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Geology, Mineralogy and Geochemistry of a Metapelite-Hosted Stratiform Arsenopyrite Mineralization (Pretul Alm, Austria)

RICHARD GÖD*) & GERHARD HEISS**)

15 Abbildungen, 4 Tabellen

Steiermark
Paläozoikum
Turmalinit
Schichtgebundene Lagerstätte
Arsenopyrit
Geochemie

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Geologie, Mineralogie and Geochemie einer schichtgebundenen Arsenopyrit-Mineralisation in Metapelit (Pretul Alm, Austria)

Zusammenfassung

Ausgehend von einer regionalen Arsenanomalie in Bachsedimenten des Raumes Mürzzuschlag – Pretul-Alm – Stuhleck wurde im Bereich der Pretul-Alm eine stratiforme Arsenkiesmineralisation gefunden. Sie tritt innerhalb von mehr/minder quarzitischen Phylliten der Grobgneisserie auf, deren diaphthoritischer Charakter durch das Auftreten von chloritisiertem Granat und Chloritoid belegt ist. Die Mineralisation besteht überwiegend aus Arsenkies, untergeordnet aus Pyrit und Magnetkies sowie Spuren von Kupferkies und Covellin. Es wurden drei mineralisierte Horizonte aufgefunden, die Mächtigkeit vom Liegenden zum Hangenden beträgt rund 40 m. Der liegende Horizont (= As-Gehalt >150 ppm) weist eine Mächtigkeit von ca. 1,5 m auf, innerhalb dessen sich eine Lage von ca. 0,5 m mit einem Gehalt von >1 Gew.-% Arsen findet. Das Arsen wird von keinen weiteren Elementen, wie sie für hydrothermale sulfidische Mineralisationen charakteristisch sind, begleitet. Die Gold- und Silbergehalte liegen um 0,3 ppm. In räumlicher Nähe zu den Arsenkiesmineralisationen treten Turmalinite mit Mächtigkeiten bis zu 20 cm auf. Ihre Geochemie lässt eine In-situ Entstehung durch hydothermale Borzufuhr annehmen. Ein genetischer Zusammenhang der Turmalinite mit der Arsenmineralistion ist nicht erkennbar.

Bodengeochemische Untersuchungen belegen, dass solche Arsenmineralisationen auch in jenen Teilen der Grobgneisserie zu erwarten sind, die innerhalb des Leithagebirges als geologisches Fenster auftreten, was einer Erstreckung über rund 70 km entspricht. Die primäre Anreicherung des Arsens wird daher als syngenetisch interpretiert und mit dem wahrscheinlich altpaläozoischen Alter der Phyllite korreliert.

Während der alpinen grünschieferfaziellen Metamorphose wurde diese Mineralisation in Scherzonen mobilisiert, was zu lokalen Arsenanreicherungen bis in den Prozentbereich führte.

*) Hon.-Prof. Dr. RICHARD GÖD, Center for Earth Sciences, University of Vienna, Althanstraße 14, A 1090 Vienna.
richard.goed@univie.ac.at
**) DR. GERHARD HEISS, ARC Seibersdorf research GesmbH, A 2444 Seibersdorf.
gerhard.heiss@arcs.ac.at

Abstract

A stratiform arsenopyrite mineralization has been found at the Pretul Alm following up a regional arsenic anomaly in stream sediments. The mineralization is hosted by diaphthoritic phyllites of prevariscan, most likely Ordovician to early Carboniferous age, belonging to the "Grobgneis Complex". Arsenopyrite is by far the dominant ore mineral, accompanied by subordinated pyrite, pyrrhotite and traces of chalcopyrite and covellin. Three different mineralized layers indicating a thickness between foot wall and hanging wall of 40 m have been found. The layer richest in arsenopyrite is about 0.5 m thick, however, taking a threshold of >150 ppm, its thickness is around 1.5 m. The arsenic mineralization is mono-elemental and not associated with elements frequently accompanying hydrothermal sulphide mineralizations. Gold and silver concentrations are around 0.3 ppm. Tourmalinites, spatially related to the mineralization, do not seem to be genetically linked to the arsenopyrite. Their geochemistry coincides with the chemistry of the hosting phyllites suggesting their in situ genesis by selectively replacing the sediments by boron-rich fluids.

Soil geochemistry suggest a continuation of the arsenic mineralizations some 70 km to the NE emphasizing its regional extension. Based on that, on the repeatedly occurring mineralized horizons and on the mono-elemental character of the mineralization, it is interpreted as of synsedimentary origin.

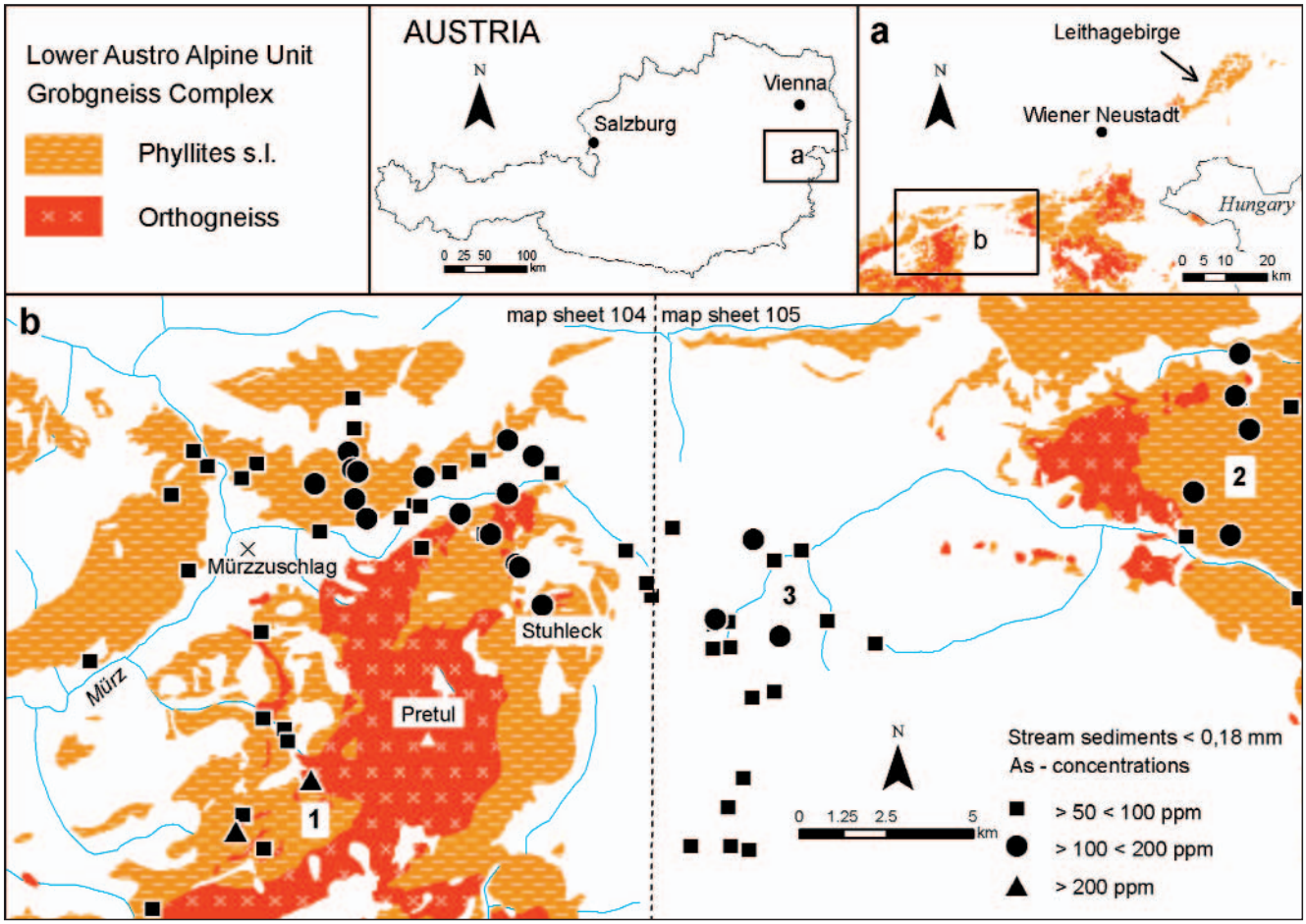
A probable Variscan impact on the mineralization as proven by the diaphthoritic mineralogy of the hosting phyllites is not demonstrable.

Finally, a late Cretaceous, eo-Alpine greenschist-metamorphism affected the mineralization. Shear zones, related to thrusting, gave rise to a remobilization causing local arsenic contents surpassing 1% As.

1. Introduction

The „Geochemical Atlas of Austria" (THALMANN et al., 1989) which is based on stream sediment analyses shows numerous arsenic anomalies all over the Eastern Alps. Almost all of them are related to known polysulphidic mineralizations and/or (abandoned) mines. These anomalies are „polyelemental", displaying the spectrum of elements commonly associated with such mineralizations. Only two significant arsenic anomalies are known so far not associated with any other elements:

1) An anomaly in the Saualpe, some 250 km S of Vienna, caused by a realgar-orpiment-native arsenic mineralization (GÖD & ZEMANN, 2000) and
2) an anomaly in the Wechsel-Semmering area, some 100 km S of Vienna, caused by a so far unknown arsenopyrite mineralization (GÖD, 2005). This latter anomaly, indicated by arsenic concentrations in stream sediments ranging from 50 ppm to a maximum of 400 ppm, spreads over an area of roughly 30 km² and corresponds to arsenic concentrations in soils up to 1600 ppm. Soil and water geochemistry of easterly



Text-Fig. 1.
Regional geology and the locations of arseniferous stream sediments.
Geology, simplified, after map sheet 104 Mürzzuschlag (MANDL, 2001) and map sheet 105 Neunkirchen (HERMANN, 1992).
a) Regional spread of the Grobgneis Complex.
b) Areas investigated: 1 = area of investigation, this paper; 2 = area investigated by GÖD & HEISS (1996); 3 = area of the abandoned copper mine Trattenbach (TUFAR, 1986).
Graphics: P. LIPIARSKI (GBA).

parts of this anomaly have been investigated by GÖD & HEISS (1996).

The arseniferous drainage system coincides mainly with a geological unit predominantly composed of phyllitic rocks belonging to a tectonic unit called the „Grobgneis Complex“.

This paper describes the geological setting, mineralogy and geochemistry of this mineralization.

2. Geology

2.1. Regional Geology and Petrography

The area under investigation is situated at the northeastern margin of the Eastern Alps, characterized by the smoothly shaped mountains of the Semmering – Wechsel region, displaying altitudes between 800 to 1800 m asl (highest elevations: Pretul, 1656 m and Stuhleck,1782 m asl respectively, see Text-Fig. 1). Its geology has been extensively compiled on a regional scale by FLÜGEL & NEUBAUER (1984), NEUBAUER et al. (1992) and more recently by SCHUSTER et al. (2001); for the local geology see sheet 104 Mürzzuschlag (MANDL, 2001). Based on these authors and restricted to the aim of this paper, the geology may be summarized as follows.

The Semmering – Wechsel region is part of the pre-Mesozoic Austro-Alpine metamorphic basement. The area under investigation belongs to the „Grobgneis Complex“ which is part of the „Semmering Complex“, itself subdivided into various nappes not further referred to in the given context. The Grobgneis Complex is composed predominantly of phyllites, phyllitic micaschists and, subordinated, of amphibolites and paragneisses. The phyllites host various (now metamorphosed) Carboniferous to Permian granites (= „Grobgneisses“), interpreted and described as laccolithic bodies (FLÜGEL & NEUBAUER, 1984). Whole rock ages of the granitic intrusions vary between 343 my and 243 my possibly indicating two separate intrusive events (summarized in SCHUSTER et al. [2001]). On a regional scale, the „Semmering Complex“ has been affected by three different metamorphic overprints, a Variscan one, dated around 370 my, a Permo-Triassic one, dated around 220 my and finally, a late Cretaceous (= „eoalpidic“) one, dated around 80 my. Metamorphism from anchizonal to greenschist facies up to amphibolite facies has been observed (MÜLLER et al., 1999; SCHMIDT, 1999; BERKA, 2000, also summarized in SCHUSTER et al., 2001).

As shown in Text-Fig. 1, the area under investigation is comprised of two petrographic units: a coarse grained orthogneiss (i.e. „Grobgneis“, name giving to the „Grobgneis Complex“ as mentioned) and monotonous phyllitic rocks s.l., locally known as „Mürztaler Quarzphyllit“. Quartzphyllites represent a widespread lithological unit in the Austro-Alpine and South-Alpine premesozoic basement and are dated elsewhere as of Ordovician to early Carboniferous age (NEUBAUER & SASSI, 1993; NEUBAUER & FRISCH,1993). Based on that age relation, a primary, intrusive contact between orthogneiss and phyllite is the accepted interpretation (SCHUSTER et al., 2001). However, due to the extremely complicated tectonic history and due to the nappe structure of the regional geologic frame, the contact as observed in the field is a tectonic one.

Essential tectonic and lithologic features of the Grobgneis Complex are „leucophyllites“, rocks composed of quartz, muscovite and (Mg-rich) chlorite. These rocks are formed by hydrothermal alteration of the Grobgneisses in shear zones, envolving an external supply of MgO (PROCHASKA et al., 1992; PROCHASKA, 1993). These shear zones occur spatially close to lithologic inhomogeneities such as contacts between orthogneisses and phyllites (REINDL, 1989; HUBER, 1994) and act as preferred gliding horizons during the alpine thrusting.

The Grobgneis Complex crops out again as geologic window in the Leithagebirge, some 70 km NE of the area under investigation (Text-Fig. 1a). Stream sediments in the northern Leithagebirge have shown to be arseniferous as well (AUGUSTIN-GYURITS & HOLNSTEINER, 1997), associated with arsenic contents in soils up to 230 ppm (this work).

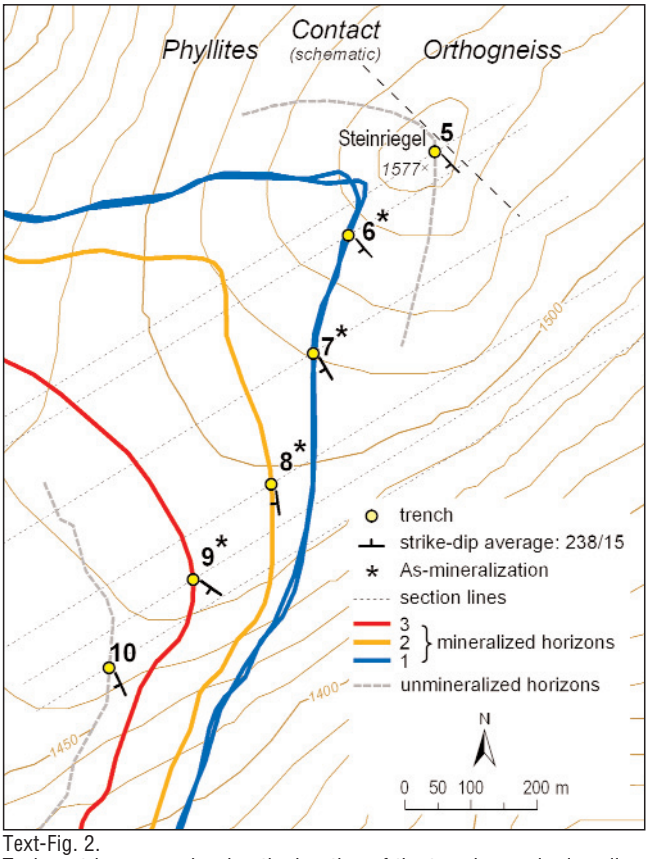
2. 2. Geology and Petrography Next to the Mineralization

2.2.1. Phyllites

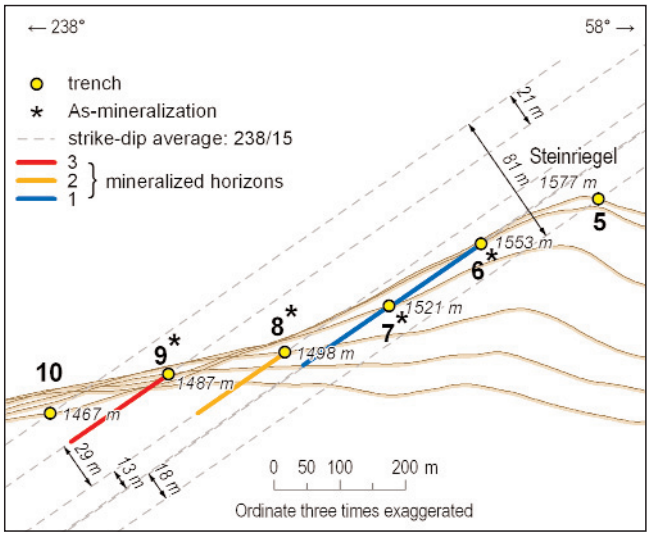
Following up the stream sediment anomalies led to the discovery of the arsenopyrite mineralization close to the „Steinriegel“, SW of the Pretul-Alpe (Text-Figs. 2,3). All the following investigations are based on observations in the trenches delineated in Text-Figs. 2 and 3 which have been dug in context with the construction of windmills.

The local geology, like the regional one, is characterized by phyllitic rocks and – marginally – orthogneisses as mentioned in the foregoing chapter. While trenches 6 to 10 are situated in the phyllites, trench 5 crosses the roughly NW–SE-running tectonic contact to a coarse grained orthogneiss („Grobgneis“). The phyllites strike uniformly NW to SE, dip gently (15°) to SW and overlay the orthogneiss.

The silvery, greyish to greenish phyllites are monotonous and homogeneous rocks, composed of mutually varying amounts of quartz, muscovite and chlorite. At the size of a hand specimen, a finely laminated texture caused by alternating quartz and muscovite/chlorite layers at the mm-scale characterizes these rocks. A pronounced, distinct twofold schistosity is observable (Text-Fig. 4). Additionally, relictic garnet (max. grainsize observed: 5 mm) is locally present. It is intimately intergrown with chlorite and occasionally with chloritoid which also may occur in the matrix



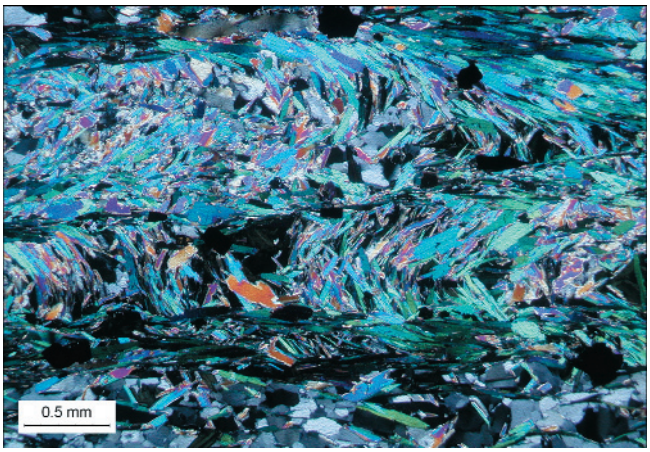
Text-Fig. 2.
Tachymetric survey showing the location of the trenches and mineralizations as observed including outcropping lines of mineralized horizons.



Text-Fig. 3.
SW–NE-trending cross section through the area investigated displaying the geometry of the three mineralized horizons and their relative distances.

itself (Text-Fig. 5). Late, syn- to post-tectonic albite porphyroblasts may occur occasionally (e.g. sample 82). No biotite has been observed. Apatite, clinozoisite, zircon and tourmaline are common accessory components.

Due to the overall monotonous character of the rocks dealt with, it was not possible to establish a stratigraphy.



Text-Fig. 4.
Phyllite displaying a twofold metamorphic penetration.
Sample 66, trench 6; thin section, crossed polarizers.

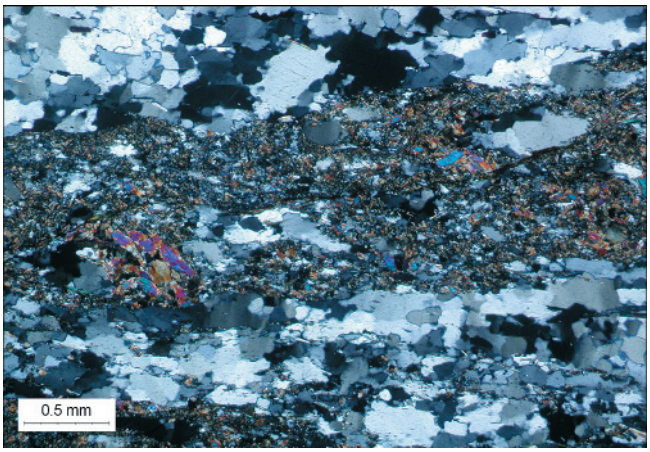
Text-Fig. 5.
Relictic garnet, diaphthoritic formation of chlorite and chloritoid.
Sample A 6, trench 6; thin section, parallel polarizers.

2.2.2. Tourmalinites

Tourmalinites are stratabound rocks that contain in excess of 15 % to 20 % tourmaline by volume (SLACK, 1982). Phyllites containing elevated contents of tourmaline in the area of investigation have been described by ROCKENSCHAUB (1989).

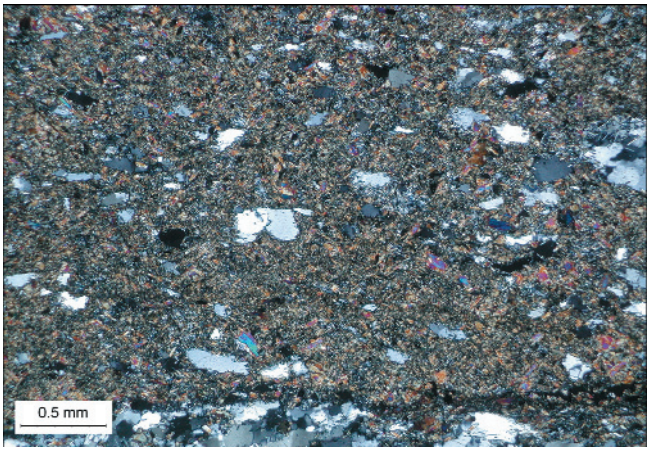
However, observations in trenches 6, 7 and 9 allow to distinguish three different subtypes of tourmaline enrichment:

Text-Fig. 6.
Banded tourmalinite, alternating quartz and tourmaline layers.
Hand specimen, sample 72, trench 7.

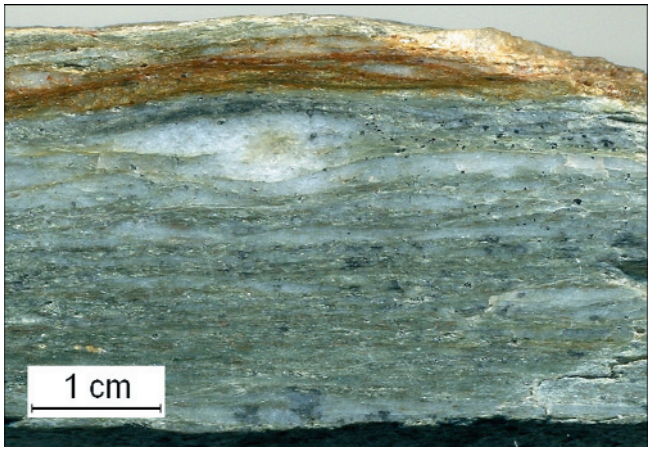


Text-Fig. 7.
Banded tourmalinite.
Sample 72, trench 7; thin section, crossed polarizers.

Text-Fig. 8.
Massive tourmalinite.
Hand specimen sample 95, trench 9.



Text-Fig. 9.
Massive tourmalinite.
Sample 95, trench 9; crossed polarizers.



Text-Fig. 10.
Mineralized quartzitic phyllite; weathered parts contain pharmakosiderite.
Hand specimen, sample 65, trench 6.

1) Gradationally increasing tourmaline contents in phyllites from microscopically sized laminae to tourmaline layers of some 1 to 2 cm thickness and/or tourmaline nodules („Turmalinaugen") of some 5 mm (trench 6).
2) „Banded tourmalinite", composed of tourmaline and quartz layers the thickness of which is around 2 cm each. The total thickness of this banded tourmalinite as observed is roughly 15 cm (trench 7; Text-Figs. 6,7);
3) „Massive tourmalinite", a layer of 20 cm thickness, sharply bordered by the hosting phyllites (trench 9; Text-Figs. 8,9);

Banded and massive tourmalinites tend to occur spatially related to and stratigraphically below the mineralization (Text-Fig. 12 and observations in trench 7). The number of tourmalinite horizons as well as their extension along strike is unknown.

All the tourmalinites are black rocks and contrast sharply with the silvery to greenish colour of the phyllites. The tourmalinites are extremely fine grained, giving the rock a cryptocrystalline appearance. Grain sizes are generally below 100 m, sometimes even below 50 m. Single tourmaline individuals the size of which does not exceed 200 m display bluish cores and thin brown rims.

The tourmaline content of the tourmalinites amounts to 80 % and may exceed 90 % by volume. Quartz (-layers) and muscovite are ubiquitous components. The tourmalinites are barren with respect to sulphides.

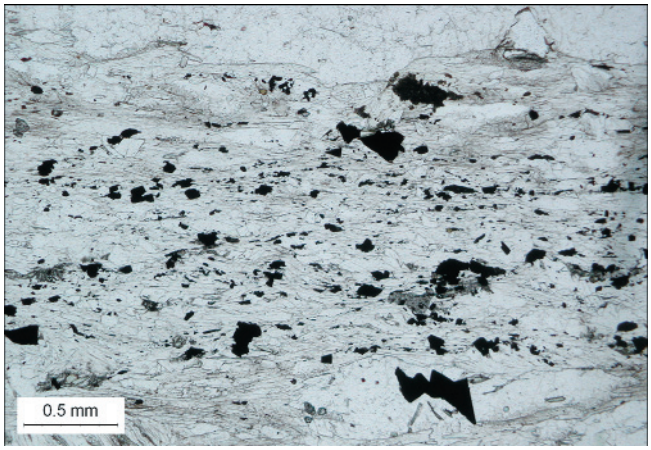
The chemistry of the tourmaline refers to a Mg-rich schorl (Ertl, 2006, pers. com.)

3. Mineralization

3.1. Macroscopic and Microscopic Description

Sulphide mineralizations have been discovered in the trenches 6 to 9 but not in trenches 5 and 10, thus indicating three different mineralized horizons (Text-Fig. 2). The vertical distance between hanging wall mineralization (horizon 3), outcropping in trench 9 and foot wall mineralization (horizon 1), outcropping in trenches 6 and 7 respectively indicates a rock pile of at least 40 m thickness potentially mineralized (Text-Fig. 3). However, due to the limited sample density no statement can be made at present on the continuity along strike or on average thicknesses nor on the number of mineralized layers.

The fine-grained mineralization strictly concordant to the schistosity, is hosted by laminated (mm-scale) quartzitic phyllites (= phyllonites) as described. The arsenopyrite grains are intimately associated with the muscovite – chlorite layers leaving the quartz laminae barren with respect to



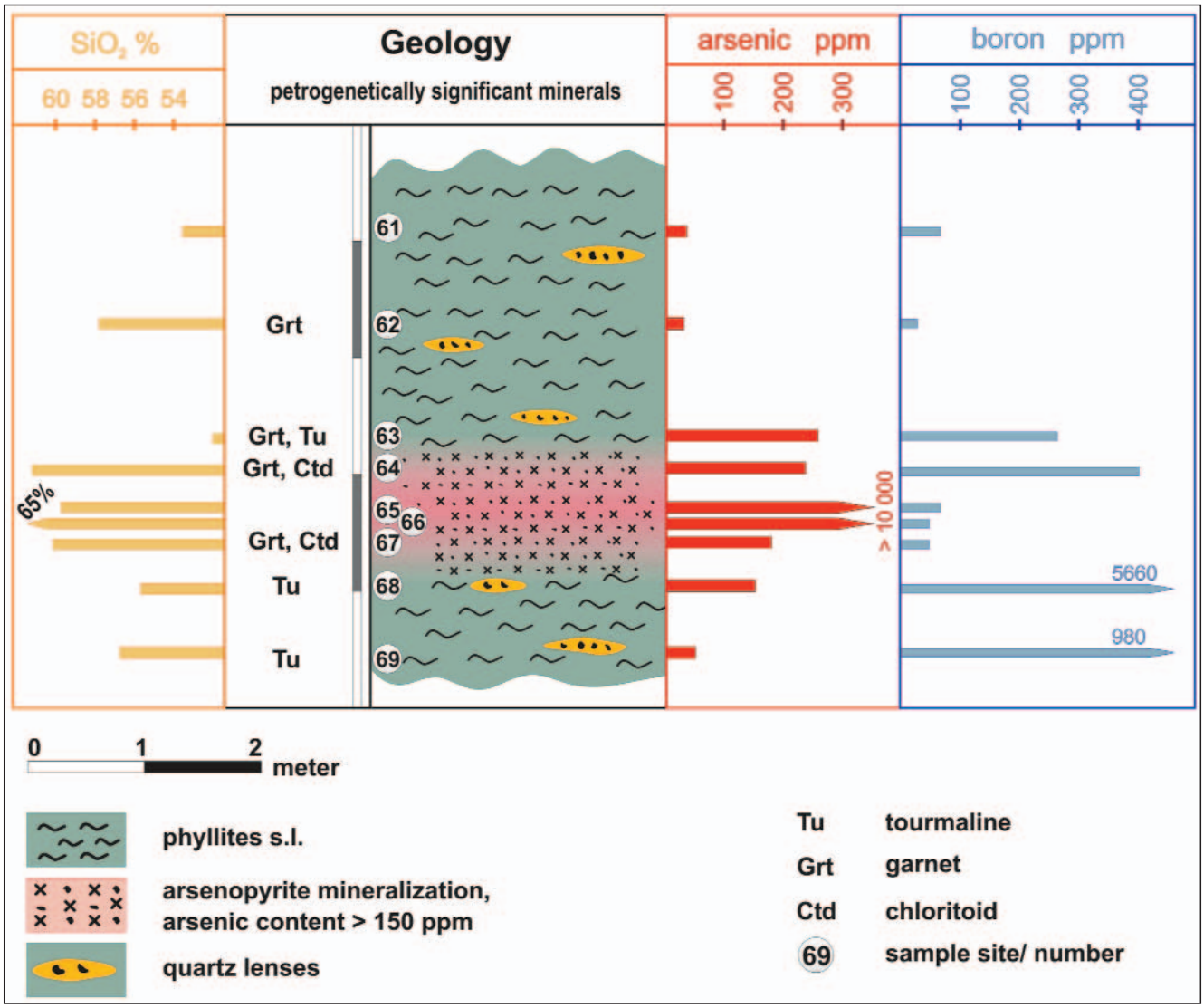
Text-Fig. 11.
Mineralized quartzitic phyllite; parallel alignement of arsenopyrite graines intimately associated with the mica/chlorite layers.
Sample 65, trench 6; parallel polarizers.

sulphides (Text-Fig. 10). By naked eye solely arsenopyrite and traces of pyrite are observable, the average grain sizes are in the order of some tenth of millimeters and may reach a maximum of one millimeter each. A schematic cross section through mineralization in trench 6 is given in Text-Fig. 12.

The phyllites immediately surrounding the mineralization do not show a significant change in their habit across the mineralization. However, samples highest in arsenic (trench 6, samples 65 and 66) display a pronounced shear zone texture and tend to be slightly more quartzitic. Phyllites in the foot wall bear tourmaline rich layers and nodules. Petrogenetically significant minerals like garnet and chloritoid occur immediately next to the mineralization (Text-Fig. 12).

The thickness of the mineralized layer richest in arsenopyrite (= As >10000ppm, samples 65 and 66) seems to be slightly above 0.5 m. However, taking – arbitrarily – a threshold of 150 ppm As, the mineralized layer would have a thickness of approximately 1.5 m. In terms of the extension along strike, the footwall mineralized horizon has been traced for 200 m (trenches 6 and 7).

Due to the sampling density given at present, no such figures are available for the middle (horizon 2) and hanging wall mineralization (horizon 3) as shown in Text-Figs. 2 and 3. However, horizon 2 is indicated by arsenic contents of >10000 ppm and 7390 ppm respectively (two samples out of three), the hanging wall horizon 3 by arsenic contents of 430 and 980 ppm respectively (two samples out of 4).



Text-Fig. 12.
Schematized cross section through the mineralization in trench 6.

The following ore minerals have been found: arsenopyrite, pyrite, pyrrhotite, chalcopyrite, covellin and, as product of weathering, pharmakosiderit. All of them occur in each of the horizons mentioned but arsenopyrite tends to be less frequent in the hanging wall horizon. In general, arsenopyrite is by far the dominating ore mineral amounting to significantly more than 95 % of all the sulphides.

Under the reflected light, arsenopyrite displays its tendency to idiomorphism, larger individuals are cracked (Text-Fig. 12). Pyrite, the amount of which is around 1 % to 2 % of the sulphide content, occurs either intergrown with or included in arsenopyrite.

Chalcopyrite and covellin are rare but common accessory minerals. Chalkopyrite occurs as isolated mineral as well as intergrown with pyrite, arsenopyrite and pyrrhotite. Covellin, frequently coating chalcopyrite to various degrees, displays concentric, shell - like features. Actually, the minerals may occur individually, intergrown with each other or as inclusion in any of the other minerals.

As emphasized, all the sulfides are strictly parallel oriented, no crosscutting mobilization has been observed. Pyrite, pyrrhotite and chalcopyrite (hanging wall, horizon 3) are rolled to sub-mm lamellae, frequently intercalated with mica staples. Arsenopyrite individuals, on the contrary, are rather undeformed than (partially) cracked and arbitrarily oriented compared to the foliation, having kept hypidiomorphic shapes.

4. Geochemistry

4.1. General Remarks

Twenty phyllites and two tourmalinites have been analysed for their main element composition, their sulphur concentration and for a total of 45 trace elements. After a metaborate/tetraborate fusion and dilute nitric digestion, the following analytical techniques have been used: main elements by ICP-emission spectrometry, trace elements by ICP-mass spectroscopy, total sulphur by Leco and, finally, boron by Na_2O_2 fusion/ICP. Precious and base metals have been separately digested in aqua regia and analyses by ICP-MS.

4.2. Geochemistry of Phyllites

The analytical results of main and trace elements are given in Table 1.

Tables 2 and 3 summarize a statistical treatment of relevant elements and corresponding correlation coefficients. Those three samples displaying arsenic contents of >10 00 ppm (samples 65, 66 and 82) have been excluded from that treatment. Their geochemistry is listed in Table 4.

Table1.
Main and trace element chemistry for a total of 22 samples.
Decimal place of sample number refers to the trench the sample was taken from e.g.: sample number 72 refers to trench 7, sample number 101 to trench 10. Table 2.

Sample #		61	62	63	64	* 65	* 66	67	68	69	71	72	73	81	* 82	83	91	92	93	94	95	101	102
Petrography		phyllite	phyllite	phyllite	phyllite	phyllite	phyllite	phyllite	phyllite	phyllite	phyllite	tourmalinite	phyllite	phyllite	phyllite	phyllite	phyllite	phyllite	phyllite	phyllite	tourmalinite	phyllite	phyllite
SiO_2	%	54,23	57,77	51,78	61,3	58,97	64,84	60,63	56,82	57,22	64,38	45	49,5	66,03	59,81	42,69	61,77	62,77	56,75	55,99	44,12	43,93	61,77
Al_2O_3	%	24,93	22,03	26,06	20,38	19,78	16,44	20,72	23,66	23,29	19,55	28,81	25,87	17,17	19,49	31,36	20,45	19,02	22,3	23,9	25,37	30,38	19,41
Fe_2O_3	%	6,63	7,09	7,57	6,48	6,65	5,67	6,58	5,99	5,53	3,6	7,87	8,69	4,72	6,3	9,54	5,04	5,69	6,81	6,6	13,18	8,69	7,22
MgO	%	2,2	2,35	2,07	1,98	2,13	1,85	1,85	3,24	2,37	1,46	4,05	3,08	1,36	1,79	2,63	1,26	1,66	2,11	1,75	4,24	2,7	2,1
CaO	%	0,09	0,1	0,1	0,09	0,02	0,02	0,13	0,1	0,02	0,01	0,19	0,01	0,11	0,14	0,01	0,01	0,1	0,07	0,02	0,22	0,09	0,11
Na_2O	%	1,22	0,9	1,38	0,96	0,67	0,53	0,94	0,95	0,85	0,58	1,73	0,75	1,8	2,03	1,65	0,76	0,68	0,73	0,93	1,59	1,61	0,89
K_2O	%	5,3	4,43	5,06	3,75	4,61	3,77	3,92	3,73	5,12	4,72	0,88	5,58	4,16	4,72	5,88	4,9	4,25	5,2	5,42	0,8	6,05	3,64
TiO_2	%	0,99	0,84	1,07	0,77	0,83	0,67	0,88	0,91	0,91	0,92	2	1,03	0,83	0,91	1,31	0,87	0,8	0,98	0,99	0,67	1,21	0,8
P_2O_5	%	0,09	0,11	0,09	0,08	0,05	0,05	0,12	0,08	0,05	0,03	0,04	0,05	0,14	0,14	0,06	0,04	0,12	0,09	0,09	0,12	0,09	0,11
MnO	%	0,05	0,05	0,08	0,05	0,03	0,03	0,08	0,03	0,05	0,02	0,02	0,07	0,04	0,05	0,06	0,03	0,06	0,05	0,06	0,02	0,09	0,06
TOT/S	%	0,01	0,01	0,01	0,01	0,95	0,8	0,01	0,01	0,01	0,38	0,01	0,01	0,04	0,47	0,01	0,21	0,01	0,14	0,01	0,01	0,01	0,01
LOI	%	4,3	4,2	4,7	3,9	5,9	5,6	3,8	4,4	4,4	4,4	2,42	5,5	3,2	4,2	5,2	4,6	4,4	4,8	4,1	3,96	5,5	3,6
SUM	%	100,05	99,89	99,98	99,76	99,67	99,48	99,66	99,93	99,82	99,69	100,01	100,15	99,57	99,6	100,43	99,75	99,57	99,91	99,86	100,23	100,37	99,73
B	ppm	67	33	267	406	63	48	60	5656	977	522	6.99 **	894	89	66	52	49	53	35	34	5.93 **	121	69
Ba	ppm	644	545	716	532	568	471	588	459	600	768	240	757	787	848	728	664	524	698	647	67	787	482
Rb	ppm	241	214	226	175	215	183	181	177	229	191	39	222	161	170	278	251	211	246	248	40	295	185
Sr	ppm	113	90	124	90	59	44	90	71	77	48	88	72	72	94	135	55	53	54	60	115	149	86
Cs	ppm	10	9	9	7	9	8	8	7	9	5	1	6	5	5	12	7	6	6	7	1	12	7
Sn	ppm	4	3	4	3	5	4	3	8	5	8	41	7	3	5	4	15	6	6	5	29	5	3
W	ppm	8	9	11	8	29	27	11	20	10	10	33	6	16	14	8	16	14	12	12	15	9	9
Th	ppm	23	18	24	14	16	14	15	20	20	25	15	23	23	19	25	17	17	20	21	9	27	21
U	ppm	4	4	4	3	3	3	3	4	4	5	4	4	3	3	5	3	3	3	4	1	5	3
Zr	ppm	162	140	137	113	120	120	141	123	155	321	335	157	367	243	174	250	153	168	177	102	206	131
Y	ppm	31	29	41	20	27	23	27	27	32	38	52	31	52	52	23	25	25	25	23	18	35	27
La	ppm	64	53	68	46	56	44	49	64	65	61	70	65	75	112	53	50	52	59	80	26	71	56
Ce	ppm	136	114	144	99	116	91	105	134	139	135	156	138	159	212	119	103	112	123	164	53	159	119
Pb	ppm	2	2	3	2	14	8	2	2	2	9	8	3	8	78	3	7	11	10	19	70	4	4
Zn	ppm	76	89	65	57	37	30	72	37	51	17	9	66	26	34	99	31	47	63	57	15	79	73
Cu	ppm	6	7	8	6	59	62	5	3	5	37	6	15	67	140	14	153	40	33	32	84	11	12
Mo	ppm	0,1	0,1	0,2	0,2	0,7	0,5	0,2	0,2	0,6	0,2	0,9	1,3	0,2	0,6	0,6	0,2	0,3	0,1	1,2	1,2	0,2	1,7
As	ppm	29	27	264	231	> 10000	> 10000	183	155	47	698	36	270	7390	> 10000	52	20	975	426	11	424	28	21
Cd	ppm	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0,1	0,1	< 0.1	< 0.1	0,1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Sb	ppm	< 0.1	< 0.1	< 0.1	< 0.1	3	2,7	0,1	< 0.1	< 0.1	0,3	0,1	0,1	0,6	1,4	< 0.1	< 0.1	0,2	< 0.1	< 0.1	0,3	< 0.1	0,1
Bi	ppm	0,1	0,1	0,2	0,2	3,4	2	0,1	0,2	0,2	0,3	1,2	0,2	0,8	1,9	0,4	1	2,3	0,7	0,4	17,4	0,2	0,9
Ag	ppm	< 0.1	< 0.1	< 0.1	< 0.1	0,3	0,1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0,3	< 0.1	0,2	< 0.1	< 0.1	< 0.1	0,1	< 0.1	< 0.1
Au	ppb	< 0.5	< 0.5	< 0.5	5,2	349,7	230,8	5,3	< 0.5	9,5	4,5	4,6	1,3	56,6	34,4	1	28,5	9,4	5,3	1,2	56,3	1,1	1,3
Hg	ppm	< 0.01	0,01	0,01	< 0.01	0,01	0,01	< 0.01	< 0.01	< 0.01	< 0.01	0,01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,01
Tl	ppm	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0,1	0,2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Se	ppm	< 0.5	< 0.5	< 0.5	< 0.5	1,6	1,5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	0,8	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	3	< 0.5	< 0.5

*) "mineralization" sensu stricto = samples with As-contents > 1%
**) wt % B_2O_3

The actual phyllite geochemistry normalized against the average shales sensu TUREKIAN & WEDEPOHL (1961) is given in Text-Fig. 13.

Amongst the trace elements, arsenic and boron are the only elements significantly enriched. It has to be emphasized that arsenic and boron do not show a mutual correlation or to any of the other elements (Table 3).

The concentrations of the elements Ag, Au, Bi, Cd, Hg, Sb, Se and Tl are either below or slightly above their relevant detection limits.

Based on the data available, no satisfying explanation can be given regarding the slight enrichment of tungsten (see also Table 1).

Arsenic, averaging 215 ppm, is enriched by a factor of 16 compared to the average shales sensu TUREKIAN & WEDEPOHL (1961) and boron, averaging 243 ppm, by a factor of 2.4.

4.3. Geochemistry of Tourmalinites

One sample of the "banded" and the "massive" tourmalinite each (samples 72 and 95) has been analysed (in case of the banded tourmalinite, the tourmaline layer as such has been taken for analyses). The main and trace element compositions are given in Table 2, a comparison of the main and trace element geochemistry of the phyllites and the tourmalinites is shown in Text-Fig. 14.

The close geochemical affinity of both rock types is obvious. Tin and tungsten contents of 35 ppm and 24 ppm respectively clearly surpass the average crustal abundances sensu TUREKIAN & WEDEPOHL (1961) of 6 ppm (Sn) and 1.8 ppm (W).

Tourmalinites not related to an ore deposit but nevertheless enriched in tin and tungsten have been reported elsewhere (Damara Orogen, Namibia; STEVEN & MOORE, 1995), containing 124 ppm Sn and 15 ppm W respectively. Additionally, they contain arsenic concentrations up to 30 ppm.

The surprisingly high average content of 230 ppm

Table 2.
Statistical treatment of the analytical results.
Samples containing >1 wt-% (samples 65, 66 and 82 of Table 1) and the tourmalinite samples 72 and 95 have been excluded.

		Phyllites				Tourmalinites	
Element		n	arith.mean	min.	max.	n	arith.mean
SiO_2	%	17	56,78	42,69	66,03	2	44,56
Al_2O_3	%	17	22,97	17,17	31,36	2	27,09
Fe_2O_3	%	17	6,62	3,60	9,54	2	10,53
MgO	%	17	2,13	1,26	3,24	2	4,15
CaO	%	17	0,07	0,01	0,13	2	0,21
Na_2O	%	17	1,03	0,58	1,80	2	1,66
K_2O	%	17	4,77	3,64	6,05	2	0,84
TiO_2	%	17	0,95	0,77	1,31	2	1,34
P_2O_5	%	17	0,08	0,03	0,14	2	0,08
MnO	%	17	0,05	0,02	0,09	2	0,02
As	ppm	16	215	11	975	2	230
B	ppm	16	243	33	977	2	20070
Ba	ppm	17	643	459	787	2	154
Be	ppm	17	4	3	6	2	8
Bi	ppm	17	0,5	0,3	2,3	2,0	9,0
Co	ppm	17	11	5	37	2	6
Cr	ppm	17	10	6	14	2	12
Cu	ppm	17	27	3	153	2	45
Cs	ppm	17	8	5	12	2	1
Ga	ppm	17	29	23	40	2	35
Hf	ppm	17	5	3	11	2	7
Mo	ppm	17	0,5	0,1	1,7	2,0	1,1
Nb	ppm	17	19	15	25	2	28
Ni	ppm	17	28	5	60	2	12
Pb	ppm	17	5	2	19	2	39
Rb	ppm	17	219	161	295	2	39
Sc	ppm	17	18	13	24	2	22
Sn	ppm	17	5	3	15	2	35
Sr	ppm	17	85	48	149	2	102
Ta	ppm	17	1,5	1,0	2,1	2,0	2,4
Th	ppm	17	21	14	27	2	12
U	ppm	17	4	3	3	2	3
V	ppm	17	115	86	161	2	133
W	ppm	17	11	6	20	2	24
Zn	ppm	17	59	26	99	2	12
Zr	ppm	17	181	113	367	2	218
Y	ppm	17	30	20	52	2	35
La	ppm	17	61	46	80	2	48
Ce	ppm	17	130	99	164	2	104
Pr	ppm		14	10	17	2	11
Nd	ppm	17	50	38	65	2	41
Sm	ppm	17	10	7	13	2	8
Eu	ppm	17	1,8	1,3	2,4	2,0	1,4
Gd	ppm	17	7	5	12	2	6
Tb	ppm	17	1,1	0,8	1,7	2,0	1,1
Dy	ppm	17	6	4	9	2	5
Ho	ppm	17	1,1	0,7	1,7	2,0	1,3
Er	ppm	17	3	2	5	2	4
Tm	ppm	17	0,5	0,3	0,8	2,0	0,6
Yb	ppm	17	3	2	6	2	4
Lu	ppm	17	0,5	0,3	0,9	2,0	0,6

arsenic is due to the high arsenic concentration of 420 ppm of one of the two samples analysed (sample 95). This content is most likely caused by the slightly porous and limonitic weathering of this sample. However, it is this sample as well which contains an unusually high Bi concentration of 17 ppm. The bismuth content of sample 72 of 1.2 ppm Bi is still ten times the content of the upper crust (WEDEPOHL, 1995).

The close geochemical affinity of both rock types is emphasized again by comparing the chondritic normalized REE contents of the phyllites and tourmalinites respectively (Text-Fig. 15).

Finally, Text-Fig. 16 compares the geochemistry of the tourmalinites presented in this work with the ones described as associated with stratabound scheelite mineralizations in the Eastern Alps (RAITH, 1988). This plot emphasizes the uniformity of both tourmalinite groups irrespectively to the mineralizations they are associated with.

4.4. Geochemistry of Samples Containing Arsenic > 1wt-%

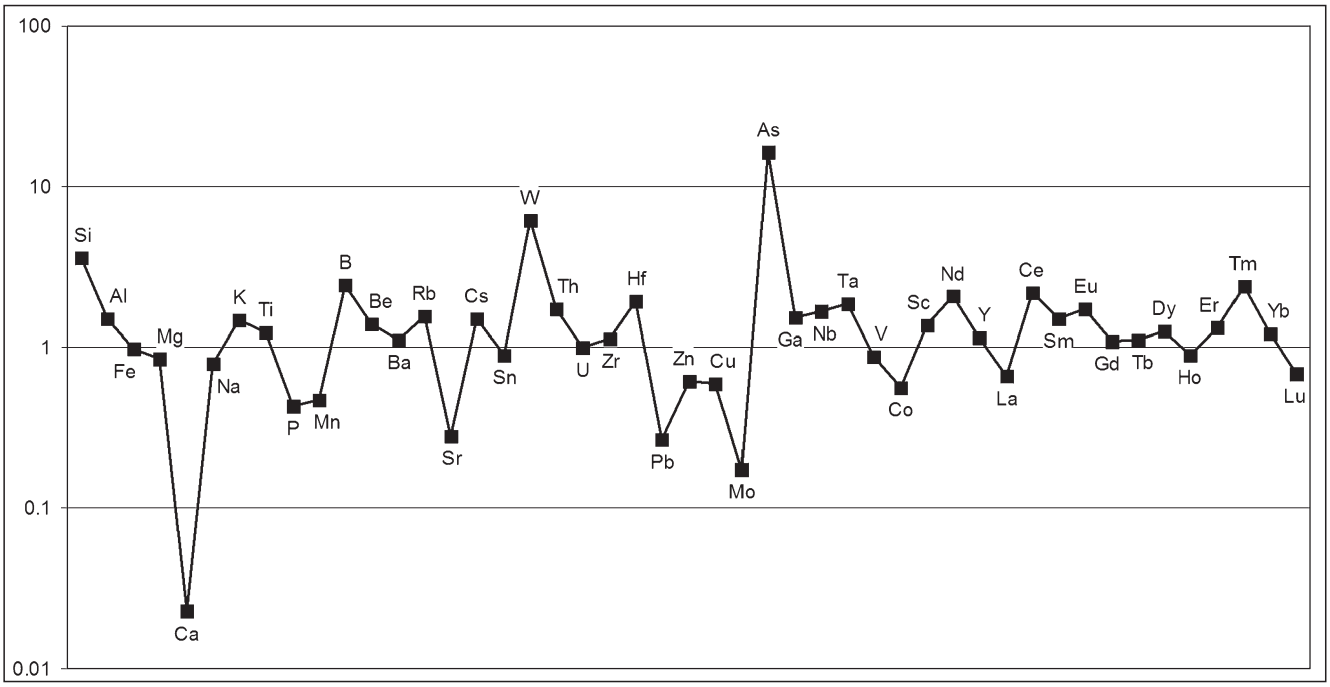
(Table 4)

The concentrations of selected elements of those three samples displaying arsenic contents >10,000 ppm are listed in Table 3. The sulphur contents of these samples correspond to arsenic contents of 2.22 wt-%, 1.86 wt-% and 1.1 wt-% respectively. Again, arsenic is not accompanied by elements frequently associated with sulphidic mineralizations. In fact, the mineralization under investigation is mono-elemental.

With regard to the schematic section through the mineralization (Text-Fig. 12) there seems to exist a clear positive correlation between arsenic and silica. This is, however, not corroborated

Table 3.
Correlation coefficients between arsenic, boron and the main elements emphasizing the lack of relevant correlation (using log-centring transformation).

	Si	Al	Fe	Mg	Ca	Na	K	Ti	P	Mn	B	As
Si	1											
Al	0,51	1										
Fe	0,34	0,87	1									
Mg	0,18	0,78	0,80	1								
Ca	-0,21	-0,47	-0,22	-0,33	1							
Na	0,13	0,56	0,55	0,25	-0,05	1						
K	0,62	0,94	0,75	0,59	-0,55	0,50	1					
Ti	0,57	0,97	0,80	0,66	-0,53	0,58	0,97	1				
P	0,20	0,02	0,30	-0,05	0,70	0,35	0,00	0,01	1			
Mn	0,11	0,56	0,80	0,46	0,07	0,45	0,49	0,50	0,50	1		
B	-0,32	-0,24	-0,42	0,09	-0,36	-0,47	-0,33	-0,31	-0,79	-0,56	1	
As	-0,31	-0,76	-0,78	-0,82	-0,01	-0,47	-0,56	-0,63	-0,26	-0,60	0,07	1



Text-Fig. 13.
Main and trace element geochemistry of the phyllites normalized against the "average shales" sensu TUREKIAN & WEDEPOHL (1961).

by the correlation coefficient calculated (Table 3). As the samples highest in arsenic show the texture of a shear zone, the correlation shown in Text-Fig. 4 is interpreted as being caused tectonically. This correlation is therefore a local one, related to the shear zone.

4.5. Sulphur Isotope Investigations

Two arsenopyrite concentrates (from samples 65 and 82) have been analysed for their S-isotopic composition yielding $\delta^{34}S$ values of +5.6‰ and 6.46‰ respectively (Table 4).

S-isotopic compositions of arsenopyrite are scarcely reported, no figures are available from the Eastern Alps. $\delta^{34}S$ compositions reported elsewhere are related to ore deposits incomparable to the mineralization presently discussed (e.g. HOFMANN & KNILL, 1996; DOWNES & SECCOMBE, 2004; FAURE & BRATHWAITE, 2006; KOLB at al., 2004). However, the figures given in the papers as cited vary between –4‰ to +5.8‰, a width into which the results presented in this paper fit fairly well. Due to the lack of comparable investigations, an interpretation of these data is impossible at present.

5. Discussion

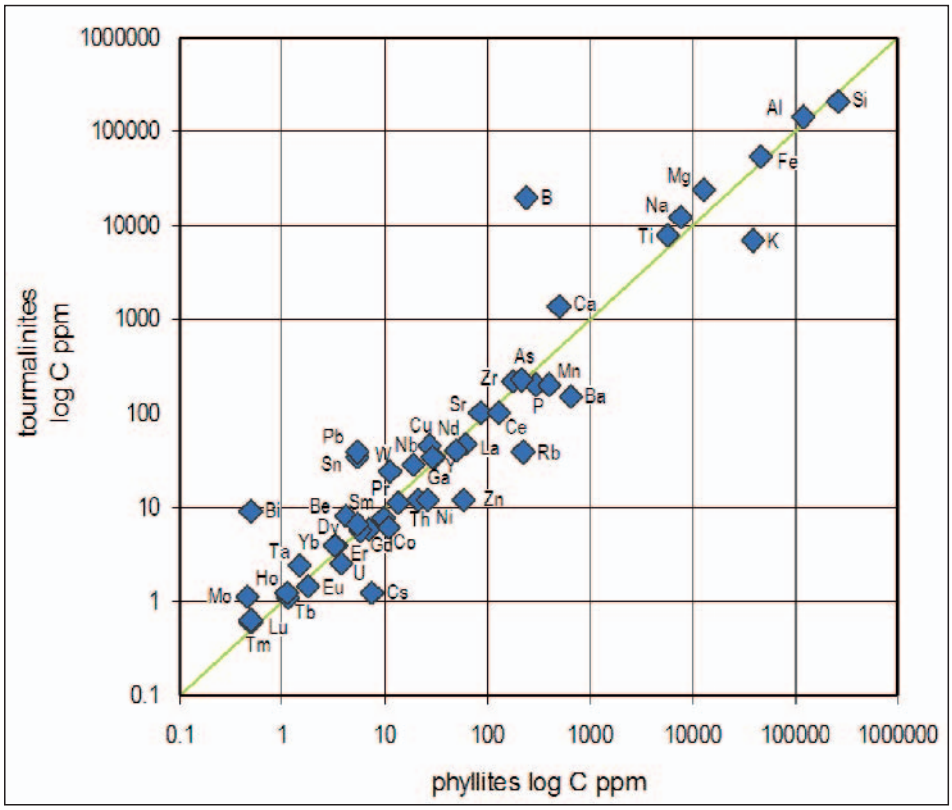
The arsenic mineralization dealt with is hosted by monotonous phyllites belonging to the "Grobgneis Komplex" as described, displaying the greenschist paragenesis quartz ±muscovite ±chlorite ±(rare) clinozoisite and, locally, relictic garnet plus chloritoid. Arsenic and boron are the only elements enriched, however, they are not correlated statistically which points to separate mechanisms of enrichment of both elements. The arsenic content as well as the boron content are obviously not controlled by the lithology of the phyllites.

Tourmalinites occur spatially related to the arsenopyrite mineralization and range in thickness from mm-scaled layers to a maximum of 20 cm. They are barren with respect to sulphides. Disregarding the boron, their bulk and trace element geochemistry (Text-Figs. 14,15) meets perfectly the composition of the phyllites.

Table 4.
Selected trace elements of the samples containing arsenic in excess of 1wt-%; $\delta^{34}S$ data of arsenopyrite. None of the elements frequently accompanying hydrothermal sulphide mineralizations is enriched.

Sample #		65	66	82
As	ppm	> 10000	> 10000	> 10000
Ag	ppm	0,3	0,1	0,3
Au	ppb	350	231	34
Bi	ppm	3,4	2	1,9
B	ppm	63	48	66
Cd	ppm	< 0.1	< 0.1	0,1
Cu	ppm	59	62	140
Hg	ppm	0,01	0,01	< 0.01
Mo	ppm	0,7	0,5	0,6
Pb	ppm	14	8	78
Sb	ppm	3	2,7	1,4
Se	ppm	1,6	1,5	0,8
Tl	ppm	< 0.1	< 0.1	0,2
Zn	ppm	37	30	34
S	%	0,95	0,8	0,47
^{34}S	-----	+ 5.9	n.a.	+ 6.46

It has to be emphasized that tourmalinites are known to occur in the Grobgneiss Complex (WIESENEDER, 1961; MOREAU, 1981). In addition, numerous occurrences, mostly boulders, have been found meanwhile across the whole Grobgneis Complex indicating maximum thicknesses of tourmalinites around 0.5 m (F. BERNHARD [2006], pers. comm.; MOREAU [ibid.] describes a maximum thickness of 2 m and a maximum extension of 7 m). A stratigraphic control of the tourmalinites can neither be established nor excluded. Furthermore, none of the reports refers to an arsenic mineralization associated with tourmalinites. Based on this observation and emphasized by the lack of statistical correlation as mentioned (Table 3), a distinct genetic connex of the arsenic mineralization and the tourmalinites is unlikely. Further on it has to be strengthened that the tourmalinites associated with stratabound scheelite miner-



Text-Fig.14.
Comparison of main and trace element geochemistry of the phyllites and tourmalinites emphasizing their close geochemical affinity.

alizations in the Eastern Alps (RAITH, 1988) and the tourmalinites related to the arsenopyrite mineralization as dicussed are geochemically not discernable (Text-Fig. 16).

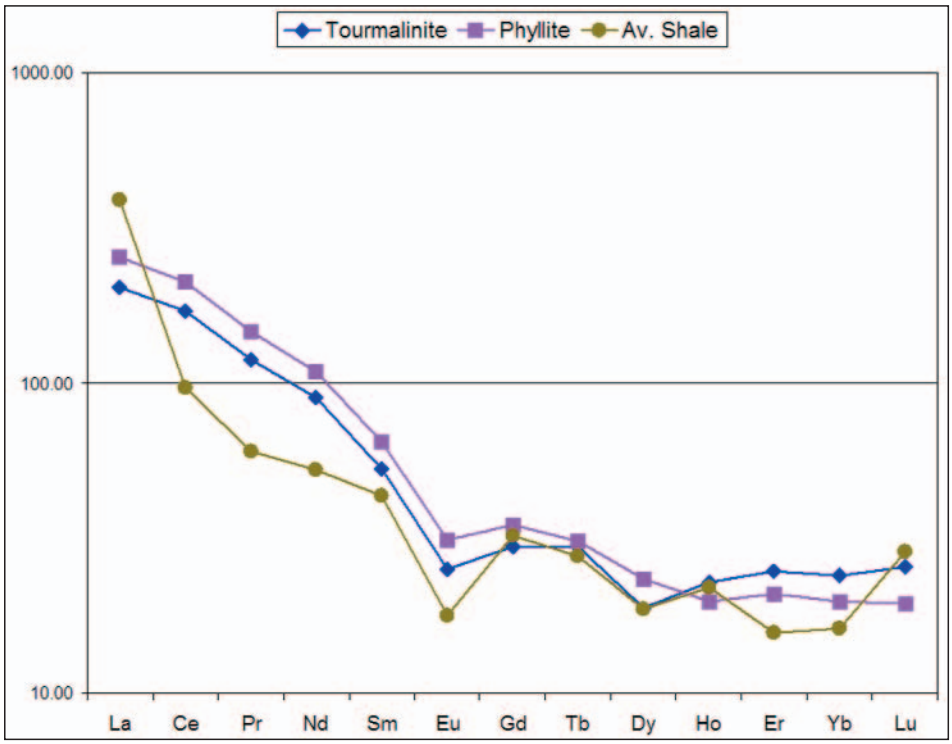
The phyllites show a pronounced twofold schistosity (Text-Fig. 4) and locally a crenulation cleavage. Relictic, chloritized garnet plus chloritoid clearly point to the diaphthoritic character of these rocks (Text-Fig. 5). The highly mineralized phyllites in trench 6 (Text-Fig. 12) show the texture of a shear zone, the mineralized samples and the tourmalinite (Text-Fig. 6) in trench 7 (samples 71–73) are of mylonitic character.

This – youngest – tectonic event corresponds to the late Cretaceous (= eoalpine) HP/LT metamorphism the age of which varies regionally between 100 my to 80 my (MÜLLER, 1994; MÜLLER et al., 1999; summarized in SCHUSTER et al., 2001). Similarly, varying data have been published regarding the metamorphic facies of this late Cretaceous metamorphism, ranging between lower greenschist facies to upper amphibolite facies in different lithologies and tectonic (sub-) units (REINDL, 1989; HUBER, 1994; BERKA, 2000; SCHUSTER et al., 2001). However, though detailed studies focusing on the metamorphism of the immediate area under investigation are lacking, the local petrography of the phyllites hosting the mineralization doubtlessly points to the upper greenschist facies and has therefore affected the mineralization to the same extent.

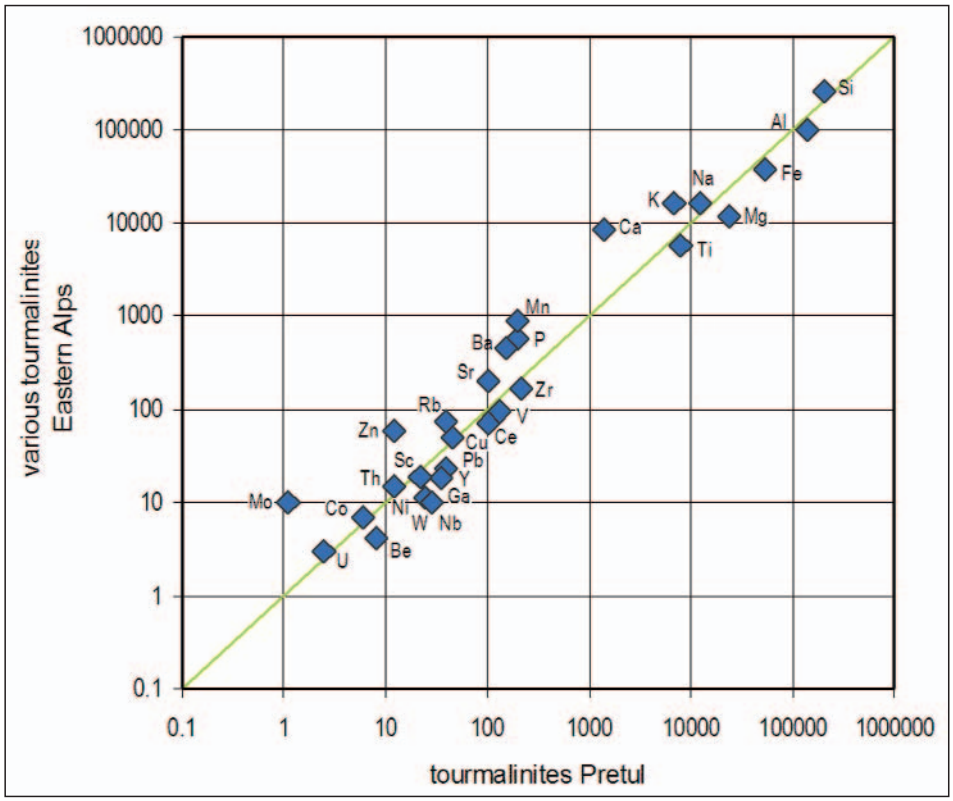
With respect to the genesis of the arsenopyrite mineralization two models have to be considered:

- A tectono-metamorphic origin in shear zones associated with hydrothermal (in this case arseniferous) fluids. This suggests an analogy to the genesis of the leucophyllites as mentioned in chapter 2.1. (see also PROCHASKA et al., 1992). That interpretation is in accordance with the shear zone texture of the mineralization as observed in trench 6 (Text-Fig. 12) and likewise by its flat SW dipping orientation which corresponds perfectly to the orientation of almost all of the regionally spread leucophyllite occurrences (HUBER, 1994). However, it has to be stressed, that no arsenic mineralization associated with leucophyllites has ever been observed (PROCHASKA, pers. comm.).
- A primary enrichment of arsenic in the primordial metapelites.

Arguments in favour of that interpretation are



Text-Fig. 15.
Comparison of the REE geochemistry of tourmalinites, phyllites and average shales (TUREKIAN & WEDEPOHL, 1961) using the normalization standard after MCDONOUGH & SUN (1995); the perfect affinity of tourmalinites and phyllites is obvious.



Text-Fig. 16.
Comparison of main and trace element geochemistry of tourmalinites associated with stratabound scheelite occurrences in the Eastern Alps (RAITH, 1988) with the tourmalinites spatially related to the arsenopyrite mineralization.

- the thickness of the potentially mineralized rock pile of approximately 40 m and the manifold occurrence of mineralized horizons (Text-Figs. 2,3);
- the regional spread of arseniferous phyllites as indicated by soil geochemistry, extending from the area of Mürzzuschlag in the W to the northern Leithagebirge in the E, a distance of about 70 km (Text-Fig. 1),
- the lack of elements accompanying the arsenic .

The high arsenic concentrations (>1wt-% As; Text-Fig. 12) are interpreted as caused by a younger, more or less local shear zone, re-mobilizing the "primary" arsenic, most likely contemporaneous with the shear zones which gave rise to the formation of the leucophyllites. Based on O-isotope fractionation (qtz – mu), temperatures between 450° and 500° have been calculated for the formation of the leucophyllites (HUBER, 1994) and $^{40}Ar/^{39}Ar$ dating yielded ages for their formation ranging between 71 and 85 my.

A probable Variscan impact on the mineralization is not demonstrable.

Further on, a recently published paper on an arsenic mineralization some 12 km W of the area investigated in the Teschengraben, S Krieglach (LASSNIG et al., 2006) needs to be considered. This mineralization, situated in the Grobgneis Complex as well, consists of concordant quartz veins which bear an arsenopyrite-pyrite-pyrrhotite-chalcopyrite-sphalerite mineralization. These quartz veins are hosted by phyllites and the Grobgneiss as well and are folded together with their host rock. Therefore, according to these authors, the mineralization is either syndeformative or, at the most, contemporaneous with the intrusion of the Grobgneis. Consequently they exclude a synsedimentary genesis of the As-mineralization and interpret its genesis as tectono-metamorphic. According to these authors, folding is related to the eo-alpine metamorphism, and is said to have taken place at temperatures between 450° and 550° (in perfect accordance with the figures given by REINDL [1994]) and at a minimum pressure of 7.5 kb. The arsenic mineralizations at Pretul Alm and Teschengraben differ mainly in their mineralogy and their tectonic style. However, no statement on their relation can be made at present.

6. Conclusions

Field observations, mineralogical and geochemical data are in favour of a primary, syngenetic interpretation of the given mineralization. This interpretation stands for a paleozoic, most likely Ordovician to early Carboniferous, regional arsenic deposition in a pelitic environment. Tourmalinites, spatially related to the mineralization do not seem to be genetically linked to the arsenopyrite mineralization. Their geochemistry corresponds to the chemistry of the hosting phyllites suggesting their in situ genesis by selectively replacing the sediments by boron-rich fluids.

During the late Cretaceous, eo-Alpine metamorphism, shear zones, related to thrusting, affected the mineralization and gave rise to an upgrade of arsenic causing locally arsenic contents surpassing 1 wt-% As.

A most likely Variscan impact on the mineralization as deduced from a regional point of view and as indicated by the diaphthoritic mineralogy of the hosting phyllites (chloritized garnet, chloritoid) is not demonstrable.

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