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Tourmaline Rocks Associated with Stratabound Scheelite Mineralization in the Austroalpine Crystalline Complex, Austria

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With 6 Figures

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Summary

This contribution demonstrates, for the first time, the close genetic relationship of concordant tourmaline rocks (tourmalinites) to stratabound tungsten mineralization and their wide regional distribution within the polymetamorphic Austroalpine Crystalline Complex of the Eastern Alps. The occurrences investigated are located in parts of the Austroalpine Crystalline Complex consisting of metavolcanoclastic and metacalcareous sequences of probable Lower Paleozoic age. Tourmalinites composed of tourmaline, quartz, plagioclase, ± almandine-rich garnet, ± muscovite, ± biotite, and minor ilmenite, rutile, graphite,· ± pyrite and, rarely, scheelite are of pre- to synmetamorphic origin. Tourmalines from the tourmalinites have been identified as intermediate members of the dravite-schorl solid solution series with minor amounts of other tourmaline end members. They can be compared to tourmalines from massive sulphide and stratabound tungsten deposits. Tourmalines from pegmatoids, on the contrary, plot close to the schorl end member. Tourmalinites are interpreted as metamorphosed products of clastic sedimentary material which has reacted with boron-rich solutions of probable exhalative-hydrothermal origin. These exhalative processes are genetically connected to the transport of B and W and to the formation of syngenetic/syndiagenetic tungsten mineralization. Metamorphic mobilization of these primary concentrations led, during the Variscan and the Alpine metamorphic events, to the formation of scheelite-bearing quartz-tourmaline-, quartz-plagioclase-tourmaline mobilizates and pegmatoids.

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Zusammenfassung

Turmalingesteine und schichtgebundene Scheelitvererzungen im polymetamorphen Kristallin der Ostalpen, Österreich

Erstmals konnte auch in den Ostalpen die enge genetische Beziehung und weite Verbreitung schichtiger Turmalingesteine (Turmalinite) zu schichtgebundenen Wolframvererzungen gezeigt werden. Die bearbeiteten Vorkommen liegen in Teilen des polymetamorphen ostalpinen Kristallins, eingeschaltet in eine bunte metavulkanoklastisch-, metakarbonatische Abfolge, wahrscheinlich altpaläozoischen Alters. Turmalinite setzen sich mineralogisch aus Turmalin, Quarz, Plagioklas, ± almandinreichem Granat, ± Muskowit, ± Biotit, untergeordnet Ilmenit, Rutil, Graphit, ± Pyrit und selten Scheelit zusammen und sind prä- bis synmetamorph gebildet worden. Die Turmaline aus den Turmaliniten sind als intermediäre Glieder der Dravit-Schörl-Mischkristallreihe mit untergeordneter Beteiligung anderer Turmalinendglieder bestimmt worden; sie sind in ihrem Mineralchemismus vergleichbar mit Turmalinen aus massiven Sulfid-, und schichtgebundenen Wolframlagerstätten. Turmalin aus Pegmatoiden steht hingegen dem Schörlendglied nahe. Die Turmalinite werden als metamorphe Produkte klastischer Sedimente, die mit borreichen Lösungen, wahrscheinlich exhalativ-hydrothermaler Herkunft, reagiert haben, gedeutet. Diese exhalativen Prozesse stehen mit der Zufuhr von Bor und Wolfram und der Bildung syngenetischer/syndiagenetischer Wolframvererzungen in enger Verbindung. Im Zuge der variszischen und alpinen Orogenesen wurden diese Ausgangsgesteine mehreren Metamorphosen unterworfen, während der es zur Bildung von scheelitführenden Quarz-Turmalin-, Quarz-Plagioklas-Turmalin-Mobilisaten und Pegmatoiden kam.

Introduction

Tourmaline is the most common boron mineral in sedimentary, metamorphic, and felsic rocks and in some associated metallic mineral deposits. Tourmaline is a common gangue mineral in postmagmatic Sn, W and Cu deposits associated with granitic rocks. Tourmaline-rich rocks have recently been recognized associated with stratabound and stratiform submarine hydrothermal ore deposits of Cu, Pb, Zn, Ag, Co, W, Sn and Au (*Fleischer* and *Routhier,* 1973; *Slack,* 1982; *Barnes,* 1983; *Campbell* and *Ethier,* 1983; *Plimer,* 1983, 1986; *Taylor* and *Slack,* 1984) in Archean (*Appel,* 1986; *Appel* and *Garde,* 1987), Proterozoic (*Ethier* and *Campbell,* 1977) and Phanerozoic (*Taylor* and *Slack,* 1984) terrains. Furthermore, tourmaline-rich rocks are associated with both sediment- and volcanic-hosted massive sulphide deposits (*Slack,* 1982; *Taylor* and *Slack,* 1984; *Plimer* and *Lees,* 1988).

Although it is well known that tourmaline occurs associated with Sn and W deposits of granitic origin, stratabound and stratiform Sn and W deposits associated with tourmaline-rich rocks have only recently been recognized (*Plimer,* 1980). These are associated with facies equivalents of various exhalites of unusual composition and of submarine hydrothermal deposits of Pb—Zn—Ag (e.g., Broken Hill, Australia; *Plimer,* 1983). Stratabound scheelite-bearing calc-silicate rocks associated with tourmaline-rich rocks have been reported from the San Luis Province, Argentina (*Delakowitz,* 1987; *Hack,* 1987). *Appel* (1986) described scheelite-bearing tourmalinite, scheelite hosted by tourmaline-bearing amphibolite with associated tourmalinite and scheelite-bearing calc-silicate rocks. Scheelite and wolframite-bearing bedded tourmalinites were reported by *Cunningham* et al. (1973) from Zimbabwe.

The aim of this paper is to document for the first time the close association of tourmaline-rich rocks and tourmalinite with widespread scheelite-bearing marbles and calc-silicate rocks of the Austroalpine Crystalline Complex (ACC) on the basis of mineralogical, petrological and geochemical investigations.

Geological Setting

Scheelite has recently been discovered over hundreds of square kilometers in the polymetamorphic series of the Stub-, Kor-, Saualpe, the Wölzer and Schladminger Tauern, the Murtaler Berge und even in the easternmost equivalent parts of the Austroalpine Crystalline Complex (ACC), in the metamorphic areas of Anger and St. Radegund (*Höll,* 1977; *Neinavaie* et al., 1985). Within the higher metamorphosed parts of the ACC east of the Hohe Tauern, scheelite occurrences are also known from the Sb—W—(Hg) mineralization of the Kreuzeck Mountains (*Lahusen,* 1972; *Reimann* and *Stumpfl,* 1985).

These polymetamorphic areas are ascribed to the Middle Austroalpine (*Tollmann,* 1977) or to the Upper Austroalpine (*Frank,* 1987) tectonic units of the Eastern Alps. They are mainly composed of metaclastic, metavolcanic, and in higher stratigraphic positions, of metacalcareous rock sequences. Large segments of the ACC have been recognized to represent metamorphic equivalents of Old Paleozoic (volcano)-sedimentary sequences (*Becker,* 1977; *Neubauer,* in *Flügel* and *Neubauer,* 1984).

Three main metamorphic events have recently been distinguished within the ACC (*Frank* et al., 1983). A first thermal metamorphic event, only preserved in the Koralpe and the southern region of the Wölzer Tauern, has been overprinted by two tectonic events of coeval regional metamorphism and deformation. These events equate with the Variscan and the Eoalpine geodynamic development of the Eastern Alps (*Frank,* 1987).

The grade of metamorphism varies on a regional basis. The highest metamorphic grades in the study area are present in the central parts of the Koralpe where Variscan as well as Eoalpine metamorphism reached amphibolite facies conditions. Associated with the Cretaceous upper amphibolite facies metamorphism was intense simple shear deformation ("Plattengneis tectonics") caused by crustal shortening and resulting in large recumbent folding of these crystalline areas. The lowest metamorphic grade zones have been recorded in the area of the scheelite mineralization at Gstoder, Murtaler Berge; here the maximum metamorphic grade was upper greenschist facies. According to *Frank* (1987) these parts of the Austroalpine Crystalline Complex differ from the crystalline areas of the Seckauer Tauern, the Gleinalpe and the Troiseck Crystalline unit where—reflecting the different geological development—tungsten mineralization and adjacent tourmaline rocks are unknown.

Tourmaline Rocks

Most of the tourmaline rocks described and the associated stratabound scheelite mineralization are situated in the polymetamorphic series of the Stubalpe and Koralpe. Minor occurrences have been observed in the crystalline complexes of Anger, the Wölzer Tauern and the Murtaler Berge (Fig. 1).

Tourmaline is present in a number of different rock types:

1. In calc-silicate rocks and amphibolites (Wölzer Tauern: Pusterwald),

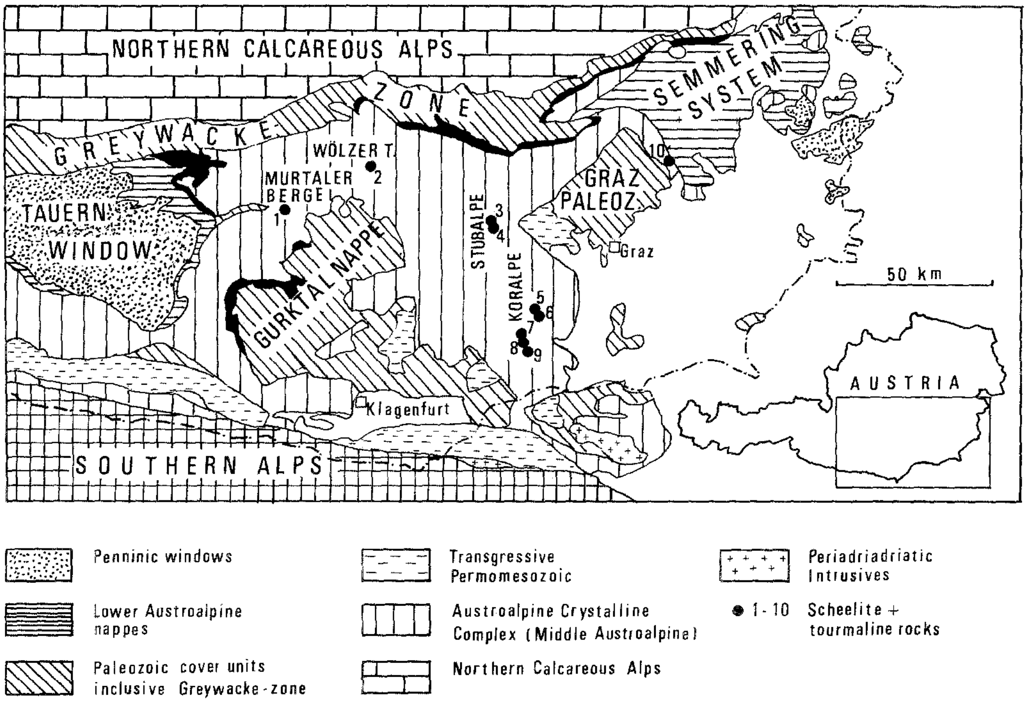

Fig. 1. Tectonic map of the eastern part of the Eastern Alps (after *Frank*, 1987) and location of tourmaline occurrences and associated scheelite mineralization within the Austroalpine Crystalline Complex *1* Gstoder, *2* Pusterwald, *3* Hirschegg/Moasterboden, *4* Hirschegg/Petereralpenbach, *5* Brandgraben/Weinebene, *6* Weißwassergraben/Prössinggraben, *7* Goding, *8* Schloßgraben, *9* Krakaberg/Friesacher Graben, *10* Naintsch/Anger

2. in stratiform tourmalinites and tourmaline-rich metaclastic rocks (Stubalpe: Hirschegg/Moasterboden, Hirschegg/Peteralpenbach; Koralpe: Krakaberg/Friesachergraben, Schloßgraben, Brandgraben/Weinebene; Crystalline Complex of Anger: Anger/Naintsch),
3. in quartz-, quartz-plagioclase mobilizates (Stubalpe: Hirschegg/Moasterboden, Hirschegg/Peteralpenbach; Koralpe: Brandgraben/Weinebene, Weißwassergraben; Wölzer Tauern: Pusterwald; Murtaler Berge: Allgäubach), and
4. in pegmatites and pegmatoids (e.g., Koralpe: Goding).

These rocks are widely distributed within the ACC and are always clearly linked to a well-defined stratigraphic horizon, mainly composed of metapelitic and metapsammopelitic sediments (Glimmerschieferserie, Gneisglimmerschieferserie, Wölzer Glimmerschiefer). Thin scheelite-bearing marbles and calc-silicate rocks, tourmalinites, graphitic schist, amphibolites and quartzites are also intercalated with these metaclastic sequences. The stratigraphic control is evident on the regional and the local scale.

Tourmaline has also been recognized from other tungsten occurrences in the Lower Austroalpine and Penninic zones. Tourmalinites have not been encountered in the Old Paleozoic metaclastic-metacalcareous sequences hosting syngenetic/syndiagenetic scheelite occurrences in the Lower Austroalpine tectonic unit (*Höll*, 1977). Tourmaline has, however, been observed as a minor mineral in phyllites interfingering with scheelite-bearing Fe-dolomites at Klamm Alm, Navis (Tyrol) in the Innsbrucker Quartzphyllite Zone (*Raith,* 1983). It has also been observed with pyrite, chalcopyrite, gold, ilmenite, magnetite and scheelite in quartz tourmaline mobilizates intercalated with chlorite-sericite phyllites at Mühlbach/Neunkirchen, Salzburg, (*Neinavaie,* pers. comm.) of the same series.

Within the tungsten occurrences of the Penninic zone of the Hohe Tauern, tourmaline has been reported from the Cu—Pb—Zn—Au—(W) deposits around Schellgaden (*Tischler* and *Ucik,* 1976) and from the Felbertal (Mittersill) tungsten mine (*Höll,* pers. comm.). At Felbertal, tourmalinites and scheelite-bearing calc-silicate rocks have recently been discovered in the eastern part of the mine and the surrounding area (*Gilg,* pers. comm.). These tourmalines from tourmalinites at the edge of the eastern orebody at Felbertal are similar in composition to those from the ACC (*Plimer,* 1987).

Mineralogy of Tourmalinites

According to *Slack* (1982) tourmalinites are defined as stratabound rocks units containing 20% or more tourmaline by volume. *Nicholson* (1980) used this term for rocks containing more than 15 vol% of tourmaline and 90 vol% of combined quartz and tourmaline. Slack emphasizes the non-genetic meaning of this term that should not be confused with terms such as tourmalite or luxullianite (quartz tourmaline rocks formed by postmagmatic pneumatolytic processes). This paper follows the definition of *Slack* regardless of restrictions by mineralogical composition proposed by *Nicholson,* as transitions to tourmaline-rich metapelites and variations in mineralogy are common on the microscopic scale.

In the field, tourmalinites are difficult to recognize. Minor graphite contents impart a black colour and may lead to confusion with dark fine grained amphibolites or graphitic quarzites and schists. Interlaminate layering of tourmaline, quartz, plagioclase, and mica minerals displays a well defined metamorphic fabric. Single tourmaline grains generally show prismatic growth forming sub- to euhedral crystals of about one mm length and are elongated parallel to the plane of foliation. The mineralogical composition of some samples investigated is listed in Table 1. Quartz, tourmaline and plagioclase are major and garnet and micas minor minerals. Ilmenite, rutile, graphite, and rarely sphene are common accessories. Clinozoisite, chlorite, apatite, and kyanite have also been identified. Kyanite is restricted to Al-rich lithologies.

Plagioclase from samples of the Stubalpe contains 20 mole% anorthite. White micas from the same locality are composed of 92 mole% muscovite and 8 mole% paragonite. Garnets (alm 64–68, sps 1–6, pyr 8–13, grs 18–22, adr 0–2) display normal zoning with an increase in Mg/Fe and a decrease of total Ca and Mn from the core to the rim of the zoned garnets. This type of zoning is the same as zoning in garnets from adjacent micaschists and calc-silicate rocks and is the same as metamorphic growth zoning produced during prograde regional metamorphism (*Tracy,* 1982). For the samples from Stubalpe where the Eoalpine metamorphic overprint only reached (lower?) greenschist facies conditions, this prograde metamorphic zoning is correlated with the Variscan lower amphibolite facies metamorphism.

Graphite, rutile, ilmenite and rare pyrite, goethite, arsenopyrite and chalcopyrite are the opaque minerals present. Graphite in amounts of up to several percent is

Table 1. *Mineralogical Composition of 15 Tourmaline Rocks from the ACC.* qu quartz, pg plagioclase, tu tourmaline, gt garnet, mu muscovite, bi biotite, il ilmenite, ru rutile, ti titanite, gp graphite, py pyrite, sc scheelite, cz clinozoisite, cl chlorite, ap apatite, ky kyanite, M major, m minor, a accessory mineral

	qu	pg	tu	gt	mu	bi	il	ru	ti	gp	py	sc	others
Hirschegg													
E 10	M	M	m	m	-	m	a	a	-	a	-	-	
E 15	M	M	M	m	m	a	a	a	a	a	-	-	
E 27	M	M	M	m	m	m	a	a	a	a	-	-	cz,cl,ap
E 297	m	M	M	-	m	-	a	a	-	m	-	-	
E 298/2	M	M	m	m	M	m	a	a	-	m	-	-	cz
E 300	M	M	M	m	a	-	a	a	-	a	a	-	cz
HI	M	M	M	a	a	a	a	a	-	a	a	m	cl
Krakaberg													
E 90	m	m	M	a	M	-	a	a	-	a	-	-	
E 310	M	m	M	a	m	a	a	a	-	a	a	-	
Schloßgraben													
E 326/1	M	M	m	m	M	m	-	a	-	a	-	-	ky
E 334	m	M	m	m	M	m	-	a	-	-	-	-	cl,ap,cz
7,8	m	m	m	m	M	m	a	a	a	-	-	-	ap
Brandgraben													
E 374	M	m	M	m	M	-	-	a	-	-	-	-	
Anger													
D 62/82	M	M	M	-	M	-	a	a	-	-	-	-	
F 55 A	m	M	M	m	m	m	a	a	-	a	a	-	cz,ap

often oriented parallel or subparallel to the schistosity or in more recrystallized types is of sphaerolitic texture. Arsenopyrite, chalcopyrite and pyrite are present as minute inclusions in tourmaline and garnet. Microprobe analyses of ilmenite showed higher Mn contents although Mn haloes are better developed in adjacent marbles and calc-silicate rocks. Maximum contents of 30 mole% pyrophanite have been detected in ilmenites from scheelite-baring tourmaline rocks whereas scheelite-free ones show lower Mn contents.

Metamorphism and Structural Development of the Tourmalinites

The relationship of crystallization to the structural development is here discussed in more detail for tourmaline rocks from the Stubalpe. Two main styles of deformation and correlated metamorphic crystallization have been distinguished in the metaclastic wallrock and in the tourmalinites of the Stubalpe. The older and most penetrative event is characterized by the main metamorphic layering, the orientation of micaceous minerals, development of a coarse microfabric and strong deformation (D 1) including isoclinal folding which is thought to be of Variscan age (*Krohe*, 1984; *Frank* et al., 1983). An early generation of staurolite, kyanite, and garnet

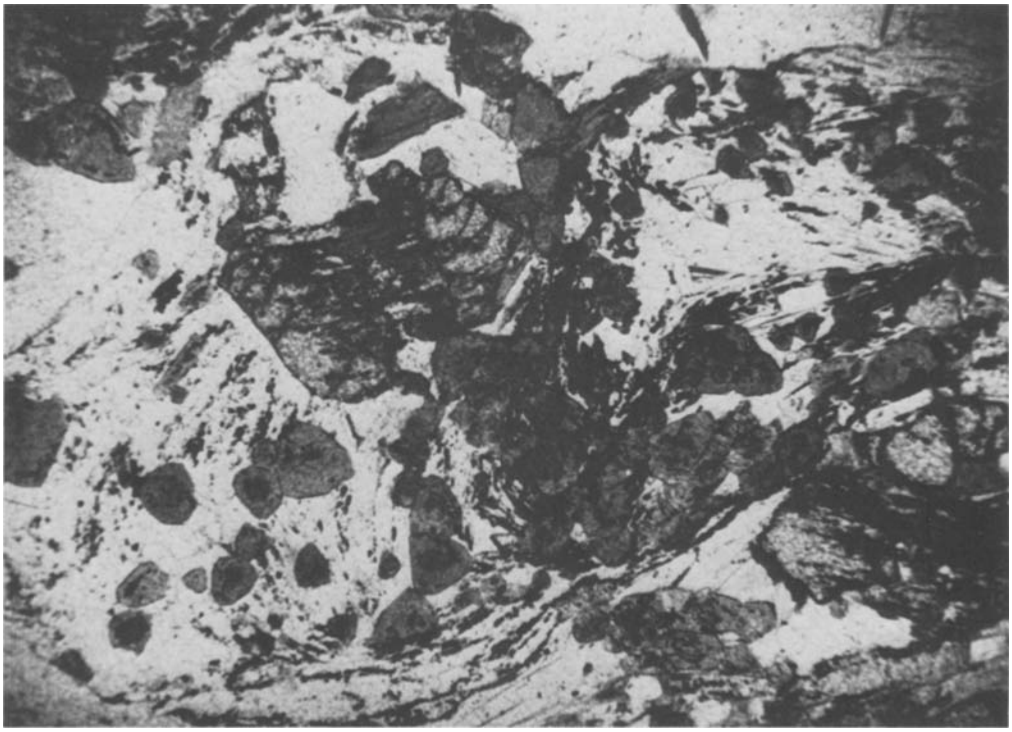

Fig. 2. Tourmaline-garnet-mica schist, Hirschegg/Peteralpenbach, Stubalpe. Tourmaline, garnet, muscovite and biotite are overgrowing isoclinally folded darker zones of opaque material.Tourmaline is therefore pre- to synmetamorphic. Later lighter coloured rims are correlated with Eoalpine recrystallization and metamorphism

has grown during this event. Inclusions of quartz, ilmenite, rutile, tourmaline and sigmoidal darker zones of graphite are restricted to garnet core zones, whereas the rim zones are free of dark zones and inclusions. Some tourmalines show similar features. Core zones with graphitic inclusions may be surrounded by graphite-free rims (Fig. 2). Tourmaline inclusions within garnet display a different texture to tourmalines in the metamorphic matrix. These fine needles are less than 0.01 mm in length, but show the same optical features as coarse-grained tourmaline. As isoclinally folded dark zones can be seen in coexisting garnet, biotite, and tourmaline, these mineral parageneses must have been formed at the latest synkinematically during the first Variscan regional metamorphism and deformation (Fig. 2). During Eoalpine metamorphism, tourmaline and the coexisting silicate minerals recrystallized under greenschist facies conditions. An accompanying second main type of deformation (D 2; open folding and crenulation cleavage) is correlated with this event. Tourmaline is partly reoriented to S 2.

In equivalent series of the Koralpe, the interrelations of crystallization and deformation are, due to the intense Cretaceous metamorphism, less obvious in the tourmaline rocks. They can, however, be correlated with single phases of the regional metamorphic history of calc-silicate rocks in the area (*Raith,* 1986).

Tourmaline and Scheelite in Quartz-Feldspar Mobilizates and Pegmatoids

Tourmaline-rich quartz-plagioclase mobilizates commonly interfinger with tourmalinites or grade into those rocks. Tourmaline from those metamorphic mobilizates normally contains a dark graphite-bearing zone compared with tourmaline from the tourmalinites. It may also be devoid of this graphitic zone especially when it forms larger individual crystalls (up to several mm). They also display a more distinctive optical zoning with blue to yellow/green cores and green/brown rims.

Quartz and oligoclase are the major components besides tourmaline. Muscovite, garnet and scheelite are minor. Porphyroblastic scheelite is present at the contact of the tourmaline rocks with the adjacent calc-silicate rocks. These rocks are composed of clinozoisite/zoisite, quartz, Ca-rich almandine and disseminated scheelite. At Hirschegg/Moasterboden they also contain folded scheelite-quartz veinlets.

At Goding, Koralpe, a thick metaclastic series ("Zentrale Serie") comprising calc-silicate rocks and amphibolites is characterized by intense quartz-feldspar mobilization and formation of pegmatoids, varying from several dm to some tens of m in thickness. Albite, microcline, and quartz are the major, muscovite, garnet, and tourmaline (up to 10 vol%) are the minor and zircon, titanite, apatite, calcite, actinolite and scheelite are the accessory minerals. At the contact of the pegmatoids with the calc-silicate rocks disseminated scheelite is concentrated. Tourmaline is always black in hand specimen showing distinctive pleochroism and optical zoning in thin section.

This type of pegmatoid is widespread in the higher metamorphic areas of the ACC. In general, they are interpreted as products of fluid-rich metamorphic processes, as they show no genetic or spatial relationship to igneous activity. The genetic situation of spodumene-bearing, scheelite-free pegmatites within the same geological series, however, is conjectural.

Mineral Chemistry and Zoning of Tourmaline

The general formula of tourmaline is: $XY_3Z_6(BO_3)_3Si_6O_{18}(OH)_4$. The main cations in the X site are Na, Ca, Mg and vacancies. The octahedral Y-site is mainly occupied by Al, Fe^{2+}, Fe^{3+}, Li, Mg, and Mn, the Z-site typically by Al but to a minor extent also by Fe^{2+}, Fe^{3+}, Ti, Mg, Cr^{3+} and V^{3+}. Some Si in the tetrahedral site can be replaced by Al. In the hydroxyl site F^-, Cl^- or O^- can replace OH^-. Boron is in regular triangular coordination and has no apparent substituents. This fact is important for the assumptions made to calculate the structural formula and the boron contents of tourmaline from microprobe analyses. Studies of the tourmaline solid solution series have demonstrated that besides the common natural solid solutions of schorl [$NaFe_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$] dravite [$NaMg_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$] and schorl elbaite [$Na(Li,Al)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$] (*Epprecht*, 1953) numerous additional substitutional schemes have to be considered. An excellent review concerning the classification of common tourmaline end members and important substitutional schemes within the tourmaline group representing the present stage of investigation is given by *Henry* and *Guidotti* (1985).

The mineral chemistry of tourmaline from different localities and geological settings has been determined using microprobe and XRD analysis. The tourmaline from the tourmalinites show small variations in the distribution of SiO_2 and Al_2O_3. The contents of FeO range between 4.87 and 8.84 weight% FeO (mean = 6.75%), the

Table 2. *Important Substitutional Schemes and Exchange Components in Tourmalines from Tourmaline Rocks in the ACC* (according to *Henry* and *Guidotti*, 1985)

site substitutions	exchange components	
$Fe^{2+}_{y}{}^{*} = Mg_{y}$	$MgFe_{-1}$	dravite-schorl substitution
$Na_{x} + Al_{z} = Ca_{x} + Mg_{z}$	$CaMgNa_{-1}Al_{-1}$	uvite substitution
$Na_{x} + Al_{y} = Ca_{x} + Fe^{2+}_{y}$	$CaMgNa_{-1}Al_{-1}$	
$Mg_{y} + Si_{T} = Al_{y} + Al_{T}$	$Al_{2}Mg_{-1}Si_{-1}$	tschermaks substitution
$Na_{x} + Mg_{y} = Al_{y} + \square_{x}{}^{**}$	$AlNa_{-1}Mg_{-1}$	alkali-defect substitution
$Mg_{y} + OH^{-} = Al_{y} + O^{2-}$	$AlMg_{-1}H_{-1}$	aluminobuergerite substitution
$Fe^{2+}_{y} + OH^{-} = Fe^{3+}_{y} + O^{2-}$	H_{-1}	buergerite substitution
$OH^{-} = F^{-}$	FOH_{-1}	

* The subscripts represent the X-site (x), the Y-site (y), the Z-site (z) and the tetrahedral site (T) in the general structural formula

** This symbol represents a vacancy in the X-site

contents of MgO between 5.09 and 9.02 weight% MgO (mean = 6.55%). The mean FeO/FeO + MgO ratios of these tourmalines vary between 0.43 to 0.58 and the $Na_2O/Na_2O + CaO$ ratios range between 0.68 and 0.81. TiO_2 content may reach 1.37 wt%. The chromium, manganese and potassium contents are extremely low. The values for zinc and nickel are always below the detection limit of the electron microprobe. It should be noted that manganese, even in an Mn-enriched matrix as indicated by the low Fe/Mn ratios of the whole rock analyses, is only slightly substituted in the analysed tourmalines. Therefore, the Mn-tourmaline [tsilaisite: $NaMn_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$] can be excluded from further interpretations. The same applies to the Li-tourmaline end members elbaite [$Na(Li,Al)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$] and liddicoatite [$Ca(Li,Al)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$], as whole rock analyses have only revealed a few ppm lithium.

Assuming 3 boron atoms in the (BO_3) site and 4 hydroxyl anions in the hydroxyl site per formula unit a simplified structural formula can be calculated on the basis of 29 oxygens (Table 3). These calculations show that different substitutional schemes have to be considered to explain variations in mineral chemistry (Table 2). Mg and Fe are the most important cations in the Y site. This complete miscibility of Mg and Fe can be described as solid solution between the two end members dravite and schorl. Whereas Mg dominates in tourmaline from tourmalinites (mean molar Mg/Fe = 1.30–2.38; Table 4), tourmalines from pegmatoids are Fe-dominated

Table 3. *Mean Mineral Composition of Tourmalines from Tourmalinites* (Hi Hirschegg/Petereralpenbach; E 27, G 30/4 Hirschegg/Moasterboden; E 310 Krakaberg/Friesachergraben; F 55 B Anger/Naintsch) and pegmatoids (E 101, Goding) from the ACC calculated on the basis of 29 oxygens

Sample	Hi	G30/4	E 27	E 310	F 55 B	E 101
	n=22	n=33	n=13	n=12	n=10	n=10
B_2O_3*	10.44	10.46	10.23	10.17	10.38	10.13
SiO_2	35.96	36.02	35.43	35.27	35.56	34.94
TiO_2	0.93	-	0.68	0.73	-	0.49
Al_2O_3	30.41	32.43	30.72	30.64	32.66	31.37
Cr_2O_3	0.06	0.03	0.02	0.06	0.06	0.01
FeO**	6.09	6.40	6.77	6.75	7.71	12.99
MnO	0.04	0.03	0.03	0.05	0.02	0.27
MgO	7.95	6.68	6.49	6.07	5.58	2.02
CaO	0.96	0.53	0.64	0.74	0.90	0.17
Na_2O	2.12	2.23	2.01	2.03	1.72	2.43
K_2O	0.01	0.01	0.00	0.02	0.02	0.01
	94.97	94.82	93.02	92.53	94.61	94.83
B	3.000	3.000	3.000	3.000	3.000	3.000
Si	5.984	5.984	6.019	6.026	5.953	5.997
AlT	0.016	0.016	0.000	0.000	0.047	0.003
AlZ	5.949	6.000	6.000	6.000	6.000	6.000
Cr	0.008	0.004	0.003	0.008	0.008	0.001
AlY	0.000	o.333	0.151	0.170	0.396	0.343
Ti	0.116	-	0.087	0.094	-	0.063
Fe	0.848	0.889	0.962	0.965	1.079	1.865
Mn	0.006	0.004	0.004	0.007	0.003	0.039
Mg	1.972	1.654	1.644	1.546	1.393	0.517
Y total	2.950	2.885	2.850	2.790	2.879	2.829
Ca	0.171	0.094	0.116	0.135	0.161	0.031
Na	0.684	0.718	0.662	0.673	0.558	0.809
K	0.002	0.002	0.000	0.004	0.004	0.002
X total	0.857	0.815	0.779	0.812	0.724	0.842

* B_2O_3 calculated on the basis of 3 boron atoms and 29 oxygens in the structural formula

** Total Fe calculated as Fe

(Mean molar Mg/Fe = 0.29). Beside Mg and Fe up to 30% Al can substitute in the Y site of the tourmaline structure resulting in an increase of total Al. This increase in the Al content can be explained by alkali defect and aluminobuergerite substitution (Table 2). Smaller amounts of Al (0 to 3%) replace Si in the tetrahedral site as a result of Tschermaks substitution.

The X site (alkali site) is mainly occupied by Na, Ca and vacancies, whereas K is negligible. The amounts of Ca in the X site can be explained by uvite substitution. The degree of Ca substitution is expressed in variations of the molar Na/Ca ratios.

Table 4. *Variation in Tourmaline Composition Expressed as Distribution of Cations Calculated on the Basis of 3 Boron and 29 Oxygens in the Structural Formula*

	Hi			G30/4			E 27		
	n=22			n=33			n=10		
	range	mean	s*	range	mean	s	range	mean	s
Mg/Fe	1.61-3.03	2.38	(0.52)	1.31- 2.85	1.96	(0.50)	1.26-2.21	1.61	(0.25)
Na/Ca	2.21-9.48	4.35	(1.76)	5.29-14.15	8.00	(1.88)	3.40-8.56	5.60	(1.62)
Si	5.80-6.07	5.98	(0.03)	5.86-6.05	5.98	(0.05)	5.91-6.01	5.97	(0.03)
Al T	0.00-0.06	0.02	(0.02)	0.00-0.14	0.03	(0.04)	0.00-0.09	0.03	(0.03)
Al Y	0.00-0.21	0.02	(0.06)	0.08-0.54	0.31	(0.15)	0.07-0.31	0.18	(0.09)
Al Z	5.80-6.00	5.91	(0.06)		6.00		5.92-6.00	5.99	(0.03)
Ti	0.06-0.71	0.12	(0.03)		-.--		0.04-1.73	0.09	(0.04)
Sum Y	2.87-3.07	2.98	(0.07)	2.83-2.94	2.88	(0.03)	2.84-2.90	2.89	(0.04)
Sum X	0.76-0.93	0.86	(0.05)	0.69-0.97	0.83	(0.08)	0.73-0.81	0.77	(0.03)

	E 310			F 55 B			E 101		
	n=12			n=8			n=15		
	range	mean	s	range	mean	s	range	mean	s
Mg/Fe	1.12-1.67	1.30	(0.18)	1.42-1.72	1.58	(0.09)	0.21- 0.39	0.29	(0.04)
Na/Ca	2.52-8.24	3.69	(1.51)	3.86-9.21	5.31	(1.67)	10.56-81.80	31.73	(18.64)
Si	5.84-6.05	5.95	(0.07)	5.88-5.99	5.94	(0.04)	5.89- 6.06	5.99	(0.05)
Al T	0.00-0.16	0.06	(0.06)	0.01-0.12	0.06	(0.04)	0.00- 0.11	0.02	(0.04)
Al Y	0.26-0.45	0.39	(0.07)	0.12-0.32	0.20	(0.08)	0.00- 0.53	0.29	(0.13)
Al Z		6.00			6.00			6.00	
Ti		-.--		0.04-0.13	0.09	(0.03)	0.23-0.15	(0.08)	(0.03)
Sum Y	2.78-2.94	2.87	(0.05)	2.81-2.87	2.85	(0.30)	2.72-2.87	2.81	(0.04)
Sum X	0.65-0.79	0.72	(0.04)	0.77-0.88	0.82	(0.04)	0.75-0.90	0.85	(0.04)

*s standard deviation, n number of analyses

In tourmalines from tourmalinites they range between 4.35–8.00. They are markedly higher in samples from pegmatoids (molar Na/Ca = 31.73). The amount of alkali-deficient tourmaline (*Werding* and *Schreyer,* 1984) is comparable in both groups of tourmalines, as shown by similar amounts of vacancies in the X site.

The amount of dehydroxylation can be estimated by further calculations. The Y site, unlike the X site, normally contains no vacancies. Tourmaline can therefore

Table 5. *Tourmaline Composition of Tourmalines from Tourmalinites and Pegmatoids Calculated on the Basis of 3 Boron Atoms and Full Occupancy of the Y site*

tourmalinites	
Hi	$(Na_{0.67}\ Ca_{0.19}\ \square^{**}\ _{0.14})\ (Mg_{1.94}\ Fe_{0.89}\ Ti_{0.12}\ Al_{0.05})\ Al_6\ Si_{6.08}\ (BO_3)_3\ (OH_{3.17}\ O_{0.83})$
G30/4	$(Na_{0.74}\ Ca_{0.10}\ \square_{0.16})\ (Mg_{1.70}\ Fe_{0.88}\ Ti^{*}\ Al_{0.42})\ Al_6\ Si_{6.09}\ (BO_3)_3\ (OH_{3.08}\ O_{0.92})$
E 27	$(Na_{0.66}\ Ca_{0.13}\ \square_{0.21})\ (Mg_{1.58}\ Fe_{1.00}\ Ti_{0.09}\ Al_{0.33})\ Al_6\ Si_{6.10}\ (BO_{3)3}\ (OH_{2.93}\ O_{1.07})$
E 310	$(Na_{0.70}\ Ca_{0.14}\ \square\ 0.16)\ (Mg_{1.55}\ Fe_{0.97}\ Ti_{0.09}\ Al_{0.39})\ Al_6\ Si_{6.06}\ (BO_3)_3\ (OH_{2.99}\ O_{1.01})$
F55B	$(Na_{0.57}\ Ca_{0.17}\ \square_{0.26})\ (Mg_{1.37}\ Fe_{1.07}\ Ti^{*}\ Al_{0.56})\ Al_6\ Si_{6.10}\ (BO_3)_3\ (OH_{2.73}\ O_{1.27})$
metapegmatoid	
E 101	$(Na_{0.83}\ Ca_{0.03}\ \square_{0.14})\ (Mg_{0.55}\ Fe_{1.92}\ Ti_{0.08}\ Al_{0.45})\ Al_6\ Si6.12\ (BO_3)_3\ (OH_{2.58}\ O_{1.42})$

** This symbol represents a vacancy in the X-site of the structural formula

* Not analysed

be calculated on the basis of 3 boron atoms and full occupancy of the Y site (Table 5). By assuming that charge balance is maintained by loss of a proton in the hydroxyl site the amount of O^- replacing OH^- can be estimated. The mean contents of oxygen substituting for hydroxyl vary between 21 and 32% in tourmalinites. By comparison, the tourmalines from a scheelite-bearing pegmatoid have a mean value of 35%. This calculated replacement of OH^- by O^- can be interpreted as effect of aluminobuergerite substitution. As some of the total Fe in the Y site may be trivalent and as some Mg may substitute for Na in the X site the calculated oxygen contents represent a minimum amount of dehydroxylation. According to other papers small quantities of OH^- are replaced by F^- and Cl^-; these have, however, not been determined in this study.

The mineral chemistry of tourmaline can also be presented in Al—Fe—Mg- and Ca—Fe—Mg diagrams (Fig. 6). In the former, tourmaline analyses from tourmalinite samples do not plot exactly on the dravite-schorl join but are slightly shifted towards higher Al contents. This fact reflects the discussed alkali-defect and aluminobuergerite substitution. The differences in mineral chemistry of these tourmalines, compared with tourmalines from the pegmatoids are also obvious; they include a markedly lower Mg/Fe and a higher Na/Ca ratio, small contents of Mn and a slightly higher aluminobuergerite component. The metapegmatoid tourmalines therefore plot close to the schorl end member in the two diagrams.

In summary, the tourmalines from the tourmalinites are characterized as intermediate to slightly Mg-enriched members of the schorl-dravite series with minor amounts of uvite-, alkali-deficient- and aluminobuergerite tourmaline component.

In contrast tourmalines from the adjacent pegmatoids are classified as Fe-rich dravite schorls with lower uvite, but similar contents of alkali-deficient- and slightly higher contents of aluminobuergerite tourmaline.

Zoning of Tourmaline

The optical mineral zoning of tourmaline is non-uniform. Dark cores displaying brown-green colours for n_ω are surrounded by green coloured rims. In other thin sections tourmaline may display bluish or yellow-brownish core zones merging into darker brown-greenish and brown-coloured rims. This second type of optical zoning is also typical for the tourmaline grains of the pegmatoids and for larger single crystals formed during recrystallization of the tourmalinites.

A more detailed investigation of the mineral chemistry of tourmalines from the Stubalpe area reveals a distinct chemical zoning (Fig. 3). High molar Na/Ca ratios,

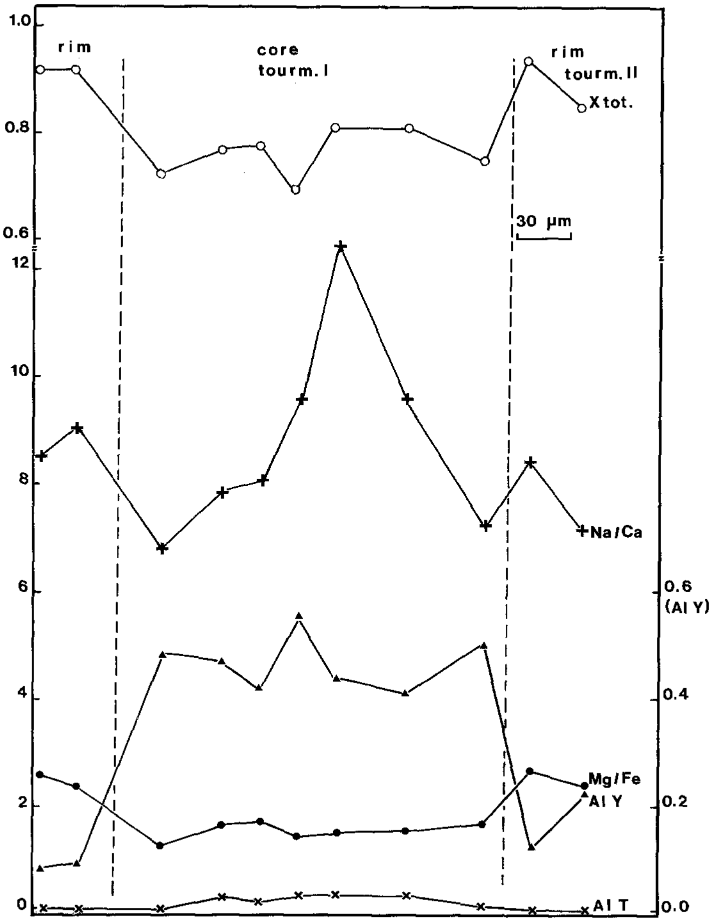

Fig. 3. Microprobe traverse across a tourmaline grain from a tourmalinite (see also Fig. 2), Stubalpe area, showing typical zoning and formation of two generations of tourmaline correlated to Variscan and Eoalpine metamorphism. The cations are calculated on the basis of 3 boron atoms and 29 oxygens in the structural formula. *X tot* represents the sum of the cations in the X site, *Al Y* the amount of Al in the Y site, *Al T* the amount of Al in the tetrahedral site of the tourmaline formula

Table 6. *Core and Rim Composition of a Tourmaline from a Tourmalinite (G 30/4) from the Stubalpe and a Scheelite-bearing Pegmatoid (E 101) from the Central Koralpe;* Mean of n analyses, standard deviation in parenthesis

	G 30/4				E 101	
	core		rim		core	rim
	n = 8		n = 4			
B_2O_3*	10.53	(0.04)	10.45	(0.04)	10.31	10.14
SiO_2	36.18	(0.20)	36.26	(0.23)	34.91	35.10
TiO_2	-.--		-.--		0.59	1.20
Al_2O_3	33.53	(0.41)	31.28	(0.34)	33.43	29.48
Cr_2O_3	0.03	(0.02)	0.06	(0.02)	0.00	0.00
FeO**	6.69	(0.37)	5.58	(0.25)	12.60	13.50
MnO	0.03	(0.03)	0.00	(0.00)	0.28	0.20
MgO	5.86	(0.41)	7.87	(0.29)	1.50	2.97
CaO	0.42	(0.11)	0.54	(0.02)	0.12	0.42
Na_2O	2.08	(0.20)	2.49	(0.12)	2.45	2.45
K_2O	0.01	(0.01)	0.02	(0.01)	0.00	0.05
	95.35	(0.32)	94.53	(0.41)	96.19	95.51
B	3.000		3.000		3.000	3.000
Si	5.970	(0.028)	6.033	(0.022)	5.886	6.019
Al T	0.032	(0.025)	0.000	(0.000)	0.114	0.000
Al Z	6.000	(0.000)	6.000	(0.000)	6.000	5.958
Al Y	0.488	(0.067)	0.132	(0.068)	0.528	0.000
Ti	-.---		-.---		0.075	0.155
Fe	0.923	(0.053)	0.776	(0.033)	1.776	1.936
Mn	0.004	(0.004)	0.000	(0.000)	0.040	0.029
Mg	1.44	(0.100)	1.951	(0.074)	0.377	0.759
Y total	2.860	(0.007)	2.867	(0.028)	2.796	2.879
Ca	0.074	(0.020)	0.095	(0.003	0.022	0.077
Na	0.665	(0.064)	0.802	(0.039)	0.801	0.815
K	0.001	(0.002)	0.004	(0.003)	0.000	0.011
X total	0.740	(0.075)	0.901	(0.039)	0.823	0.903

* B_2O_3 calculated on the basis of 3 boron atoms and 29 oxygens in the structural formula

** Total Fe calculated as FeO

which decrease from the core to the rim zone, with increasing Mg and Fe contents are typical. The core zones of tourmalines are also characterized by lower amounts of Si and higher amounts of Al, resulting in high amounts of Al in the Y site, some replacement of Si by Al in the tetrahedral site and more vacancies in the X site (Table 6). In the core zones about 30% and in the rims about 15% of OH^- are replaced by O^-.

Mineral chemistry does not change continuously towards the rim zone. Regarding the Na/Ca ratios and the Al contents in the Y site the abrupt change in mineral composition is evident (Fig. 3). The rim tourmalines also show higher Mg/Fe ratios,

Table 7. *Major, Minor (in %) and Trace Element Distribution of Tourmalinites (in ppm) from the ACC Determined by ICP-OES, XRF, and AAS Analytical Methods*

	ICP-OES			XRF			AAS		
	x	s	n	x	s	n	x	s	n
Si				26.3	3.63	13			
Ti				0.58	0.14	13			
Al				10.0	2.52	13			
Fe				3.87	1.62	13			
Mg				1.21	0.42	13			
Ca				0.85	0.56	13			
Na				1.62	0.56	13			
K				1.67	1.29	13			
As							< 2	-	9
Au							< 0.02	-	5
Ba				452	253	13			
Be	4	2	9						
Ce	71	42	9						
Cr	79	34	9						
Co	7	4	9						
Cu	49	37	9	44	31	12			
Ga	18	10	9						
Li							22	12	9
Mn				900	600	13			
Mo				10					
Nb	10	4	9						
Ni	15	8	9						
P	570	155	8						
Pb	23	10	9	24	10	13			
Rb				74	65	12			
Sb							0.15	0.13	8
Sc	19	6	9						
Sr	201	75	9	180	72	12			
Th				15	6	11			
U				3	1	12			
V	96	34	9						
W				11	13	12			
Y	21	12	9	18	10	12			
Zn							58	17	9
Zr				165	65	13			

x mean, s standard deviation, n number of samples analysed an excess in Si (Si higher than 6) and less vacancies in the X site. An interpretation of this mineral zoning as well as data on the petrography and metamorphic history of the Stubalpe area will be given later.

Geochemistry of Tourmaline Rocks

The distribution of the major, minor and trace elements has been determined by XRF, ICP-OES, and AAS techniques and are summarized in Table 7. SiO_2 contents vary between 42 and 62% and can be explained by variations in the boron contents, which reflect the changing amounts of tourmaline in these rocks. The mean value for aluminium is 19% Al_2O_3. Higher contents have been measured only where modal kyanite is present.

To examine the genetic aspects, silica, aluminium and iron have been plotted in the *Moore* and *Dennen* diagram (1970) for the chemical classification of clastic sedimentary rocks (Fig. 4). The Fe/Al ratios correspond to those of clastic sediments. Higher amounts of aluminium are restricted to a sample showing incipient regional metamorphic mobilization. The lower Si contents may be explained by large amounts of boron replacing silica in tourmaline rocks. Considering the shift to lower Si contents, the analysed tourmalinites have mainly been derived from shales, with minor contributions from greywackes and arkoses and only rarely from quartzites. These results are in good agreement with petrographic observations.

The chemical composition of the tourmalinites compared with average values of shales (*Turekian* and *Wedepohl,* 1961; *Schroll,* 1975) reveal the close geochemical

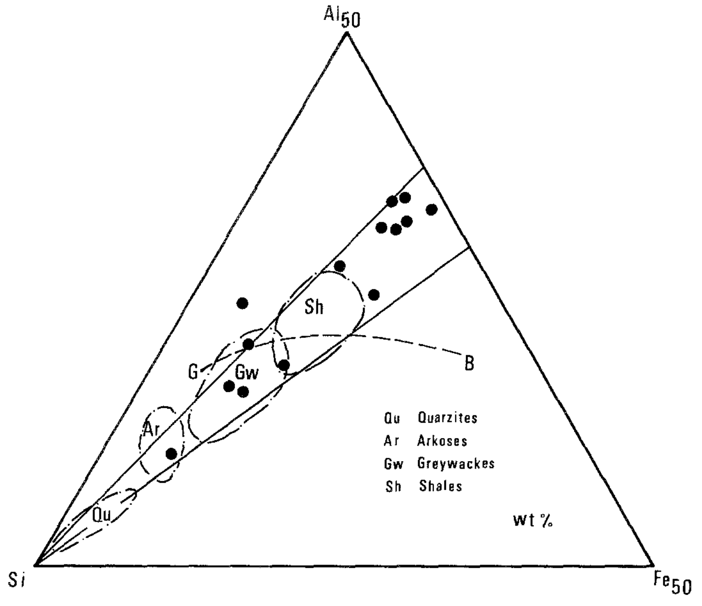

Fig. 4. Si – Al_{50} – Fe_{50} diagram for the classification of clastic sediments (after *Moore* and *Dennen,* 1970). The 14 tourmalinite samples from the Austroalpine Crystalline Complex display typical Fe/Al ratios compared with clastic sediments. The precursor rocks of the tourmalinites must be interpreted mainly as shales, minor greywackes and arkoses and only rarely as quartzites. The dashed line *G–B* represents the empirical composition line of felsic (*G*) to mafic (*B*) rocks

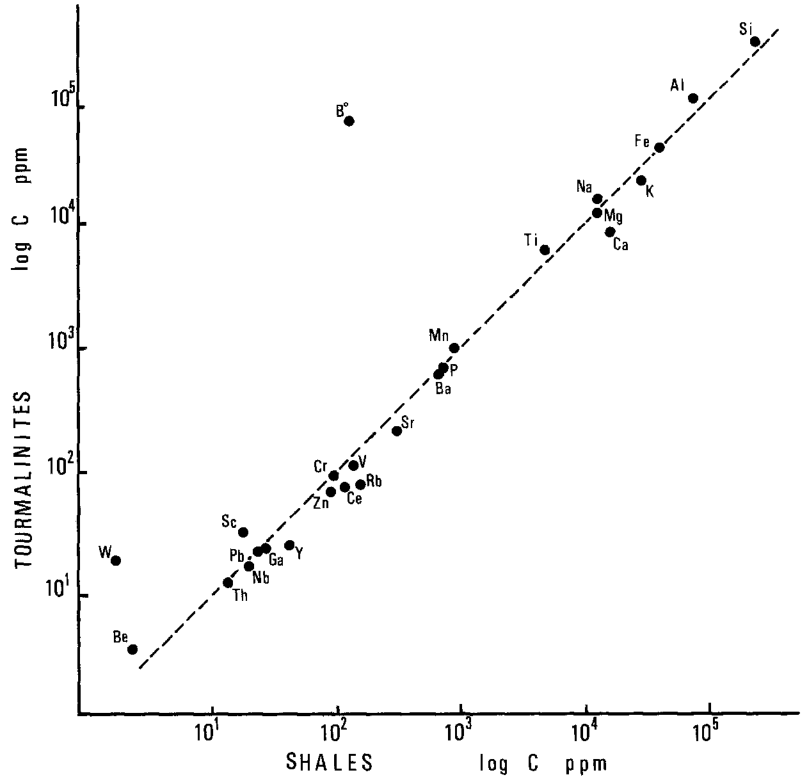

Fig. 5. Comparison of major, minor and trace element distribution of average tourmalinites from the Austroalpine Crystalline Complex with average shales (data from *Turekian* and *Wedepohl*, 1961; *Schroll*, 1975). The good correlation of most elements supports the derivation of the tourmalinites from clastic sedimentary material. The increase in boron (estimated from total rock analyses) and tungsten is thought to be caused by hydrothermal exhalative processes. For number of samples, analytical errors and standard deviation see Table 7

relationship of these two rock groups (Fig. 5). Only boron calculated from the whole rock analyses and in some cases tungsten are significantly increased in the tourmalinites. The relationship to clastic sedimentary material is also evident for single elemental ratios (e.g., the K/Rb ratio of 1:250 for shales does not differ significantly from tourmalinite). All these data show that the precursors of the tourmaline rocks were clastic sediments. Boron and in some cases tungsten-bearing solutions were introduced to these sediments.

Syngenetic sulphide mineralization associated with tourmalinites is scarce (e.g., Anger/Naintsch). These tourmalinites are enriched in zinc (215 ppm) due to minor quantities of sphalerite which have been observed together with pyrite. In all tourmalinite samples molybdenum is below the detection limit of about 10 ppm. Gold analysed in five samples is always below the detection limit of 0.02 ppm.

Discussion of Mineral Chemistry

Tourmaline mineral chemistry is useful in defining different genetic groups of tourmaline because it is very sensitive to changing chemistry within different geological environments (*Henry* and *Guidotti*, 1985). Tourmalines from stratabound ore deposits are distinguished from those of magmatic deposits and those of metamorphic origin by their lower Fe/Mg ratios, their higher F/Cl ratios, heavier $\delta^{18}O$ values and differing trace element contents (*Taylor* and *Slack*, 1984). However, in some settings tourmalines of high Fe/Mg ratios close to the schorl end member composition are also associated with massive exhalative ore deposits (e.g., Bergslagen area, Sweden; Bushmanland area, South Africa; Broken Hill, Australia). A genetic discrimination between tourmalines of exhalative or evaporitic-sabkha origins on the basis of mineral chemistry is not possible. Within both genetic groups intermediate to Mg-rich members of the dravite schorl series are common. Higher uvite components may occur in Ca-dominated lithologies which occur in both settings.

The comparison of published data with tourmaline analyses obtained in the course of this study reveals that tourmalines of the ACC show similar mineral chemistry to those from other stratabound deposits (Fig. 6). They can all be classified as intermediate so slightly Mg-enriched dravite schorls with minor amounts of uvite-, alkali-deficient- and aluminobuergerite tourmaline. One sample from a metapegmatoid is classified as an Fe-rich member of the dravite-schorl solid solution series with minor amounts of the other tourmaline end members. These observations are also in accordance with data from tourmalines of metamorphic pegmatoids and

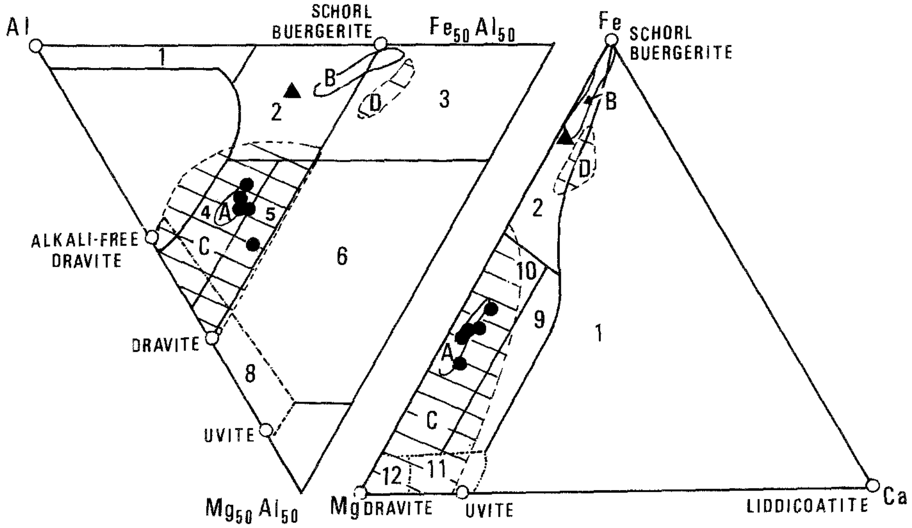

Fig. 6. Ca − Mg − Fe and Al − Fe_{50} − Mg_{50} diagrams illustrating average tourmaline compositions of investigated tourmalines from tourmalinites (●) and metapegmatoids (▲) compared with other data. Fields *1–12* according to *Henry* and *Guidotti* (1985) with data from metamorphic (*A*) and metapegmatite (*B*) tourmalines from NW Maine. *1* Li-rich granites, *2* Li-poor granitic rocks, pegmatites etc, *3* hydrothermally altered granitic rocks, *4* metapelites and metapsammites, Al-saturated, *5* metapelites and metapsammites, Al-unsaturated, *6* Fe^{3+}-rich quartz-tourmaline rocks, calc-silicate rocks, *7* low Ca-ultramafics and Cr- and V-rich metapelites, *8* metacarbonates, metapyroxenites, *9* Ca-rich metapelites, *10* Ca-poor metapelites, metapsammites, and quartz-tourmaline rocks, *11* metacarbonates, *12* metaultramafics. Striped fields: Data from massive sulphide deposits from Appalachian-Caledonian (*C*; *Taylor* and *Slack*, 1984) and Broken Hill massive sulphide deposits (*D*; *Plimer*, 1983)

accessory metamorphic tourmalines from metapelites of NW Maine (*Henry* and *Guidotti,* 1985). Even the discrimination from metamorphic tourmalines which are widespread (*Black,* 1971; *Abraham* et al., 1972; *Kennan,* 1982, *Slack* et al., 1984) may therefore be ambiguous if interpretation is based on mineral chemistry only. In the ACC growth and zoning of tourmaline can be correlated with the metamorphic history of the area. This is demonstrated in the following for the Stubalpe area.

Fine needles of tourmaline within core zones of garnet confirm that tourmaline has been present during the early stages of metamorphism prior to the growth of garnet and the development of the coarse metamorphic texture. A first generation of coarse grained tourmaline (tourmaline I, Figure 3) has grown pre-, or at the latest, synkinematically during the main metamorphic event of Variscan age. This coarse grained tourmaline crystallized together with other silicate phases (garnet, biotite) and has overgrown dark graphitic isoclinal folds formed during the first main Variscan deformation (D 1). A second generation of tourmaline (tourmaline II) with differing mineral chemistry (Table 6) is correlated with the greenschist facies metamorphism of Eoalpine age. The inclusion-free rims are thought to have formed during this second event. The observed mineral zoning therefore has to be interpreted as metamorphic zoning. Delicate lamellar zoning, as reported from hydrothermal minerals, has not been found.

Summary and Conclusions

Stratabound Character of Tourmaline Rocks and Tungsten Mineralization

Based on geological, mineralogical and petrological evidence, the stratabound and, rarely, stratiform character of scheelite mineralization and associated exhalites in the ACC has been demonstrated (*Raith,* 1986). Tungsten mineralization and the accompanying tourmalinites are stratigraphically controlled and are hosted mainly by Paleozoic metapelitic-metapsammopelitic sediments which have been deposited during epochs of increasing carbonate sedimentation.

There is no relationship to felsic plutonic activity. The tungsten- and boron-rich horizons on the regional and local scale are always controlled by sedimentological and stratigraphic parameters. Relict sedimentary structures (graded bedding, cross bedding) described from tourmalinites of other metamorphic areas (*Slack* et al., 1984) are not preserved in the areas investigated. The comparison and good correlation of the major, minor and trace elements from tourmaline rocks to average contents of shales, however, strongly suggest that the precursors were original clastic sediments.

A relationship between boron and organic carbon (e.g., tourmalinites and gneisses of the Azov region, U.S.S.R., *Serdyuchenko,* 1977; Moldanubian graphite deposits, Austria, *Beran,* 1986 pers. comm.), boron and coals deposited in areas which have had subtle marine incursions (*Edgar,* 1962), boron and oil shales associated with evaporites (*Vine* and *Tourtelot,* 1978) and the common observation of graphite in the tourmalinites, marbles and calc-silicate rocks suggest a possible facies control for the mineralization as documented from other types of deposits (uranium, base metal, and precious metal deposits).

Processes of Boron Preconcentration

The tourmalinites and tourmaline-rich metapelites are interpreted as metamorphosed boron-enriched rocks. Their metamorphic history is identical to that of the surrounding wall rocks. It is not possible to derive the quantities of boron required to form tourmaline from isochemical metamorphic processes. Preconcentration of boron is therefore postulated.

Submarine-exhalative, evaporite-sabkha, detrital and authigenic-diagenetic processes have been considered to explain the anomalously high concentration of boron and the formation of tourmaline in the exogenic cycle (*Slack,* 1982; *Plimer,* 1983). Normally detrital and authigenic-diagenetic processes are regarded as unimportant in the formation of tourmalinites, because of the lack of typical heavy mineral suites or simple mass balance calculations. Most of the authors favour an interpretation as metamorphosed, boron-rich chemical sediments, boron having been enriched by exhalative processes in sedimentary and volcano-sedimentary environments.

It is therefore suggested that boron in hydrothermal solutions of submarine exhalative origin has played an important role in transporting tungsten and other base metals (*Basset,* 1980; *Plimer,* 1983). Reaction of these solutions with clastic material produced an extremely boron-rich sediment, the precursor of the tourmalinites. Because tourmaline has such a wide stability range, it may have formed early, possibly during sedimentation or diagenesis. Postmetamorphic-metasomatic processes must be excluded on the basis of field geological relationships.

Derivation of Boron and Tourmaline Precursor Rocks

Different processes have been discussed to explain the tourmaline precursor rocks. Boron-rich saponites, formed during sea-floor alteration in the presence of boron enriched fluids (*Stubican* and *Roy,* 1962), different boro-silicates such as searlesite, reedmergnerite etc, which are restricted to evaporitic-lacustrine settings, or boron-rich gels (*Ethier* and *Campbell,* 1977) have been considered (*Slack* et al., 1984). Most authors favour tourmaline as a possible precursor mineral for tourmaline in the tourmalinites (*Plimer,* 1983), suggesting direct nucleation and crystallization of tourmaline from boron-rich fluids on the sea-floor. Clay minerals are the most likely source of boron in a marine environment. Marine illite can absorb 400–500 ppm B (*Reynolds,* 1965). High concentrations of boron are also observed in Fe—Mn-bearing deep sea sediments reflecting submarine exhalative influences (*Erzinger,* 1985). Structural changes in clays, especially those of the illite-muscovite family, result in a decrease in the boron content with increasing diagenesis and prograde metamorphism. Clastic sedimentary material thus has to be regarded as a potential source for boron to form accessory tourmaline in a closed geochemical system (e.g., isochemical metamorphism) or to allow further concentration in open systems (e.g., brines, connate waters, exhalative hydrothermal solutions). This interaction of host rock and ore fluids is as important as in magmatic hydrothermal ore deposits (*Shibue,* 1984).

Derivation of boron from clay minerals is also supported by empirical observations. The occurrence of tourmalinites is in general restricted to sediment and volcanic-sediment hosted tungsten deposits. They are only rarely found in stratabound deposits of volcanic affilation (e.g., Felbertal scheelite mine, Austria).

Exhalative-Hydrothermal versus Saline-Evaporitic Boron and Tungsten Concentration

The exhalative model provides a sound basis for the interpretation of tourmalinites genetically connected to massive sulphide deposits, especially if they are situated in volcanogenic-sedimentary environments, associated with other chemical sediments (banded iron formation, Mn rocks, quartz-gahnite rocks). Syngenetic/syndiagenetic exhalative W-enrichment is known from old (Proterozoic) exhalative massive sulphide deposits (e.g., Broken Hill, Australia, *Plimer,* 1980) as well as from recent exhalative hot spring environments (Frying Pan Lake, New Zealand, *Höll,* 1985).

In some areas tourmalinites have, however, been deposited in sedimentary sequences with evaporitic influence or in evaporitic-sabkha environments (Adirondacks, New York, U.S.A., *Brown,* 1983; Damara orogen, Namibia, *Behr* et al., 1983; Azov region, U.S.S.R., *Serdyuchenko,* 1977; Sar e Sang, Afghanistan, *Schreyer* and *Abraham,* 1976).

Extremely high concentrations of boron (1.3–1.5% B_4O_7), tungsten (32–55 ppm W) and lithium are known from evaporite brines of Searles Lake (*Smith,* 1979), making Searles Lake the best example for the close association of boron and tungsten in a lacustrine evaporite environment.

Tourmalines from tourmalinites from the ACC are characterized as intermediate to slightly Mg-enriched members of the dravite-schorl series. Uvite and alkali-deficient tourmaline substitution are of minor importance. Discrimination between tourmalines from tourmalinites and metapegmatoids is possible by their composition (e.g., Mg/Fe ratio). Mineral chemistry, however, does not allow discrimination between exhalative and evaporite-sabkha-derived tourmalines. The mineralogical composition and geochemistry of the calc-silicate rocks, the geochemistry and $\delta^{18}O$–$\delta^{13}C$ isotope composition of marbles and the geochemical characterization of metabasaltic rocks intercalated with the W-bearing sequences all suggest formation by submarine hydrothermal precursors (*Raith,* 1986, *Raith* et al., 1989).

Exploration

Tourmalinites and related tourmaline-rich rocks can provide a guide to tungsten mineralization of the ACC. Even in highly metamorphosed volcano-sedimentary environments they may preserve some information on the stratiform/stratabound character and proximity to stratiform/stratabound tungsten mineralization. In spite of minor W-contents, stratabound and stratiform tourmaline rocks cannot be regarded as ore-bearing host rocks for tungsten mineralization in the ACC. However, they are considered to be an important guide for further exploration for tungsten, base and precious metals in the Eastern Alps and in comparable series elsewhere.

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References

Abraham K, Mielke H, Povondra P (1972) On the enrichment of tourmaline in metamorphic sediments of the Arzberg Series, W.-Germany (NE Bavaria). N Jb Min Mh 1972: 209–219

Appel PUW (1986) Strata-bound scheelite in the Archean Malene supracrustal belt, West Greenland. Mineral Deposita 21: 207–215

— *Garde AA* (1987) Stratabound scheelite and stratiform tourmalinites in the Archean Malene supracrustal rocks, Southern West Greenland. Grønlands Geol Unders Bull 156, Copenhagen, pp 26

Barnes RG (1983) Stratiform and stratabound tungsten mineralization in the Broken Hill Block, N.S.W. J Geol Soc Austral 30: 225–239

Basset RL (1980) A critical evaluation of the thermodynamic data for boron ions, ion pairs, complexes, and polyanions in aqueous solution at 298.15 K and 1 bar. Geochim Cosmochim Acta 44: 1151–1160

Becker LP (1977) Zum geologischen und tektonischen Aufbau des Stubalpenzuges (Stmk.) mit einem Vergleich seiner Position zur NE-Saualpe (Ktn.). Carinthia 87/167: 113–125

Behr HJ, Ahrendt H, Martin H, Porada H, Röhrs J, Weber K (1983) Sedimentology and mineralogy of the Upper Proterozoic playa-lake deposits in the Damara Orogen. In: *Martin H, Eder FW* (eds) Intracontinental fold belts. Springer, Berlin Heidelberg New York Tokyo, pp 577–610

Black PM (1971) Tourmalines from Cuiver Island, New Zealand. Min Mag 38: 374–376

Brown CE (1983) Mineralization, mining, and mineral resources in the Beaver Creek area of the Grenville lowlands in St. Lawrence County, New York. U.S. Geol Surv Prof Pap 1279: 21 pp

Campbell FA, Ethier VG (1983) Environment of deposition of the Sullivan orebody. Mineral Deposita 18: 39–55

Cunningham WB, Höll R, Taupitz KC (1973) Two new tungsten bearing horizons in the older Precambrian of Rhodesia. Mineral Deposita 8: 200–203

Delakowitz B (1987) Geologisch-geochemisch-lagerstättenkundliche Untersuchungen zur Genese von Wolframvorkommen in der Sierra del Morro-oeste, Provinz San Luis, Argentia. Ph.D. thesis Univ Munich

Edgar RM (1962) Boron content in relation to organic carbon in certain sediments of the British Coal Measure. Nature 196 (4853): 428–431

Epprecht W (1953) Die Gitterkonstanten der Turmaline. Schweiz Min Petr Mitt 33: 481–505

Erzinger J (1985) Geochemistry of boron in metalliferous deep sea sediments. Fortschr Min 63 Bh 1: 58

Ethier VG, Campbell FA (1977) Tourmaline concentrations in Proterozoic sediments of the Southern Cordillera of Canada and their economic significance. Can J Earth Sci 14: 2348–2363

Fleischer R, Routhier P (1973) The "consanguineous" origin of a tourmaline-bearing gold deposit: Passagem de Mariana (Brazil). Econ Geol 68: 11–22

Flügel H, Neubauer F (1984) Steiermark. Erläuterungen zur geologischen Karte der Steiermark 1:200 000, Geol. B.-A, Vienna, 127 pp

Frank W (1987) Evolution of the Austroalpine elements in the Cretaceous. In: *Flügel HW, Faupl P* (eds) Geodynamics of the Eastern Alps. Deuticke, Vienna, pp 379–406

Frank W, Esterlus M, Frey I, Jung G, Krohe A, Weber J (1983) Die Entwicklungsgeschichte von Stub- und Koralpenkristallin und die Beziehung zum Grazer Paläozoikum. Jahresber 1982 Hochschulschwerpunkt S 15, Leoben, pp 263–292

Hack M (1987) Geologisch-geochemisch-lagerstättenkundliche Untersuchungen zur Genese von Wolframlagerstätten in der Pampa del Tamboreo, Provinz San Luis, Argentinien. Ph.D. thesis Univ Munich

Henry D, Guidotti CV (1985) Tourmaline as a petrogenetic indicator mineral: an example from the staurolite-grade metapelites of NW Maine. Am Min 70: 1–15

Höll R (1977) Early Paleozoic ore deposits of the Sb—W—Hg formation in the Eastern Alps and their genetic interpretation. In: *Klemm DD, Schneider HJ* (eds) Time- and strata-bound ore deposits. Springer, Berlin Heidelberg New York Tokyo, pp 169–198

— (1985) Geothermal systems and active ore formation in the Taupo Volcanic Zone/New Zealand. Monogr Sers Mineral Deposits 25: 53–73

Kennan PS (1983) Tourmalinite from Belgium and from SE Ireland—a discussion. Min Mag 47: 236–238

Krohe A (1984) Metamorphosegeschichte und tektonische Entwicklung in der nördlichen Koralpe, der angrenzenden Stubalpe und am Südwestrand des Grazer Paläozoikums. Diss Univ Vienna, 236 pp

Lahusen L (1972) Schicht- und zeitgebundene Antimonit-Scheelit-Vorkommen und Zinnober-Vererzungen in Kärnten und Osttirol/Österreich. Mineral Deposita 7: 31–60

Moore BR, Dennen WH (1970) A geochemical trend in silicon-aluminium-iron ratios and the classification of clastic sediments. J Sed Petr 40: 1147–1152

Neinavaie H, Pfeffer W, Thalmann F (1985) Ergebnisse der geochemischen Prospektion auf Stahlveredler im Bundesgebiet. Berg u hüttenmänn Mh 130/4: 111–116

Nicholson PM (1980) The geology and economic significance of the golden Dyke Dome, Northern Territory. In: *Ferguson J, Goleby AB* (eds) Uranium in the Pine Creek geosyncline. Int Atomic Energy Agency Vienna, pp 313–334

Plimer IR (1980) Exhalative Sn and W deposits associated with mafic volcanism as precursors to Sn and W deposits associated with granites. Mineral Deposita 15: 275–289

— (1983) The association of tourmaline-bearing rocks with mineralization at Broken Hill, N.S.W. Aus IIM Conference, Broken Hill, pp 157–176

— (1986) Tourmalinites from the Golden Dyke Dome, Northern Australia. Mineral Deposita 21: 263–270

— (1987) The association of tourmalinite with stratiform scheelite deposits. Mineral Deposita 22: 282–291

— *Lees TC* (1988) Tourmaline-rich rocks associated with the submarine hydrothermal Rosebery Zn—Pb—Cu—Ag—Au deposit and granites in Western Tasmania, Australia. Mineral Petrol 38: 81–103

Raith J (1983) Die Scheelitvererzung auf der Klamm Alm, Navis, Tirol, und ihr geologischer Rahmen. Vorarbeit Univ Vienna, 68 pp

— (1986) Scheelitvererzungen in Marmoren und Kalksilikatgesteinen des Kristallins östlich der Hohen Tauern, Österreich. Ph.D. thesis Univ Vienna, 179 pp

— *Papesch W, Schroll E* (1989) Kohlenstoff- und Sauerstoffisotope scheelitfreier und scheelitführender Karbonatgesteine aus den Ostalpen. Anz österr Akad Wiss math naturw Kl: in press

Reimann C, Stumpfl E (1985) Paleozoic amphibolites, Kreuzeck Mountains, Austria: Geochemical variations in the vicinity of the mineralization. Mineral Deposita 20: 69–75

Reynolds RC (1965) Geochemical behaviour of boron during the metamorphism of carbonate rocks. Geochim Cosmochim Acta 29: 1101–1114

Schreyer W, Abraham K (1976) Three stage metamorphic history of a whiteschist from Sar e Sang, Afghanistan, as a part of a former evaporite deposit. Contr Min Petr 59: 111–130

Schroll E (1975) Analytische Geochemie, Band I, Methodik. Enke, Stuttgart, 292 pp

Serdyuchenko DP (1977) Archean tourmaline-bearing and other metasedimentary gneisses of the Azov region, as related to their paleogeographic environment of formation. Dokl Akad Nauk SSSR 227: 90–93

Shibue Y (1984) Chemical compositions of tourmaline in the vein-type deposits of the Kaneuchi Mine, Japan. Mineral Deposita 19: 298–303

Slack JF (1982) Tourmaline in Appalachian Caledonian massive sulphide deposits and its exploration significance. Trans Instn Min Metall sect B: B 81–89

— *Herriman N, Barnes RG, Plimer IR* (1984) Stratiform tourmalinites in metamorphic terranes and their geologic significance. Geol 12: 713–716

Smith GI (1979) Subsurface stratigraphy and geochemistry of Late Quaternary evaporites. Searles Lake, California. US Geol Surv Prof Paper 1043: 1–130

Stubican V, Roy R (1962) Boron substitution in synthetic micas and clays. Am Min 47: 1166–1173

Taylor BE, Slack JF (1984) Tourmalines from Appallachian-Caledonian massive sulphide deposits: textural, chemical, and isotopic relationships. Econ Geol 79: 1703–1726

Tischler SE, Ucik FH (1979) Schichtgebundene Sulfidmineralisation (Typus Schellgaden) in der Schieferhülle des östlichen Tauernfensters. Carinthia II 89/169: 371–407

Tollmann A (1977) Geologie von Österreich, Band I. Deuticke, Vienna, 766 pp

Tracy RJ (1982) Compositional zoning and inclusions in metamorphic minerals. In: *Ferry JM* (ed) Characterization of metamorphism through mineral equilibria. Rev Min 10, Min Soc Amer, pp 335–397

Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the earth's crust. Bull Geol Soc Amer 72: 175–192

Vine JD, Tourtelot EB (1970) Geochemistry of black shale deposits—a summary report. Econ Geol 65: 253–272

Werding G, Schreyer W (1984) Alkali-free tourmaline in the system $MgO—Al_2O_3—B_2O_3—SiO_2—H_2O$. Geochim Cosmochim Acta 48: 1331–1344

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