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Scandium mineralization associated with hydrothermal lazulite-quartz veins in the Lower Austroalpine Grobgneis complex, Eastern Alps, Austria

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ABSTRACT: Lazulite ($MgAl_2(PO_4)_2(OH)_2$)-quartz veins within the Lower Austroalpine Grobgneis complex, Austria, have Sc-contents up to 200 ppm. The predominant Sc-carrier is pretulite, $ScPO_4$, and this phase occurs as a wide-spread accessory mineral. Vein formation took place at temperatures of 300-500° C and low pressure during Permo-Triassic extensional tectonics and fluid flow. Mg-enriched alteration zones suggest that vein material was not derived from the immediate host rocks. Eo-Alpine metamorphism and deformation overprinted the veins to varying degrees. Despite the low tonnage of the Sc-rich veins, this new type of Sc-mineralization may point to larger Sc-accumulations in similar phosphate-rich hydrothermal environments.

1 INTRODUCTION

Scandium is a moderately abundant transition element with an average content ca. 7 ppm in the upper and ca. 25 ppm in the lower continental crust (Wedepohl 1995). Sc-content broadly decreases from mafic (ca. 50 ppm) to felsic (<5-10 ppm) igneous rocks (e.g. Norman & Haskin 1968, Poli et al. 1989). Siliciclastic sedimentary rocks have Sc-contents of 5-25 ppm, decreasing with increasing sediment maturity (Cullers 2000, Sawyer 1986).

Demand for Sc in the western world has increased only recently, especially for high-strength Sc-Al alloys. This contrasts with the long-term use of Sc in the former Soviet Union as an alloying metal in missile and MIG-fighter construction.

Despite the similar crustal abundance of Sc compared with base metals, e.g. Cu, Pb, Sn, independent Sc-minerals and Sc-deposits are rare and Sc is usually won as by-product during processing of various ores, tailings or residues. Recently, the Zhovti Vody mine in the Krivoy-Rog-Basin, Ukraine, began to produce Sc as a main product from metasomatic rocks within iron formations. Reserves are 7.4 Mt grading 105 ppm Sc (Ashurst Technology Ltd. website 2001). Possibly economic Sc-enrichments were also reported in fresh and weathered carbonatites (Amli 1977, Kravchenko et al. 1996) and in lateritic weathering crusts (Australian Rare Earth Newsletter website 2001). Liferovich et al. (1998) reported a low-temperature hydrothermal Sc-mineralization associated with various hydrous phosphates within metasomatized phoscorites of the Kovdor Massif, Russia.

The long-known lazulite ($MgAl_2(PO_4)_2(OH)_2$)-quartz veins in northeastern Styria and southern Lower Austria contain significant Sc-enrichments in the form of pretulite, $ScPO_4$ (Bernhard et al. 1998b). This contribution gives data on the geology, mineralogy and geochemistry of this new type of Sc-mineralization.

2 REGIONAL GEOLOGY

The polymetamorphic Lower Austroalpine Grobgneis complex which contains the Sc-rich lazulite-quartz veins comprises mainly phyllites, micaschists and paragneisses with abundant Carboniferous to Permian granitoid intrusions (Fig. 1). Three metamorphic events can be distinguished: 1) a Variscan amphibolite facies metamorphism (garnet + staurolite); 2) an only locally observed Permian HT-LP metamorphism (andalusite + biotite + sillimanite); 3) an Eo-Alpine greenschist facies metamorphic overprint (chloritoid + chlorite), locally reaching amphibolite facies conditions (staurolite). The Permian high-grade rocks may represent a separate tectonic unit, emplaced onto the Grobgneis complex s. str. during Eo-Alpine nappe stacking, but evidence is ambiguous (Schuster et al. 1999).

This polymetamorphic basement is parautochthonously overlain by a monometamorphic, Permian to lower Triassic siliciclastic (Verrucano, Semmeringquarzit) and Triassic-Jurassic carbonatic cover sequence (Fig. 1).

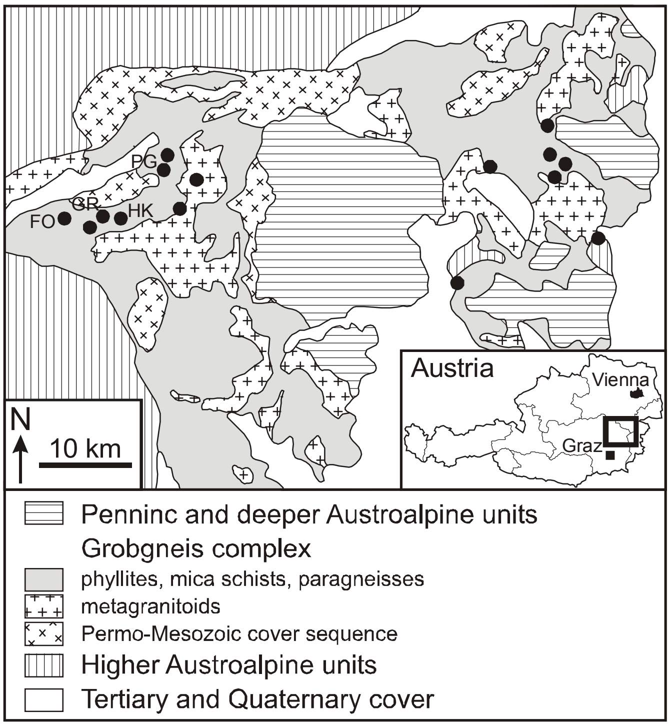

Figure 1. Simplified geological map of northeastern Styria and southern Lower Austria. Important lazulite occurrences are shown as black dots. FO: Freßnitzkogel, GR: Granegg-NW, HK: Höllkogel, PG: Pretulgraben.

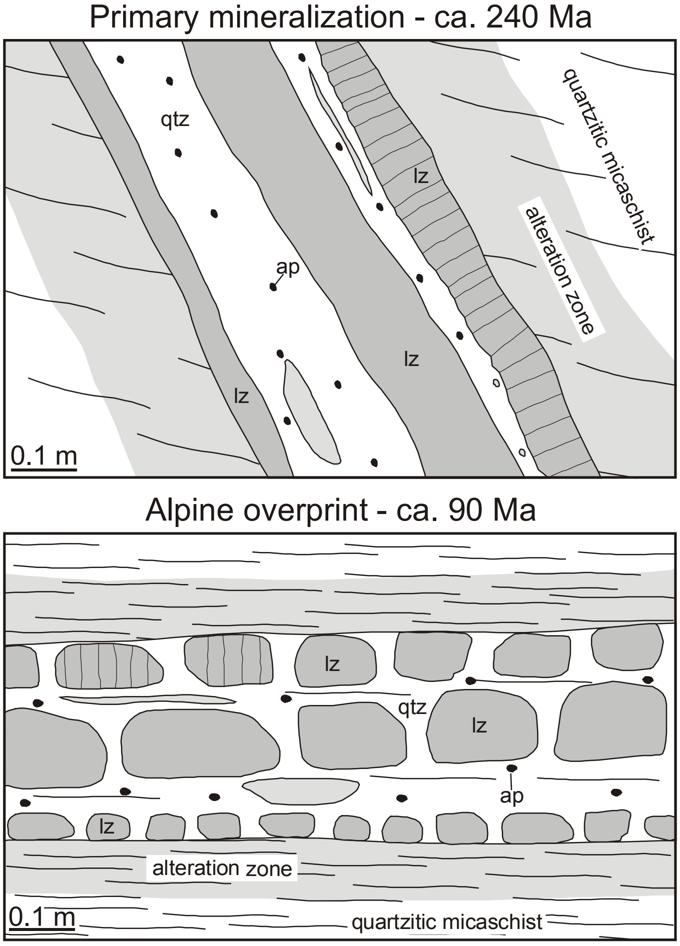

Figure 2. Synoptic presentation of primary and secondary features of Sc-rich lazulite-quartz veins.

3 MINERALIZATION

About 15 major Sc-rich lazulite-quartz veins are known within the basement rocks, spread over an area of ca. 1000 km^2 (Fig. 1). They appear to occur in lithologies with and without obvious Permian HT-LP metamorphism, but field evidence is not always clear due to poor exposure of critical outcrops. The relationship with the Sc-poor lazulite occurrences in the Semmeringquarzit is unknown.

The veins are hosted by quartzitic rocks (quartz + muscovite + chlorite ± albite) or by micaschists (muscovite + biotite + quartz + garnet + chloritoid after andalusite?). Veins are at least up to one meter thick and can be traced in continuous outcrop up to 5 m, but occurrence of loose blocks suggest much higher strike lengths. Primary hydrothermal features are often disturbed by Eo-Alpine metamorphism and deformation, but in less overprinted areas primary hydrothermal features can be observed (Fig. 2):

1) Crosscutting relationships of lazulite-quartz veins with the layering and foliation of host rocks.
2) Hydrothermal breccias consisting of lazulite and quartz, both supporting angular clasts of host rocks.
3) Comb textured lazulite crystals.
4) Hydrothermal banding, consisting of lazulite-rich and quartz-rich domains.
5) Concentric oscillatory growth zoning of xenotime-(Y) and pretulite.

However, Eo-Alpine overprint lead to

1) ductile deformation and complete recrystallization of quartz,
2) brittle deformation, marginal recrystallization and static replacement of lazulite by muscovite and apatite,
3) replacement of lazulite by muscovite and apatite in narrow shear zones,
4) remobilization of lazulite, apatite and quartz in dilatational fractures.

The primary assemblage of lazulite-rich domains is pale green to pale blue lazulite (> 80 Vol%, XMg = 0.92-0.98), fluorine-bearing apatite, subordinate quartz and possibly muscovite. Ubiquitous primary accessory minerals are pretulite, florencite-(Ce), xenotime-(Y) and rutile. The size of pretulite crystals ranges from 1-200 µm. Small grains occur as inclusions in lazulite, whereas the larger grains appear to be confined to lazulite grain boundaries or fractures. Quartz-rich domains consist of recrystallized quartz, apatite and little rutile and xenotime-(Y) and are devoid of pretulite.

Other minerals, confined to individual veins, related to Alpine overprint or supergene processes, are kyanite (replacing andalusite), augelite, wardite, clinochlore, pyrite, hydroxylherderite, chlorapatite, hydroxylapatite, bearthite, paragonite, goyazite, crandallite, corundum, pyrophyllite, kaolinite, goethite.

Field relations constrain the time of vein formation between post-peak Permian HT-LP metamorphism and Cretaceous, Eo-Alpine metamorphism. Electron microprobe dating of accessory xenotime-(Y) gave an age of 246 ± 23 Ma (Permian - Lower Triassic), consistent with field and petrographic observations (Bernhard et al. 1998a).

Thermodynamic considerations comprising primary hydrothermal minerals suggest vein formation at 300°-500°C and ≤ 3 kbar.

4 CHEMICAL CHARACTERIZATION

Lazulite-quartz veins are enriched in P, Al, Mg, according to their major mineral, lazulite. The overall trace element characteristic shows a marked depletion of HFSE elements (Ti, Zr, Hf, Nb), a slight depletion of base metals (Cu, Pb, Zn, Sn) and an enrichment of Sc (up to 200 ppm), V and Sr compared to upper crustal values (Tab. 1). REE-contents are varying and possibly influenced by post-vein REE mobility, as indicated by late stage or Eo-Alpine formation of florencite-(Ce) in some samples. REE-patterns reflect the dominant contribution of florencite-(Ce) and xenotime-(Y) to the REE-budged and show negligible to positive Eu-anomalies (Fig. 3). A fractionation of Y and Dy or a lanthanide tetrad effect is not obvious. Metasedimentary and metagranitoid rocks in the area have Sc-contents in the usual range (Schermaier et al. 1997).

Sc (and V) correlates positively with lazulite abundance (Fig. 4), suggesting coprecipitation of pretulite and lazulite and possible transport of Sc as phosphate complexes (Gramaccioli et al. 2000). The dominant carrier of Sc in the lazulite-quartz veins appears to be pretulite, but the actual Sc-content of the accompanying lazulite is not yet known. Quartz-rich domains contain less than 5 ppm Sc (Tab. 1).

5 WALL ROCK ALTERATION

Lazulite-quartz veins are accompanied by macroscopically inconspicuous, several dm wide alteration zones. Irrespective of the host rock, they consist of quartz + muscovite + Mg-rich chlorite ± kyanite and were recrystallized and often deformed during Eo-Alpine orogenesis. An important feature is the partial replacement of primary monazite-(Ce) by florencite-(Ce) during hydrothermal alteration.

The chemical characterization of the alteration zone at Höllkogel, located in quartzitic rocks, suggest that HFS elements (Ti, Zr) were immobile during alteration. Mass balance calculations with Ti and Zr as immobile components indicate a three-fold enrichment of Mg and a depletion of Fe, Mn and possibly Na. XMg increase from ca. 0.4 in unaltered quartzitic rocks to ca. 0.75 in the alteration zone. All other elements remained unchanged within uncertainty. This results point out that vein material was not derived from the immediate host rock but must have an external source, which is unconstrained at the moment.

Table 1. Major and trace element analyses of lazulite-quartz veins. Major elements, Be and Sc by ICP-AES, other elements by ICP-MS after fusion digestion.

sample	GR1a	HK1a	PG3	FO2	HK1f	UCC
type	lz-rich	lz-rich	b. vein	b. vein	qtz-rich	
wt% SiO_2	7.57	1.62	39.83	40.60	98.01	64.92
TiO_2	0.03	0.02	0.02	0.06	<0.01	0.52
Al_2O_3	31.53	32.04	19.31	20.17	0.67	14.63
Fe_2O_3	0.43	0.46	0.31	0.78	<0.01	4.42
MnO	0.02	0.01	0.01	0.04	<0.01	0.07
MgO	11.47	11.68	5.89	5.13	0.03	2.24
CaO	2.90	2.62	5.35	3.83	0.66	4.12
Na_2O	0.08	0.06	0.08	0.24	0.02	3.46
K_2O	0.44	0.22	0.92	1.05	0.19	3.45
P_2O_5	39.08	43.05	25.26	21.88	0.58	0.15
LOI	6.06	6.25	3.65	4.73	0.04	
Total	99.61	98.03	100.63	98.51	100.20	
ppm Be	1	<1	2	2	<1	3.1
V	165	140	86	70	<5	53
Cr	<20	21	16	33	<10	35
Ni	<15	<5	<5	42	<5	19
Cu	<10	<5	<5	29	<5	14
Zn	<30	<2	<2	10	<2	52
Ga	2	3	2	5	<1	14
Ge	<0.5	0.1	0.4	1	0.7	1.4
Rb	13	7.2	31.3	43.7	6.5	110
Sr	1440	817	689	3380	41.3	316
Sc	242	185	83	59	5	7
Y	14.7	20.2	20.6	137.6	100.8	21
Zr	<1	3.7	5.2	2.3	4.2	237
Nb	1.7	0.45	1.0	2.8	1.3	26
Mo	<2	0.21	0.36	0.6	0.45	1.4
Sn	<1	0.4	0.7	0.8	0.3	2.5
Sb	0.2	0.59	<0.01	2.99	0.37	0.31
Cs	0.4	0.33	0.37	1.4	0.36	5.8
Ba	88	92.9	74.7	211	24.9	668
La	1.48	1.82	14.87	44.4	1.40	32
Ce	2.6	3.8	29.8	97.9	3.00	66
Pr	0.36	0.46	3.37	10.90	0.38	6.3
Nd	1.92	2.58	16.89	50.04	2.43	26
Sm	1.12	1.09	4.22	12.03	1.81	4.7
Eu	0.74	1.16	3.86	3.70	1.88	0.95
Gd	2.76	2.21	3.86	13.21	7.50	2.8
Tb	0.56	0.53	0.60	2.66	2.25	0.50
Dy	2.93	3.47	3.36	17.36	16.68	2.9
Ho	0.51	0.69	0.62	3.86	3.55	0.62
Er	1.34	1.94	1.73	11.12	10.51	--
Tm	0.17	0.25	0.18	1.65	1.51	--
Yb	1.04	1.72	1.51	10.30	9.47	1.5
Lu	0.15	0.23	0.20	1.39	1.28	0.27
Hf	<0.1	<0.05	<0.05	<0.1	<0.05	5.8
Tl	0.20	0.04	0.14	0.19	0.06	0.75
Pb	10	10	7	5	<5	17
Bi	<0.06	<0.05	0.12	0.07	<0.05	0.12
Th	1.85	0.24	3.18	19.15	0.33	10
U	1.5	1.2	1.0	7.5	3.5	2.5

lz-rich: lazulite-rich domain; qtz-rich: quartz-rich domain; b. vein: bulk vein; UCC: composition of the upper continental crust (Wedepohl 1995).

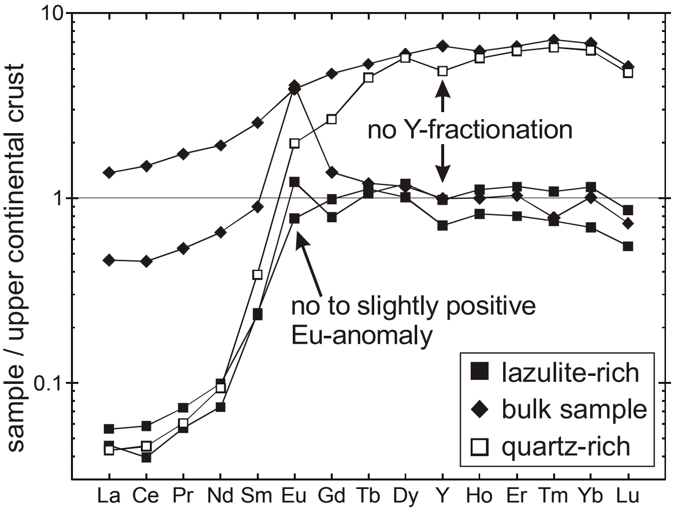

Figure 3. REE-patterns of lazulite-quartz veins, normalized to the upper continental crust (Wedepohl 1995)

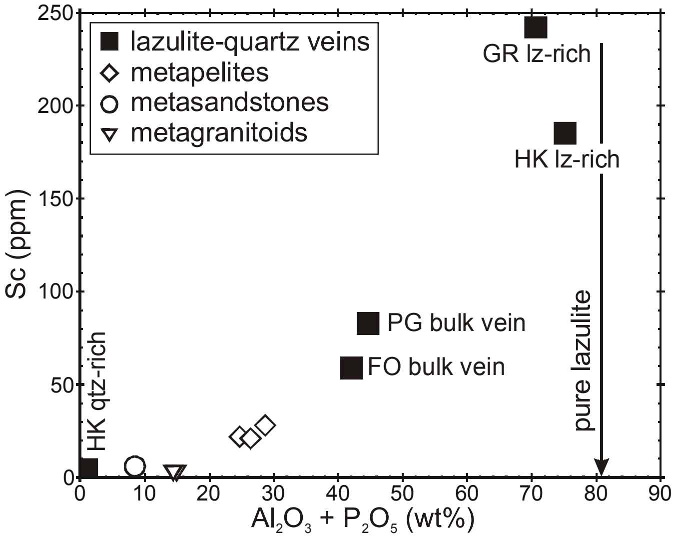

Figure 4. Plot of Sc versus Al_2O_3+P_2O_5 for lazulite-quartz veins and various country rocks of the Grobgneis complex.

6 TENTATIVE GENETIC INTERPRETATION

The formation of lazulite-quartz veins may be related to Permo-Triassic extensional tectonics, metamorphism and fluid circulation. Permo-Triassic quartz, barite, fluorite and base metal vein systems are widely distributed in the Alps and in central Europe. The occurrence of Sc-rich lazulite-quartz veins within a restricted area of the Eastern Alps suggest locally very unusual mobilization, transport and precipitation conditions.

7 CONCLUSIONS

Sc-mineralization in the studied region does not comprise large deposits, but only small-scale occurrences scattered over a quite large area. The discovery of a high-tonnage Sc-deposit in this part of the Eastern Alps seems unlikely. However, the close association of Sc with phosphate minerals may point to the presence of similar, economic Sc-enrichments in other phosphate-rich hydrothermal systems.

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