Wagnerite from a metapelitic rock of the Simano Nappe (Lepontine Alps, Switzerland), Part I : mineralogy and geochemistry

Autor(en): Irouschek-Zumthor, Alfred / Armbruster, Thomas

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Part I: mineralogy and geochemistry

by *Alfred Irouschek-Zumthor*[1], and *Thomas Armbruster*[2]

Abstract

A rock forming wagnerite ($P2_1/c$, Z = 16) $Mg_{1.83}Fe_{0.15}Mn_{0.02}(PO_4)F_{0.72}OH_{0.28}$ from a phlogopite schist in the Lepontine area of the Central Alps in Switzerland is described. Single crystal methods were applied to measure unit cell dimensions and optical properties of one selected grain: a = 9.650 (3) Å, b = 12.714 (4) Å, c = 11.974 (4) Å, β = 108.34 (2)°, $n_{c,38.5}$ = 1.5885, n_b = 1.5891, $n_{a,-20}$ = 1.5983, 2 V_z = 29°. The OH-content was qualitatively determined by IR-spectroscopy and the numeric value was calculated as difference between the measured F-concentration and the stoichiometric formula $(Mg,Fe)_2(PO_4/OH,F)$. F,OH-wagnerite is rimmed by F-apatite. It is suggested that a specific rock chemistry is more decisive for wagnerite formation than p,T-conditions. The rare mineral wagnerite has hitherto been described from diagenetic to eclogite-granulite facies rocks.

Keywords: Wagnerie, triplite, phosphates, crystal chemistry, optical properties, Central Alps.

INTRODUCTION

This article provides further information about the first occurrence of wagnerite in the Lepontine area of the Central Alps of Switzerland (IROUSCHEK and ARMBRUSTER 1984). Wagnerite is a rare magnesio-fluorophosphate mineral which was first described by FUCHS (1821) in quartz-carbonate veins at Höllgraben near Werfen, Austria. Despite its early discovery, only a few additional occurrences in different geological environments have been reported. In addition to some later discoveries near the type locality, Werfen (Bischofshofen [HEGEMANN and STEINMETZ 1927] and Webing/Abtenau [KIRCHNER 1981/82]),

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[1] Mineralogisch-petrographisches Institut der Universität Basel, Bernoullistrasse 30, CH-4056 Basel.

[2] Laboratorium für chemische und mineralogische Kristallographie der Universität Bern, Freiestrasse 3, CH-3012 Bern.

wagnerite has been detected within the residues of dissolved salts from the Zechstein formation south of Hannover, Germany (BRAITSCH 1960) and in pegmatites of Bamle, Norway (PISANI 1879), Mangualde, Portugal (JESUS 1936), Dolni Bory, Czechoslovakia (STANĚK 1965), and Enderby Land, Antarctica (GREW 1981). ZAMBONI (1910) reported wagnerite from a cavity of volcanic lava resulting from the Vesuvian eruption of 1872. The most recent reports of new occurrences are from high grade metamorphic rocks e.g. Kyakhta, USSR (FINKO 1962), Bodenmais, Germany (PROPACH 1976a), the Santa Fe Mountains of Colorado, USA (SHERIDAN et al. 1976), and in a pyrope-rich rock similar to eclogite near Skřinářov, Czechoslovakia (NOVÁK and POVONDRA 1984).

The simplified formula of wagnerite is $Mg_2(PO_4/F)$. However, most crystals contain some Fe, Mn and Ca. The miscibility between wagnerite and the Fe or Mn-phosphates triplite $(Mn,Fe)_2(PO_4/F)$ — triploidite $(Mn,Fe)_2(PO_4/OH)$ — zwieselite $(Fe,Mn)_2(PO_4/F)$ seems to be controlled by structural constraints. In triplite and zwieselite (C2/c) all Mg, Fe, and Mn are octahedrally coordinated by oxygen or fluorine (WALDROP 1970), whereas in wagnerite and triploidite $(P2_1/c)$ Mg, Fe, and Mn are partly five-fold and partly six-fold coordinated. Some of the alleged ferroan-wagnerites are actually Mg-rich triplites and not wagnerites (SHERIDAN et al. 1976). The structures of both minerals are very similar and reveal also very similar X-ray powder patterns. OH-groups, substituting for fluorine, in wagnerite have only been analysed by NOVÁK and POVONDRA (1984) and FINKO (1962), while SHERIDAN et al. (1976) noted a low Cl → F substitution.

GEOLOGICAL SETTING AND SAMPLE DESCRIPTION

The outcrop of wagnerite-bearing rock occurs in the Simano-Nappe at the locality Miregn in Val Ambra. This region, located in the Lepontine Alps, has undergone alpine metamorphism at amphibolite facies conditions of about 600–650 °C and pressures between 5 and 7 kbar during the tertiary (FREY et al. 1980). Granitic gneisses are the dominant rock types in the lower part of the Simano Nappe, while metapelites are more abundant in the upper portions. At Miregn, a layer of Mg-rich metapelitic rocks with an average thickness of about 2.5 m cuts through the monotonous granitic gneisses. This layer can be subdivided into three different rock types.

The lower part consists of schists with phlogopite, quartz, cordierite, and kyanite as main constituents (IROUSCHEK-ZUMTHOR 1983). Subordinate constituents are fibrolitic sillimanite and idiomorphic as well as xenomorphic apatite. Rutile, some zircon and monazite are present as accessory minerals. Irregularly distributed nodules of kyanite megacrystals up to 10 cm, sometimes associated with green idiomorphic apatite up to 2 × 1 cm, are common in this horizon.

Intercalated with the phologopite schists are leucocratic, gneissic looking boulders composed of quartz, cordierite, and idiomorphic apatite together with little phlogopite, pyrrhotite, and rutile.

The middle part of the metapelitic layer consists of leucocratic gneiss with the mineral assemblage of quartz, fibrolitic sillimanite, albite (6–10% An), cordierite, and white kyanite with some muscovite and accessory xenomorphic apatite.

The upper portion of the sequence is formed by an irregular alternation of phlogopite schists with leucocratic gneisses of different thicknesses. The phlogopite schists contain the constituents quartz, kyanite, albite (6–10% An), fibrolitic sillimanite, phlogopite, muscovite, and orange to red-brownish colored, sometimes cloudy looking grains which have been identified by X-ray powder diffraction as wagnerite. Most wagnerite grains have a pale yellow to golden-yellow color with a resinous to glassy luster but do not display obvious cleavage. Wagnerite crystallizes in anhedral grains of 0.2–3 mm in size. In thin-section, wagnerite appears colorless and shows as specific "chagrin" (grain leather appearance). However, it is not clear whether this is a specific property of the mineral itself or whether it is caused by a lot of small fluid inclusions. The inclusions contain almost equal parts of a liquid and a gaseous phase. Characteristically, the interference color of wagnerite under crossed nicols is slightly grayish-blue which helps with identification. A narrow rim with slightly higher refractive indices has been observed around some wagnerite grains (Fig. 1). Electron microprobe analyses show that this is apatite, probably an alteration product of wagnerite. Interestingly, apatite is rather scarce in these wagnerite-bearing rocks, while in the lower layers of wagnerite-free phlogopite schists, apatite is relatively abundant, occurring as either idiomorphic or xenomorphic crystals.

In the cordierite-bearing rocks of the lower and middle part of the layered sequence, kyanite is a relictic mineral which is always rimmed by cordierite and occasionally transformed into andalusite (ARMBRUSTER and IROUSCHEK 1983). In contrast, in the wagnerite-bearing phlogopite schists, kyanite is of idiomorphic or subhedral shape and shows, with the exception of deformed crystals, no alteration phenomena. Despite an intensive search, no cordierite has been detected in these rocks. Fibrolitic sillimanite occurs as clusters within phlogopite layers. Phlogopite is occasionally altered to chlorite.

Petrographic observations suggest that wagnerite coexists with kyanite, phlogopite, albite, and quartz. Inclusions of wagnerite in kyanite demonstrate that wagnerite has grown together with kyanite during amphibolite facies condition of the alpine metamorphic event.
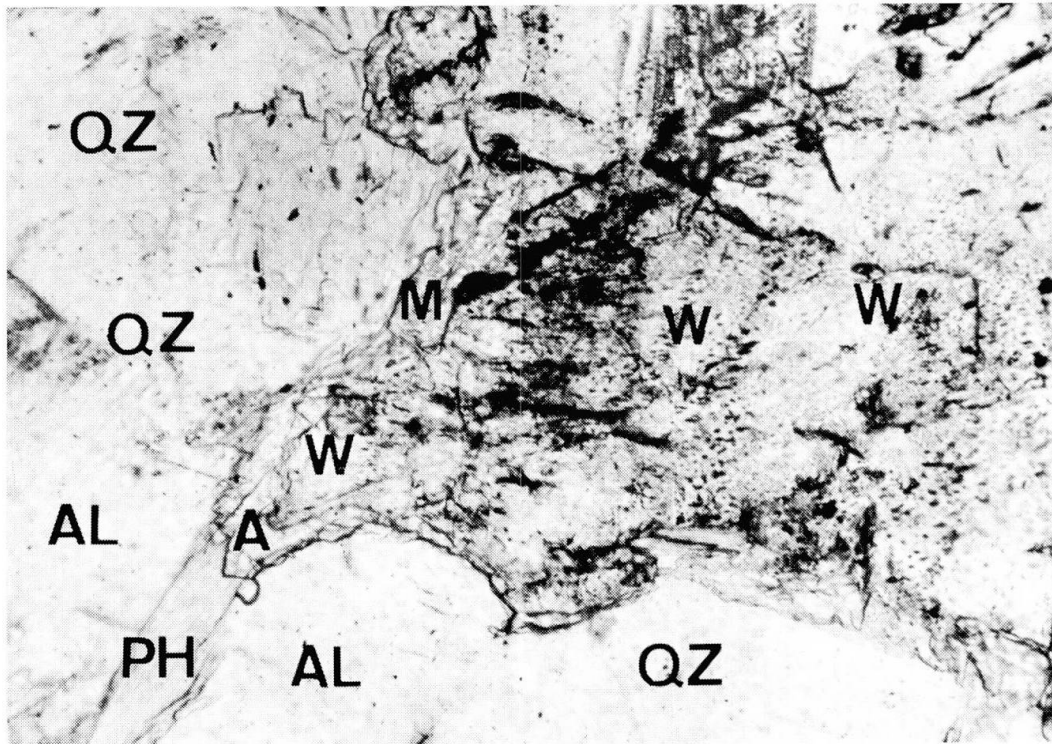
Fig. 1a Micrograph (diameter ca 0.5 mm) of wagnerite (W) rimmed by apatite (A)—higher relief—in a matrix of quartz (QZ), albite (AL), phlogopite (PH), and white mica (M). Wagnerite appears cloudy due to a large number of tiny fluid and ore inclusions.
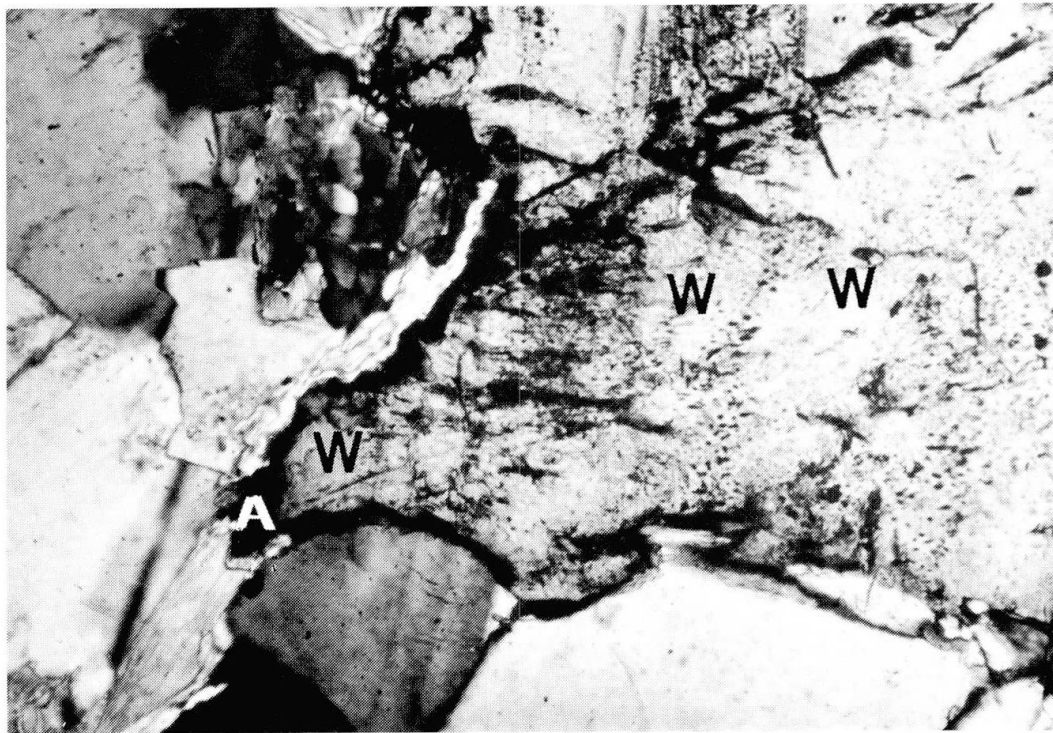
Fig. 1b Section as in Fig. 1a but under crossed nicols. The black apatite rim around wagnerite is clearly differentiated.

EXPERIMENTAL

Mineral separation

Because wagnerite occurs as an accessory phase in the phlogopite schists, around 1.5 kg of wagnerite-bearing rocks were collected, crushed, sieved, and washed. The size fraction between 0.1 and 0.3 mm was put through a Frantz magnetic separator. Wagnerite was enriched in the magnetic fraction. Around 0.2 g of macroscopically pure wagnerite was then obtained by handpicking.

Optical measurements

Several xenomorphic single crystals of wagnerite (about 0.2 mm in diameter) were mounted on glass fibers and studied under a spindle stage equipped microscope (BLOSS 1981). The optic angle at 589 nm was calculated from extinction measurements under crossed nicols with the program EXCALIBR (BLOSS 1981). The resulting optic angles $2 V_Z$ varied between 25 and 35°. Since the extinction determination was highly influenced by inclusions, the optic angle is judged to be accurate to within 2°. A rather clear crystal ($2 V_Z = 29°$) was selected for refractive index measurements with the double variation method (wave length, temperature). The following refractive indices were refined for 25 °C and 589.3 nm: $n_{c,38.5} = 1.5885$, $n_b = 1.5891$, $n_{a,-20} = 1.5983$ (nomenclature according to BLOSS [1985]), the dispersive power was about 0.015 for all directions. Refractive indices were measured to within ± 0.0005. Refractive indices of additional crystals, although poorer in quality, were in fair agreement with the selected specimen.

X-ray diffraction measurements

The lattice constants for the same wagnerite crystal as used for the spindle stage optics were measured with an Enraf Nonius CAD4 four circle X-ray diffractometer using graphite filtered MoKα radiation and refined from 25 individually centered reflections, yielding a = 9.650 (3) Å, b = 12.714 (4) Å, c = 11.974 (4) Å, β = 108.34(2)°. The optic orientation b∥y, a∧Z = -20° is in agreement with literature data (HEGEMANN and STEINMETZ 1927). An X-ray powder pattern was also recorded with an Enraf Nonius Guinier camera using FeKα radiation. For the determination of the cell parameters the single crystal method is by far more reliable, because the low symmetry does not allow unambigous indexing of the powder pattern.

Infrared spectroscopy

IR powder pellets were prepared according to the KBr-disc-technique. Three runs with differently treated wagnerite were carried out: a) undried, b) dried for 16 hours at ca. 100 °C, c) dried for 1 h at ca. 100 °C with a larger quantity of material. All spectra show an identical pattern of absorption bands. The spectra (Fig. 2, Table 1) indicate the presence of OH-groups with stretching vibrations at 3580 cm⁻¹. A more diffuse water absorption band at 3440 cm⁻¹ is probably caused by humidity in the KBr or on the crystal surface. Additional absorption bands between 1800 cm⁻¹ and 3000 cm⁻¹ are not part of the wagnerite spectrum but are caused by the preparation technique. Table 2 compares the infrared spectrum of Miregn wagnerite with IR-data (GADSDEN 1974) of wagnerite from Werfen, and with other simple phosphates of similar composition, e.g. triplite $(Mn,Fe)_2(PO_4/F)$ and triploidite $(Mn,Fe)_2(PO_4/F,OH)$. The spectrum of Miregn wagnerite shows some additional peaks when compared to the wagnerite from Werfen. The reason for this difference could be partial substitution of Fe for Mg or partial substitution of OH for F in the Miregn sample. In contrast, the wagnerite from Werfen is almost a pure magnesio-fluoro-phosphate. The additional peaks at 965 and 740 cm⁻¹ also appear in the spectrum of triploidite, an OH-bearing Mn,Fe-phosphate, at 957 and 755 cm⁻¹. Similar agreement can be observed for the position of the OH-stretching bands: Miregn wagnerite at 3580 cm⁻¹ — triploidite at 3509 cm⁻¹.

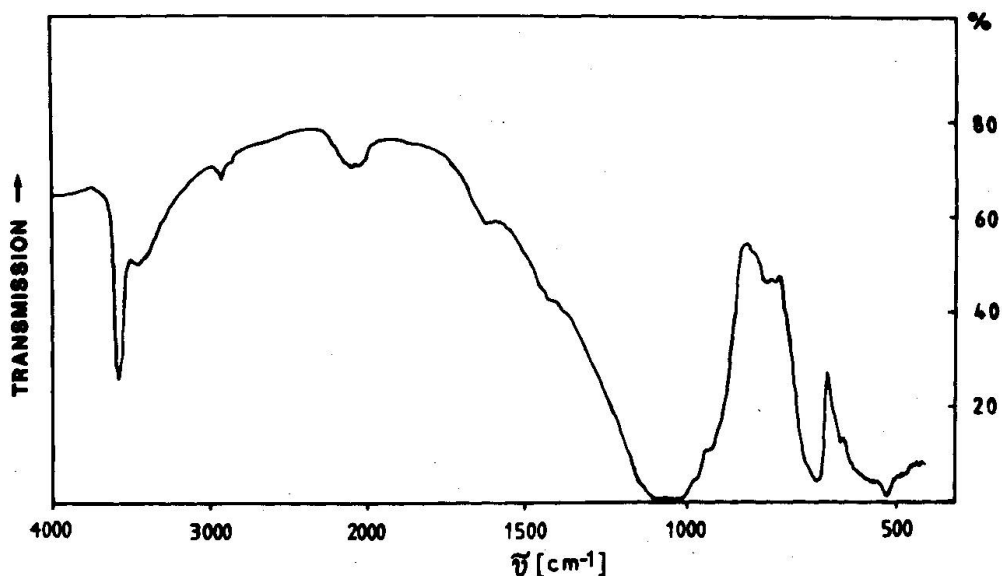*Fig. 2*   Infrared spectrum (KBr-pellet technique) of wagnerite from Miregn. Absorption bands between 1800 and 3000 cm⁻¹ are not part of the wagnerite spectrum but due to impurities caused by the preparation method.

Table 1   IR powder spectra of wagnerite – related minerals.

TRIPLITE $(Mn,Fe)_2(PO_4/F)$		WAGNERITE – Werfen $(Mg,Fe,Mn)_2(PO_4/F)$		WAGNERITE – Miregn $(Mg,Fe,Mn)_2(PO_4/F,OH)$		TRIPLOIDITE $(Mn,Fe)_2(PO_4/OH)$	
1095	vb/sh	1095	sh	1090	b/sh	1090	b/sh
1075	b/vs	1075	sh	1075	m/sh	1058	b/sh
1050	b/vs						
1020	vb/sh	1050	s	1045	s	1030	vs/b
						1010	b/sh
				965	m/sh	957	m/sh
				930	w/sh	870	b/sh
805	vw	650	b/sh	740	w/b	755	sh
605	m/sh	608	m/b	630	m/sh		
580	m/b	525	b/sh	598	m	595	b/sh
455	w/b			540	w/sh	570	s/b
		410	m/vb	520	w		

Hydroxyl stretching vibration

				3580	s	3509	
				3440	b		

vs = very strong
s = strong
m = medium
vb = very broad
b = broad
vw = very weak
w = weak
sh = shoulder

Mineral chemistry

Because of the small amount of available material, the great number of inclusions, and the intimate intergrowth with randomly distributed apatite, wet chemical analyses or XRF-analyses of the main components would be inaccurate and were therefore not done. The chemical composition has been determined on an ARL electron microprobe using different wagnerite grains mounted on a polished and beryllium coated thin-section. The following operating conditions were used: accelerating voltage: 15 kV, sample current: 40 mA, beam diameter: 4 µm, beam current integration: 50 sec, program correction: ZAF. The standardization for phosphorus was done with synthetic $Mg_2P_2O_5$. Mg was standardized with MgO, while the remaining elements were standardized with natural as well as synthetic silicates and oxides. As a control of the fluorine content, as measured by the electron microprobe, an additional fluorine double determination was performed with a specific ion-selective electrode. This value was in good agreement with the average fluorine content obtained by electron microprobe analyses. The small amount of fluorine is remarkable and is the

Table 2 Analyses of wagnerites.

	1	2	3	4	5	6	7
MgO	43.76(18)	46.28	48.35	42.84	48.31	42.50	46.08
FeO	6.04(25)	-	0.95	8.67	1.72	4.40	3.32
MnO	0.92(09)	-	0.70	0.45	0.49	0.60	0.04
CaO	-	3.10	-	-	-	4.1	-
P_2O_5	42.68(18)	43.58	43.45	41.56	42.89	-	41.80
F	8.27(21)	10.61	11.49	10.05	10.72	-	8.80
Cl	-	-	-	-	0.48	-	-
OH	2.82	-	-	0.65	-	-	1.18
- F=O	3.48	4.47	4.84	4.22	4.51	-	3.71
-OH=O	1.33			0.31			
-Cl=O					0.10		
Sum	99.68	99.10	100.10	99.69	100.00	51.6	97.51

cations on the basis of 9 negative charges

	1	2	3	4	5	6	7
Mg	1.82	1.89	1.96	1.80	1.97	1.76	1.93
Fe	0.14		0.02	0.21	0.04	0.10	0.08
Mn	0.02		0.02	0.01	0.01	0.01	0.00
Ca		0.09				0.12	
P	1.01	1.01	1.00	0.99	0.99		1.00
F	0.72	0.92	0.99	0.89	0.92		0.77
Cl					0.02		
OH	0.28			0.12			0.22

1 Miregn (this work) standard deviations in parentheses
2 Bamle, Norway (PISANI 1879) recalculated
3 Werfen, Austria (Hegemann and STEINMETZ 1927) recalculated by SHERIDAN et al. (1976)
4 Kyakhta, USSR (FINKO 1962) recalculated by SHERIDAN et al. (1976)
5 Santa Fe, USA (SHERIDAN et al. 1976)
6 Bodenmais, FRG (PROPACH 1976) only partial analysis
7 Skřinářov, CSSR (NOVÁK and PROVONDRA 1984)

lowest ever reported for wagnerite (Table 2). A qualitative OH or H_2O test was carried out by IR-spectroscopy, while an estimate of the OH-content was obtained by difference from the stoichiometric formula (one (F, OH) per formula equivalent). Although wagnerite exhibits a distinct OH → F substitution, other minerals in the same assemblage show normal to high F-concentrations. Apa-

tite is a pure F-apatite and phlogopite contains 0.45 wt.% F. The averaged composition of five electron microprobe analyses is presented in Table 2 together with wagnerite compositions from other localities. The Miregn wagnerite shows significant Fe replacing Mg, while Mn substitution for Mg is less pronounced. No additional cations were detected in transparent zones of the grains (without solid or liquid inclusions). It is important to note, that within this zone no Ca was found, whereas in some older analyses a certain amount of CaO was often reported. According to own optical observations on thin-sections, the rim of the grains consists for the most part of apatite (Fig. 1). Furthermore, an increase of K, Na, Si, Al and Ti along wagnerite phase boundaries may indicate a zone of complicated intergrowth-alteration products.

DISCUSSION

The Miregn wagnerite possesses a significantly lower F-concentration (8.27 wt.%) compared to the theoretical value for $Mg_2(PO_4/F)$ of 11.68 wt.%. IR-spectra indicate that this deficit may be balanced by OH. A similar substitution has been known for the fluoro-phosphates triplite/zwieselite leading to the hydroxyl-phosphate triploidite. Difference calculations for the Miregn wagnerite suggest that about 28% of the F-positions are substituted by OH. The rela-
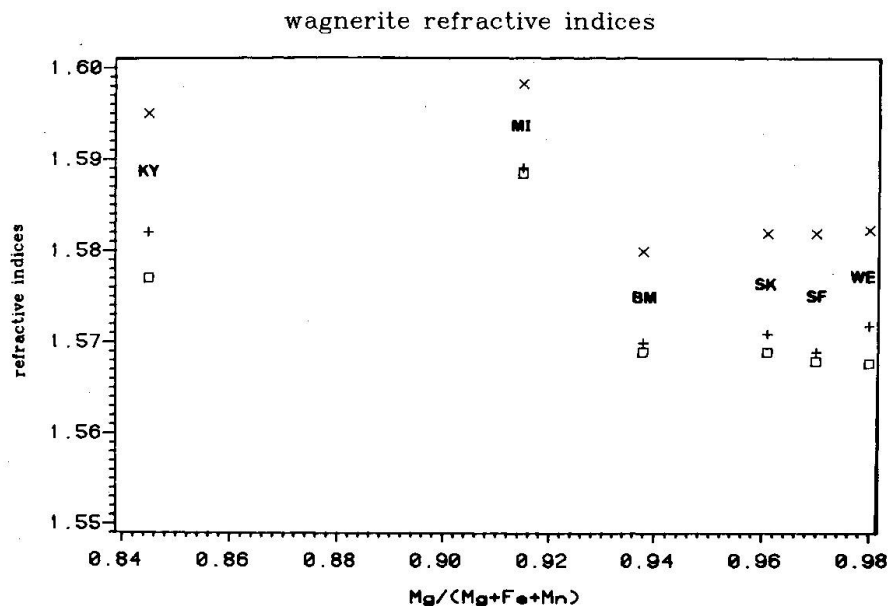

Fig. 3 Wagnerite refractive indices are plotted against Mg/(Mg+Fe+Mn). The Miregn wagnerite exhibits the highest refractive indices which might be related to the pronounced OH → F substitution.
KY: Kyakhta, USSR (FINKO 1962)
MI: Miregn (this paper)
BM: Bodenmais, FRG (PROPACH, 1976b)
SK: Skřinářov, Czechoslovakia (NOVÁK and POVONDRA 1984)
SF: Santa Fe, USA (SHERIDAN et al. 1976)
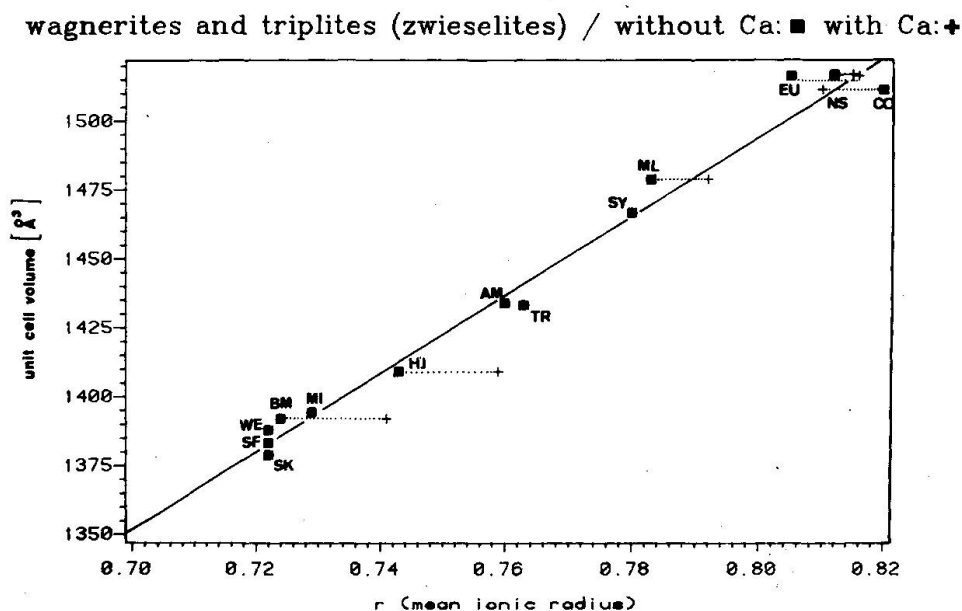WE: Werfen, Austria (HEGEMANN and STEINMETZ 1927)

wagnerites and triplites (zwieselites) / without Ca: ■ with Ca: +

Fig. 4 Unit cell volumes of wagnerites and doubled cell volumes of tripilites (zwieselites) are plotted versus the mean ionic radii of cations in five- and six-fold coordination (SHANNON 1976). Filled squares indicate samples where Ca was either neglected in the calculation of the ionic radius or was not found in the analysis. Crosses indicate samples where Ca was considered in the calculation of the mean ionic radius. For Mg-rich samples, the correlation between unit cell volume and mean ionic radius is improved if Ca is not considered as a structural component. The solid line (V [$Å^3$] = 341.6 + 1443.2 r, R = 99.0%) was refined from data where Ca was not considered. Wagnerite samples are indicated by "w" in the following legend, all other samples are triplites (zwieselites).

WE: Werfen (w), Austria (unit cell volume: CODA et al. 1967, chemistry: HEGEMANN and STEINMETZ 1927)
SF: Santa Fe (w), USA (SHERIDAN et al. 1976)
SK: Skřinářov (w), Czechoslovakia (NOVÁK and POVONDRA 1984)
BM: Bodenmais (w), FRG (PROPACH 1976a)
MI: Miregn (w) (this paper)
HJ: Hallsjöberget, Sweden (unit cell volume: SHERIDAN et al. 1976, chemistry: HENRIQUES 1957)
AM: Albères massif, France (unit cell volume: SHERIDAN et al. 1976, chemistry: FONTAN et al. 1970)
TR: Turkestan ridge, USSR (unit cell volume: SHERIDAN et al. 1976, chemistry: GINZBURG et al. 1951)
SY: synthetic triplite (YAKUBOVICH et al. 1978)
ML: Mica lodge, USA (unit cell volume: WALDROP 1969, chemistry: HEINRICH 1951)
EU: Eurajoki, Finland (HAAPALA and OJANPERA 1969)
NS: Novia Scotia, Canada (MANDARINO et al. 1984)
CO: Cornwall, England (GEORGE et al. 1981).

tively high Fe-content combined with Mg-deficiency of the Miregn wagnerite also suggests substantial substitution of the type Fe → Mg. When the refractive indices are plotted (Fig. 3) against the X-values, X = Mg/(Mg+Fe+Mn), it becomes obvious that the increased content of Fe and Mn is not primarily responsible for the strikingly high refractive indices of the Miregn specimen. Previously, PROPACH (1976b) explained the variation of optical properties in natural wagnerites as due to Fe,Mn → Mg substitution. Probably, the higher OH-concentration is the major reason that the Miregn wagnerite does not fit into this trend (e.g.: fluorapatite: n_o = 1.635, n_e = 1.630, hydroxylapatite: n_o = 1.651, n_e = 1.644). However, it remains puzzling why the sample from Skřinářov (NOVÁK and POVONDRA 1984) does not exhibit elevated refractive indices, although

the Skřinářov wagnerite shows almost as high OH → F substitution as the Miregn wagnerite (Table 2).

To test whether the frequently reported Ca-content in natural wagnerites and related structures is part of the mineral itself or is caused by impurities or alteration of the Mg,Fe,Mn-phosphates, the mean ionic radius of the cation in octahedral and five-fold coordination was plotted against the unit cell volume (Fig. 4). Due to the halfed b-axis in triplite, the corresponding cell volume had to be doubled. In the first model the mean radius (SHANNON 1976) was calculated from all bivalent cations, such as Mg, Fe, Mn, and Ca, as indicated by crosses in Fig. 4. Filled squares display mean radii as calculated without Ca. Inspecting the Ca-free values, wagnerites build a group with mean radii between 0.72–0.725 Å. Triplites, however, range between 0.74–0.82 Å. If Ca is considered as a structural component in wagnerite, the correlation between unit cell volume and mean ionic radius is not as well defined (Fig. 4). The pronounced difference in ionic radii between Mg: 0.72 and Ca: 1.00 Å, both in octahedral coordination (SHANNON 1976), seems to preclude substantial Ca incorporation into natural wagnerite. Probably, most Ca analysed in natural samples results from apatite alterations or impurities. However, AUH and HUMMEL (1974) describe experiments where they substituted up to 15.5 mol% Mg by Ca at 930 °C.

GENETIC CONSIDERATIONS

Wagnerite occurs as an accessory mineral in different rock types which are formed within a wide range of metamorphic conditions. It has been described from diagenetic (BRAITSCH 1960) to eclogite-granulite facies rocks (NOVÁK and POVONDRA 1984). Thus, specific temperature and/or pressure ranges do not seem to be the main controlling factors for the limited occurrence of the mineral. More restricting for the formation of the magnesio-fluoro-phosphate seems to be the chemical composition of the host rocks. Mg and P are common elements in varying concentrations in nearly every metamorphic and magmatic rock. Despite, this wide distribution of the main costituents of wagnerite, the magnesio-fluoro-phosphate remains scarce. PROPACH (1976a), SHERIDAN et al. (1976), as well as NOVÁK and POVONDRA (1984) proposed that Mg-rich and Ca-poor rock chemistry favors the formation of wagnerite. This is supported by the described assemblages of Mg-rich minerals like cordierite, sapphirine pyrope, orthopyroxen, taaffaite, and phlogopite. On the other hand, the criterion of Ca-poor but Mg-rich rock chemistry seems to be premature for a general explanation of the limited occurrence of wagnerite. In fact, only one partial quantitative analysis of wagnerite bearing rock (MgO: 23 wt.% and CaO: 0.58 wt.%, NOVÁK and POVONDRA, 1984) is available.

The wagnerite-bearing rocks of Miregn are metapelites with a mineralogy corresponding to that of the wagnerite-bearing metapelites in the Santa Fe

Table 3   Selected analyses of wagnerite-bearing (WR) and wagnerite-free (AI) rocks with high Mg- and low Ca-content fr

	WR1	WR2	WR3	AI365	AI573	AI587	AI526	AI633	AI523
SiO_2	52.0	51.0	54.4	38.1	65.4	59.9	51.7	76.2	68.0
Al_2O_3	21.5	21.5	19.6	26.0	14.8	19.5	15.1	10.7	18.4
Fe_2O_3	0.3	0.5	0.4	0.4	0.8	0.4	0.8	0.6	0.2
FeO	3.9	3.8	3.6	10.7	4.2	3.2	6.4	3.5	1.9
MnO	0.04	0.05	0.05	0.07	0.07	0.06	0.08	0.05	0.08
MgO	8.2	8.3	7.5	10.0	5.7	7.7	14.2	3.6	5.1
CaO	0.9	1.0	1.0	0.4	0.5	0.7	0.6	1.3	1.0
Na_2O	5.5	6.0	5.5	2.5	1.5	1.8	0.4	0.5	1.7
K_2O	4.6	4.9	4.7	6.6	2.2	2.7	6.0	0.1	0.6
TiO_2	0.2	0.2	0.2	1.1	0.8	0.4	0.8	0.5	0.1
P_2O_5	0.3	0.3	0.3	0.2	0.3	0.5	0.5	0.7	0.6
F	0.4	0.4	0.3	0.1	0.1	nd	0.3	0.1	nd
H_2O	1.9	2.3	2.2	3.9	2.8	1.9	2.4	1.9	2.3
Sum	99.74	100.25	99.7	100.07	99.17	98.56	99.28	99.75	99.98

Mountains (SHERIDAN et al. 1976). For understanding the conditions of wagnerite formation whole rock analyses of Mg-rich and Ca-poor wagnerite-free rocks of the Simano Nappe (IROUSCHEK-ZUMTHOR 1983) are compared with the chemistry of the wagnerite-bearing rocks of Miregn (Table 3). The comparison of the ratios Ca/Mg versus Ca/P (Fig. 5) indicates that Ca-poor, Mg-rich rock chemistry alone is not sufficient to explain wagnerite formation in these rocks. Wagnerite-bearing rocks plot on the right side of Fig. 5 and it remains puzzling why this high Ca/P ratio led to wagnerite and not predominantly to apatite crystallization. However, it can be assumed that a certain amount of Ca might have been fixed in albitic feldspars (An: 0.06–0.10) prior to wagnerite formation. Thus, subtraction of anorthitic Ca-content becomes necessary to estimate the "available" Ca-content. Fig. 6 compares this residual atomic Ca-value versus the atomic P-content. It is striking that wagnerite-free rocks in Fig. 6 plot close to a line which characterizes a Ca/P ratio of 5/3 (apatite). In fact, thin section study shows that apatite is present in all these rocks. The scatter of values is also explained by other phosphates in minor concentrations such as monazite. The wagnerite bearing rocks form a cluster below the Ca/P = 5/3 line which is characteristic of apatite.

Fig. 5 clearly indicates that low Ca/Mg- and Ca/P-ratios in metapelites are not enough to explain the occurrence of wagnerite. Additional elements which
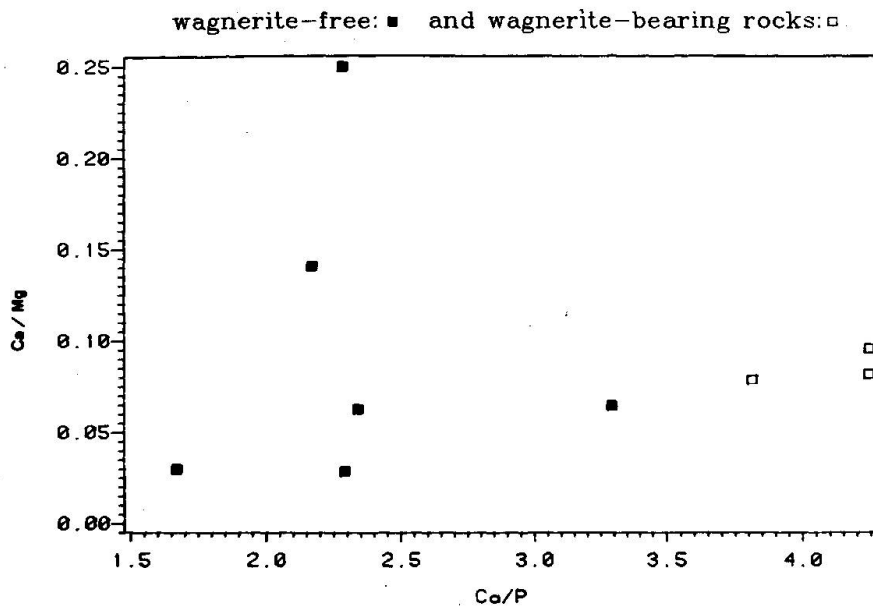
wagnerite—free: ■ and wagnerite—bearing rocks: □

Fig. 5 The atomic ratios Ca/Mg versus Ca/P of wagnerite-free (filled squares) and wagnerite-bearing rocks (open squares) are plotted. This diagram indicates that Ca-poor and Mg-rich rock chemistry is not sufficient to explain wagnerite formation.
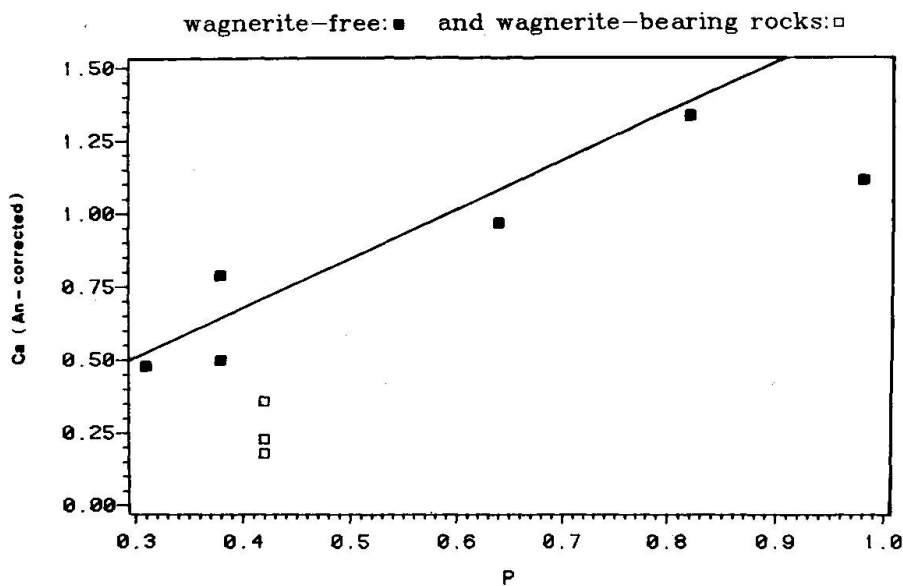
wagnerite—free: ■ and wagnerite—bearing rocks: □

Fig. 6 All rock analyses (Table 3) were corrected for Ca fixed in albitic feldspar (An: 0.08) and the residual Ca-content is plotted versus the atomic P-concentration. Wagnerite bearing rocks plot below the Ca/P = 5/3 (apatite Ca/P-ratio).

stabilize Ca-bearing minerals also influence the wagnerite formation. At Mi-regn, the high Na-content of the wagnerite-bearing rocks led to albitic feldspar formation. The feldspar structure accommodates Ca to build an albite—anor-thite solid solution series and withdraws Ca. Thus, a deficit of "available" Ca relative to the P-content (for apatite formation) is responsible for wagnerite for-mation.

Acknowledgements

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