite and both assemblages are often described (Rost, 1949; DIETRICH and PETERS, 1971). For the assemblage chrysotile + tremolite we must assume a stability field, as this pair occurs in several serpentinites: Totalp (PETERS, 1963), Oberhalbstein (DIETRICH, 1969; DIETRICH and PETERS, 1971), Wurlitz in the Münchberger Gneissmass (Rost, 1949). In order that a stability field occurs in our multisystem for chrysotile + tremolite, the solid-solid reaction C + Tr = A + Di(BTFW) has to be placed between the formation reaction of antigorite (C+T)



Totalp, (2) Tiefencastel, (3) Line P. Curver-Cunter, (4) Line P. Arlos-Rona (5) Marmorera,
 (6) Line Forcellina-Pass-Julier Pass, (7) Engadine Line (Ober-Engadin)

Fig. 4. Critical assemblages in ultramafics in the profile Totalp (Aroser Schuppenzone)–Oberhalbstein. Broken streaks mark local occurrence, the dotted line the occurrence of vein-antigorite. Data for Totalp were compiled after PETERS (1963), for Oberhalbstein after DIETRICH (1969) and DIETRICH and PETERS (1971). Section Totalp–Tiefencastel not on scale. = A) and the breakdown reaction of chrysotile (C = B + A), see also the sequence of assemblages in the Oberhalbstein (fig. 4).

The P-T diagram for CaO-bearing serpentinites must contain the following relevant, divariant fields with progressive metamorphism: C+Tr+T, A+C+Tr, A+C+Di, A+B+Di, A+F+Di, A+F+Tr and F+T+Tr. The assemblage brucite + tremolite has not been described although it would represent the upper pressure limit of antigorite + diopside.

Both tremolite and diopside occur in weakly metamorphosed (prehnitepumpellyite facies) areas, in the Totalp and in the Oberhalbstein. However, in the Totalp, PETERS (1963) observed tremolite, but never diopside, as new epitaxial growth on primary diallage or as aggregates of amphibole fibres as pseudomorphs after pyroxenes. However, diopside appears in the Totalp in fissures in clinopyroxene serpentinites. Thus the rock-forming assemblage chrysotile + diopside does not occur in the Totalp, but appears first in the higher grade Oberhalbstein. The observed sequence of assemblages in progressive metamorphism is presented in fig. 4.

THE PHASE-DIAGRAM

The P, T and $f_{H_{20}}$ phase relations between the 8 phases brucite, chrysotile, antigorite, talc, forsterite, diopside, tremolite and H_2O can be calculated quantitatively in the system CaO-MgO-SiO₂-H₂O from equilibrium data from only four linearly independent reactions, which together contain all 8 phases (SKIP-PEN, 1971). Three of the four selected reactions have been determined experimentally and can describe the system MgO-SiO₂-H₂O quantitatively, together with additional information from field data (EvANS *et al.*, 1976). The calculated location of the dehydration reactions, except for the breakdown of antigorite (A = F + T + H₂O, see Appendix) agrees to within $\pm 10^{\circ}$ C with the results of HEMLEY *et al.* (1977a, b). As the fourth linear independent reaction, A + Di = F + Tr + H₂O was selected. TROMMSDORFF and EVANS (1977a) list the equilibrium data for this reaction. With this choice of data we have an internally consistent set, that can also be compared with the set for the ophicarbonate system of TROMMSDORFF and EVANS (1977a, b). For the equilibrium constants for all the univariant reactions, see table 2.

The reaction C + Tr = A + Di (BTFW) takes place according to this data, at 2 kbars and 192° C. So that (BTFW) lies just above the reaction C + T = A(BFWDiTr). Although absolute temperature calibration in low grade ultramafic rocks is very questionable, it is clear that field data from the Oberhalbstein, see fig. 4, suggest a slightly larger temperature interval than the calculated 7° C at 2 kbars, as the first appearance of antigorite + diopside takes place for the first time in the southern Oberhalbstein, about 6 km south of the first

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Table 2.

		Evans et al. (1976)	Evans et al. (1976)	Evans et al. (1976)	TROMMSDORFF et al. (1977)														
	Jcy	1	i	ı	I	1	-0.25	l	1	1	0.25	0.25	1	1	I	4.25	0.25	-0.25	
	pender	ł	1	I	1	1	t	13	1	20	I	1	- 45	-3	ũ	45	-3	Q	
	Linear dependency	1 -	۱ ۱	I I	1 1	-1 3	-0.75 3	-1 4	-1 4	1 -4	-0.25 1	-0.25 -	2 9 -	- I	ן ו	-2.25 9	-0.25 1	0.25 - 1	
stant 1)	C	5.0019	1.7259	0.5478	4.7864	0.1758	0.2297	0.2583	1.9017	9.0543	1.6720	2.79 - 0.0539	0.8859	0.0825	1.0131	19.31 - 0.0300	0.0286	1.0670	
Equilibrium constant ¹)	в	433.89	158.31	51.57	445.04	41.04	38.25	44.64	199.35	832.05	161.10	2.79 -	-28.08	3.60	99.54	19.31 -	6.39	96.75	
Equilib	A	-210330	-76500	-23319	-213995	-19170	-18254	-25713	-95670	-370710	-77416	-916	-59805	-6543	-40095	-75381	-7459	-39179	
	Stoichiometry ²)	$A = 18F + 4T + 27H_2O$	$5C = 6F + T + 9H_2O$	$\mathbf{B} + \mathbf{C} = 2\mathbf{F} + 3\mathbf{H_2O}$	$8Di+A = 18F + 4Tr+27H_{2}O$	15C + T = A	15C + Tr = A + 2Di	17C = A + 3B	$20C = A + 6F + 9H_2O$	$A + 20B = 34F + 51H_2O$	$5C + 2Di = 6F + Tr + 9H_2O$	2 Di + T = Tr	$2\mathbf{A} = 45\mathbf{B} + 17\mathbf{T}$	2C = 3B + T	$5\mathrm{B} + \mathrm{T} = 4\mathrm{F} + 6\mathrm{H_2O}$	34 Di+ 2A = 17 Tr + 45 B	$2 \mathrm{Di} + 2 \mathrm{C} = \mathrm{Tr} + 3 \mathrm{B}$	$Tr + 5B = 2Di + 4F + 6H_2O$	
	Absent	(C, B, Di, Tr)	(A, B, Di, Tr)	(A, T, Di, Tr)	(C, B, T)	(B, F, W, Di, Tr)	(B, T, F, W)	(T, F, W, Di, Tr)	(B, T, Di, Tr)	(C, T, Di, Tr)	(A, B, T)	(C, A, B, F, W)	(C, F, W, Di, Tr)	(A, F, W, Di, Tr)	(A, C, Di, Tr)	(C, T, F, W)	(A, T, F, W)	(C, A, T)	

¹) $\ln K = \frac{A}{T} + B + \frac{C(P-1)}{T}$, where T is in ${}^{\circ}K$ and P is in bars. ²) See Table 1 for abbreviations and mineral formulae. Fugacity data from BURNHAM et al. (1969).

Tremolite- and Diopside-bearing Serpentine Assemblages

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appearance of antigorite (not vein-antigorite) in the univariant assemblage antigorite + chrysotile + talc and also about 6 km north of the first appearance of antigorite + brucite. This suggests that the reaction C + Tr = A + Di (BTFW) lies somewhere half way between the reactions C + T = A and C = A + B. Here one should bear in mind, that the solid-solution effect can be very large on the solid-solid reaction (BTFW), because ΔS of the reaction is small ($\Delta T = \frac{BT \ln K}{\Delta S r}$).

The equilibrium of the reaction $A + Di = F + Tr + H_2O$ (BCT) can be calculated for 2 kbars at about 486° C ($P_{H_2O} = P_{total}$). The reaction (BCT) lies above 1 kbar about 30° C beneath the breakdown reaction of antigorite (BCDiTr). The measured widths of the tremolite + antigorite + forsterite and tremolite + talc + forsterite zones in the Bergell tonalite aureole (TROMMSDORFF and EVANS, 1972) could point to a little larger temperature interval between reaction (BCT) and reaction (BCDiTr).

With respect to the field observations both CaO-bearing reactions may be better located if the $\Delta G^{\circ}_{f,298}$ for diopside is decreased or if $\Delta G^{\circ}_{f,298}$ for tremolite is increased, resulting in new values for the equilibrium constants A and B of both CaO-bearing reactions: A = -19597, B = 38.85 for reaction (BTFW) and A = -208621, B = 442.64 for reaction (BCT). The effect of solid-solution on

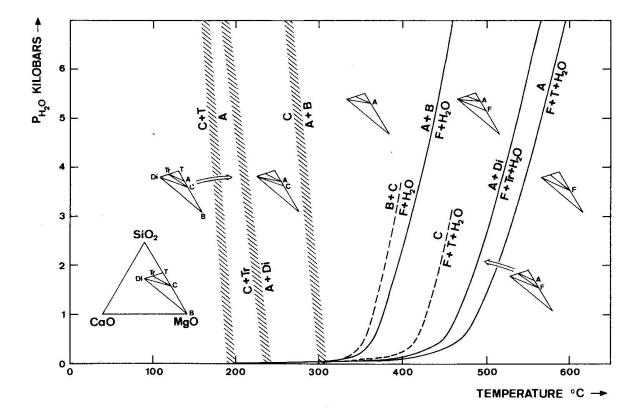


Fig. 5. Temperature-pressure $(P_{H_2O} = P_{total})$ diagram for stable (continuous lines) and metastable (dashed lines) equilibria in the multisystem antigorite, brucite, chrysotile, talc, forsterite, diopside, tremolite and H₂O. The location of C+Tr = A+Di is based on equilibrium constants A and B cited on page 134.

the location of (BCT) and (BCDiTr) is similar, thus the width of the temperature interval will not be changed by solid-solution. TROMMSDORFF and EVANS (1972) determined the partitioning of Mg between olivine with $x_{Mg}^{Ol} = 0.9$ and other phases to be $x_{Mg}^{T} = 0.976$, $x_{Mg}^{Di} = 0.969$, $x_{Mg}^{Tr} = 0.961$ and $x_{Mg}^{A} = 0.952$ for $P_s = 2$ kbars and $T = 525 \pm 50^{\circ}$ C. Assuming $\gamma_{Mg} \approx 1$, the temperature shift at 2 kbars will be about -8° C for both reactions.

The locations of the internally consistent reaction boundaries in the $P_{H_{2}O}(=P_{total})$ -T diagram are shown in fig. 5. Only the position of (BTFW) is inferred from field data. The location of the dehydration reactions are probably good to at least $\pm 20^{\circ}$ C (Evans *et al.*, 1976), whereas the position of the solid-solid reactions must be regarded as very approximate, as is explained by the example of C+Tr = A + Di (BTFW). This problem is clear from the fact that the assemblage chrysotile + talc appears south of the Engadine Line (Upper Engadine), several kilometers south of the first appearance of antigorite. This same holds for chrysotile + tremolite relative to antigorite + diopside.

CONCLUSIONS

It is evident from field observations and in accordance with our phase diagram, that tremolite is the most important CaO-bearing mineral of low grade ultramafics. At slightly higher grades (from the upper pumpellyite facies) diopside will dominate until the lower amphibolite facies, where diopside plus antigorite will give forsterite + tremolite.

Acknowledgements

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Appendix

Problems with the antigorite breakdown equilibrium

For the reaction antigorite (Kunze-type) = forsterite + talc + H₂O, Mg₄₈Si₃₄O₈₅(OH)₆₂ = 18 Mg₂SiO₄ + 4 Mg₃Si₄O₁₀(OH)₂ + 27 H₂O, we can recalculate $\Delta G_{f,298}^{0}$ of antigorite (Kunze-type), using HEMLEY'S (1977b) experimentally determined equilibrium of antigorite + talc + forsterite for 1 kbar at 514° C. With the following values for antigorite (Kunze-type): V⁰ = 102.89 cm³ (KUNZE, 1961), S⁰₂₉₈ = 50.6 cal/deg · gfw (recomputed value of KING et al., 1967; OTERDOOM, 1975) $\Delta S^{0}_{f,298} = -249.196$ cal/deg, cp-constants with equation cp = a + b*T + c*T⁻²: a = 72.793 cal/deg · gfw, b = 30.985*10³ cal/deg² · gfw, c = $-16.975*10^{-5}$ cal · deg/gfw (recomputed value of KING et al., 1967; OTERDOOM, 1975) and thermodynamic data for talc and forsterite as listed in table 3 of HEMLEY et al. (1977b), $\Delta G^{0}_{f,298} = -930533$ cal/gfw for antigorite (Kunze-type). With these data the breakdown reaction of antigorite lies just above the upper limit of Johannes experimentally deterW. H. Oterdoom

mined brackets. The calculation scheme followed has been described by HEMLEY et al. (1977b) with their equation 2. The recalculation has been made because $\Delta S_{t,298}^{0}$ of antigorite in HEMLEY's table 3, p. 360, is based on two different antigorite compositions (idealand Kunze-type) and V⁰ was based on unitcell data given by PAGE and COLEMAN (1967, table 3), that yield an unreasonably large molar volume.

The still existing discrepancy of $\pm 20^{\circ}$ C between the locations of the antigorite breakdown reaction of HEMLEY et al. (recalculated) and EVANS et al. could be possibly explained by the different chemical compositions and thus the different antigorite varieties of Hemley's and Johannes samples. Johannes antigorite (EVANS et al., 1976, table 4) shows lower SiO₂, higher MgO and H₂O content than the one of (HEMLEY et al., 1977b, table 1) and plots so more towards chrysotile whereas Hemley's antigorite plots more towards talc.

The recalculated antigorite breakdown based on HEMLEY et al. is consistent with the antigorite breakdown of Johannes, as supported by field evidence: Johannes antigorite shows less solid solution towards tale and his sample comes from an area (Piz Lunghin, Engadine) where antigorite \pm brucite is the stable assemblage without relict olivine (DIET-RICH and PETERS, 1971). The first appearance of forsterite in this area is some kilometers to the south in Val Malenco. On the other hand, Hemley's antigorite, 94-NZ-62-5 supplied by R. COLEMAN, originates from an area with the assemblage antigorite \pm tale \pm relict olivine (COLEMAN, 1966, p. 70).

Added in press:

A reinvestigation of 94-NZ-62-5 reveals an almost ideal Kunze-type formula. Compare however the USGS analysis (in PAGE and COLEMAN, 1967, tab. 1).

	1) wt %	2) wt %	³)	
SiO2 TiO2	44.35 0.03	44.35 trace	33.79 _	} 34.00
Al_2O_3	0.55	0.55	$0.49 \begin{array}{c} 0.2 \\ 0.2 \end{array}$	
Fe ₂ O ₃	4.15*)	-		
FeO	_ `	3.1**)	1.97	
MnO	0.07	0.03	0.02	
MgO	40.10	40.10	45.54	
CaO	0.04	0.03	0.02	47.94
Na ₂ O	0.03	trace		41.94
K ₂ Ō	< 0.01	0	-	
P_2O_5	0.01	0		
Cr ₂ O ₃	0.065	0.06	0.04	
NiO	0.25	0.11	0.07	
ZnO	0.005	trace		J
H_2O+	10.01	11.9	60.48	
	99.65	100.23		

Composition of 94-NZ-62-5, from Griffin Range, New Zealand

¹) Gravimetric- and spectrographic analysis of B. Ayranci and M. Weibel (Zurich) corrected for CO₂ in magnesite.

²) "Best" antigorite-composition based on gravimetrical- and spectrographical analysis of the USGS (in PAGE and COLEMAN, 1967) and Ayranci-Weibel and on microprobe analysis of Evans (Seattle).

*) Total iron as Fe_2O_3 .

**) Total iron as FeO.

³) Numbers of ions on the basis of 116 anhydrous oxygens.

References

- BURNHAM, C. W., J. R. HOLLOWAY and N. F. DAVIS (1969): Thermodynamic properties of water to 1000° C and 10,000 bars. Geol. Soc. Amer., Spec. Paper 132, 96 p.
- COLEMAN, R. G. (1966): New Zealand serpentinites and associated metasomatic rocks. New Zealand Geol. Survey Bull. 76, 102 p.
- DAY, H. D. (1972): Geometrical analysis of phase equilibria in ternary systems of six phases. Amer. J. Sci. 272, 711-734.
- DIETRICH, V. (1969): Die Ophiolithe des Oberhalbsteins (Graubünden) und das Ophiolithmaterial der ostschweizerischen Molasseablagerungen, ein petrographischer Vergleich.
 Dissertation. Europäische Hochschulschriften, Reihe 17, Erdwissenschaften, Nr. 1, 180 S. Verlag Herbert Lang & Cie. AG, Bern.
- DIETRICH, V. und TJ. PETERS (1971): Regionale Verteilung der Mg-Phyllosilikate in den Serpentiniten des Oberhalbsteins. Schweiz. mineral. petrogr. Mitt. 51, 329-348.
- DUNGAN, M. A. (1977): Metastability in serpentine-olivine equilibria. Am. Min. 62, 1018-1029.
- EVANS, B. W. and V. TROMMSPORFF (1970): Regional metamorphism of ultramafic rocks in the Central Alps: Parageneses in the system CaO-MgO-SiO₂-H₂O. Schweiz. mineral. petrogr. Mitt. 50, 481-492.
- EVANS, B. W., W. JOHANNES, W. H. OTERDOOM, V. TROMMSDORFF (1976): Stability of chrysotile and antigorite in the serpentine multisystem. Schweiz. mineral. petrogr. Mitt. 56, 79–93.
- HEMLEY, J. J., J. W. MONTOYA, C. L. CHRIST, P. B. HOSTETLER (1977a): Mineral equilibria in the MgO-SiO₂-H₂O system: I, talc-chrysotile-forsterite-brucite stability relations. Amer. J. Sci. 277, 322–351.
- HEMLEY, J. J., J. W. MONTOYA, D. R. SHAW and R. W. LUCE (1977b): Mineral equilibria in the MgO-SiO₂-H₂O system: II, talc-antigorite-forsterite-anthophyllite-enstatite stability relations and some geologic implications in the system. Amer. J. Sci. 277, 353–383.
- KING, E. G., R. BARANY, W. W. WELLER and L. B. PANKRATZ (1967): Thermodynamic properties of forsterite and serpentine. U.S. Bureau of Mines, Report of Investigations 6962, 19 p.
- KORZHINSKII, D. S. (1957): Physicochemical basis of the analysis of the paragenesis of minerals. (Engl. transl., New York consultants Bureau, 1959.)
- KUNZE, G. (1958): "Die gewellte Struktur des Antigorits II." Z. Krist. 110, S. 282-320.
- KUNZE, G. (1961): Antigorit. Strukturtheoretische Grundlagen und ihre praktische Bedeutung für weitere Serpentin-Forschung. Fortschr. Mineral. 39, 206–324.
- OTERDOOM, W. H. (1975): Geologisch-petrographische Untersuchungen des Malencoserpentins in Val Scerscen. Diplomarbeit, ETH Zürich.
- PAGE, N. J. and R. G. COLEMAN (1967): Serpentine-mineral analyses and physical properties. U.S. Geol. Survey Prof. Paper, 575-B, B103-B107.
- PETERS, TJ. (1963): Mineralogie und Petrographie des Totalpserpentins bei Davos. Schweiz. mineral. petrogr. Mitt. 43, 529-685.
- ROBIE, R. A. and D. R. WALDBAUM (1968): Thermodynamic properties of minerals and related substances at 298.15 K (25.0° C) and one atmosphere (1.013 bars) pressure and at higher temperatures. U.S. geol. Surv. Bull. 1259, 256 S.
- ROST, F. (1949): Das Serpentinit-Gabbro-Vorkommen von Wurlitz und seine Mineralien. Heidelberger Beiträge zur Mineralogie und Petrographie 1, 626–688.
- SKIPPEN, G. B. (1971): Experimental data for reactions in siliceous marbles. J. Geol. 79, 457-481.

- TROMMSDORFF, V. and B. W. EVANS (1972): Progressive metamorphism of antigorite schists in the Bergell tonalite aureole (Italy). Amer. J. Sci. 272, 423-437.
- TROMMSDORFF, V. and B. W. EVANS (1974): Alpine metamorphism of peridotitic rocks. Schweiz. mineral. petrogr. Mitt. 54, 333-352.
- -- (1977a): Antigorite-ophicarbonates: Phase relations in a portion of the system CaO-MgO-SiO₂-H₂O-CO₂. Contr. Mineral. Petrol. 60, 39-56.
- -- (1977b): Antigorite-ophicarbonates: Contactmetamorphism in Val Malenco, Italy. Contr. Mineral. Petrol. 62, 301-312.
- WICKS, F. J. and E. J. W. WHITTAKER (1975): A reappraisal of the structures of the serpentine minerals. Can. Mineral. 13, 227-243.

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