

Pretulite, ScPO₄, a new scandium mineral from the Styrian and Lower Austrian lazulite occurrences, Austria

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ABSTRACT

Pretulite is a new Sc phosphate with zircon-type structure from the phyllite-micaschist hosted hydrothermal lazulite-quartz veins in the Lower Austroalpine Grobgnais complex, eastern Austria. The new species is the Sc-dominant analogue of xenotime-(Y) and occurs as an accessory mineral in all investigated lazulite specimens, forming anhedral to euhedral crystals up to 200 μm long with the dominant form {211}. It is associated with lazulite, fluorapatite, chlorapatite, quartz, muscovite, clinocllore, paragonite, kyanite, pyrophyllite, augelite, wardite, hydroxylherderite, goyazite, florencite-(Ce), xenotime-(Y), bearthite, rutile, pyrite, corundum, and an AlO(OH)-phase. Pretulite is translucent to transparent with an adamantine luster, colorless to pale pink, uniaxial positive with $\omega = 1.790$ (5), $\epsilon = 1.86$ (1) and shows a weak orange fluorescence at 254 nm as well as a bright blue cathodoluminescence. Mohs hardness is about 5. The empirical formula for pretulite (based on four O atoms) is $(\text{Sc}_{0.98}\text{Y}_{0.02})_{1.00}\text{P}_{1.00}\text{O}_{4.00}$. It contains variable amounts of Y with $\text{Y}/(\text{Y} + \text{Sc}) = 0.5 - 3.2$ mol% and traces of Yb, Er, and Dy. The space group is $I4_1/amd$ with $a = 6.589$ (1) Å, $c = 5.806$ (1) Å, $V = 252.1$ (1) Å³, $d_{\text{calc}} = 3.71$ g/cm³, $Z = 4$. The four strongest lines in the X-ray powder pattern are $d_{200} = 3.293$ (100), $d_{112} = 2.4636$ (42), $d_{312} = 1.6927$ (45), $d_{332} = 1.3697$ (15) Å. The crystal structure was refined using 108 reflections to $R(F_o) = 0.018$. Cell parameters and average M-O distances confirm a small amount of Y substituting Sc in the eightfold-coordinated M-position. The formation of pretulite is attributed to a moderate enrichment of Sc in lazulite-rich domains of the veins (about 180 ppm) and the inability of the accompanying minerals to incorporate larger quantities of Sc in their crystal structure. The name is after the mountain Pretul, Fischbacher Alpen, Styria, Austria.

INTRODUCTION

Scandium is a moderately abundant transition element with an average content of 11 ppm in the upper continental crust (Taylor and McLennan 1985) and generally substitutes for Fe, Al, and Y in major and accessory rock-forming minerals (Fron del 1970). Thus, minerals with Sc as a major constituent are rare. Only five are presently known, including thortveitite [(Sc,Y)₂Si₂O₇], bazzite [Be₃(Sc,Al)₂Si₆O₁₈], cascandite [Ca(Sc,Fe²⁺)Si₃O₈(OH)], jervisite [(Na,Ca,Fe²⁺)(Sc,Mg,Fe²⁺)Si₂O₆], and kolbeckite [ScPO₄·2H₂O]. The Sc silicates are found in pegmatites, hydrothermal veins, and miarolitic cavities in granites, whereas kolbeckite is of low-temperature hydrothermal or supergene origin (Fron del 1970; Mellini et al. 1982; Postl 1981).

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During systematic SEM-EDX work on Styrian lazulites, a volatile-free Sc phosphate was detected, which turned out to be the Sc-dominant analogue of xenotime-(Y). This phase has been named pretulite after the mountain Pretul (1656 m above sea level, Fig. 1), where it was first discovered. The mineral and the name have been approved by the IMA Commission on New Minerals and Mineral Names. Type material of pretulite is deposited at the Steiermärkisches Landesmuseum Joanneum, Graz, Styria and at the Naturhistorisches Museum, Vienna.

GEOLOGICAL OVERVIEW

Two different types of lazulite occurrences exist in the Lower Austroalpine units of northeastern Styria and southern Lower Austria. The first type (pretulite-bearing) commonly consists of up to 1 m³ large, loose blocks of lazulite-quartz veins. About 15 of such occurrences are known, located in the Grobgnais complex west and east of the underlying Wechsel complex (Fig. 1). The host

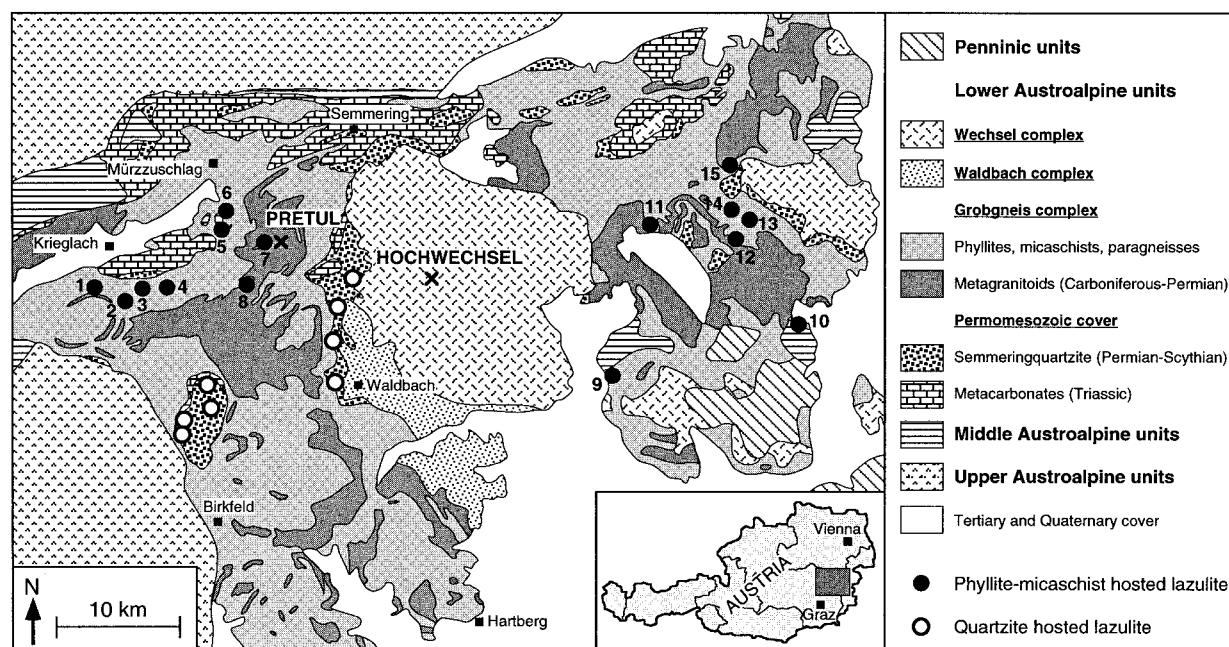


FIGURE 1. Simplified geological map of the Lower Austroalpine nappe complex in eastern Austria (Neubauer et al. 1992). Locations of lazulite occurrences are in part derived from Berl (1996): (1) Fressnitzkogel, (2) Rotriegel, (3) Fressnitzgraben (lazulite type locality), (4) Höllkogel (pretulite type locality), (5) Fürstenbauer, (6) Ganztal, (7) Amundsenhöhe, (8) Grossmarker, (9) Schäffern, (10) Kirchschiag, (11) Krumbach, (12) Thal, (13) Spratzau A, (14) Spratzau B, (15) Stickelberg.

rocks of these hydrothermal veins are polymetamorphic phyllites and micaschists with a probable early Paleozoic protolith age (Neubauer et al. 1992). The Variscan metamorphism of the Grobgneis complex reached amphibolite facies conditions with local migmatization in the southern part and was accompanied by voluminous Carboniferous and subordinate Permian granitoid intrusions (Fig. 1). Subsequent Alpine deformation and metamorphism at greenschist facies conditions in the northern part and amphibolite facies conditions in the southern part transformed the granitoids into gneisses (Grobgneis) and the metasedimentary rocks into phyllites and micaschists, leaving only local remnants of Variscan mineral assemblages (Neubauer et al. 1992). The second type of lazulite occurrences (pretulite-free) is associated with the Lower Triassic, monometamorphic Semmering quartzite of the Fischbach window and the Rettenegg area (Fig. 1).

Meixner (1937) gave the most recent survey of all known Austrian lazulite occurrences. He suggested that all lazulite-bearing veins in northeastern Styria and southern Lower Austria are genetically related to the widespread, in his view post-Jurassic granitoids of the Grobgneis complex.

OCCURRENCE AND PARAGENESIS

Pretulite was first discovered at Fürstenbauer, Pretulalpe (Fig. 1). Investigation of samples from other localities in Styria and southern Lower Austria showed that pretulite is an ubiquitous mineral in phyllite-micaschist hosted lazulite-quartz veins. Höllkogel is considered to

be the type locality because it is the only known bedrock occurrence and it provided the material most suitable for a complete description of the new mineral species.

The type locality of pretulite is a natural outcrop, situated 100 m southwest of the Höllkogel, 12 km south-southwest of Mürzzuschlag, Fischbacher Alpen, Styria, Austria (15°37'25"E, 47°30'56"N, 1020 m above sea level). Here, the quartz-rich phyllite (quartz, muscovite, chlorite, albite, apatite, zircon, rutile, indicating greenschist facies metamorphic overprint) contains a subconcordant to concordant, 10–40 cm wide lazulite-quartz vein. The vein dips 30° north, is boudinaged, and shows sharp contacts to the host rock. It can be traced over the whole outcrop length of 4 m, and there is no macroscopically visible alteration zone adjacent to the vein. Two different, irregularly distributed domains can be distinguished within this and all other lazulite-quartz veins: (1) Subangular to rounded, lazulite-rich domains that are 0.5–20 cm in size and consist of coarse-grained, pale blue, commonly anhedral lazulite (>80 vol%), fluorapatite, chlorapatite, muscovite, as well as locally clinocllore and paragonite as major constituents. Accessory phases include augelite, wardite, hydroxylherderite, goyazite, florencite-(Ce), xenotime-(Y) (with 1–2 wt% Sc₂O₃), rutile, pyrite, corundum, an AlO(OH)-phase, and pretulite. Quartz appears here as a late-stage fracture-filling phase only. (2) Quartz-rich domains are composed of recrystallized quartz (>95 vol%), fluorapatite, muscovite, and xenotime-(Y) (with uraninite inclusions) and rutile as accessories. They may be as large as 30 cm, enclose

lazulite-rich domains or fill gaps between them, suggesting a late-stage origin. Quartz-rich domains are devoid of corundum and pretulite.

This clear distinction between lazulite- and quartz-rich domains is locally disturbed by subsequent deformation, recrystallization, and alteration, most probably during Alpine greenschist facies metamorphism. A second generation of muscovite, apatite, and clinocllore as well as kyanite and pyrophyllite developed along narrow shear planes and at the rims of lazulite-rich domains. Fractures in lazulite are filled with quartz, apatite, bearthite, sometimes pretulite, and a second generation of subhedral to euhedral lazulite. In a few cases, several 1000 cm³ large volumes of lazulite-quartz veins may have been totally remobilized, resulting in an intimate intergrowth of lazulite, apatite, and quartz. Supergene minerals in lazulite-quartz veins are goyazite, crandallite, hydroxylapatite, kaolinite, goethite, and melanterite.

Pretulite comprises <0.05 vol% of lazulite-rich domains and every thin section contains some anhedral to euhedral crystals from a few to 200 μm in size. Small grains are dominantly enclosed by primary lazulite crystals, whereas the larger grains are more often confined to lazulite grain boundaries or later fractures. In some cases, pretulite may be intergrown with muscovite, clinocllore, fluorapatite, and rutile. Inclusions in pretulite are rare, consisting of clinocllore, lazulite, and fluorapatite. The textural observations indicate that pretulite crystallized during formation of lazulite-rich domains and may also suggest a possible remobilization during metamorphic overprint.

The relation of pretulite to xenotime-(Y) is not easily discernable. In polished thin sections, these minerals were not observed together, which may be because only one xenotime-(Y) grain was detected out of several thin sections examined. In the polished grain mount of a heavy mineral concentrate of the type specimen (sample HK1A), however, some pretulite crystals contain 1–5 μm sized, rounded blebs of xenotime-(Y). These blebs may represent exsolution products of a more Y-rich precursor phase. Very rarely, up to 30 μm large xenotime-(Y) grains are oriented intergrown with pretulite, suggesting a contemporaneous growth of two immiscible phases. Large individual xenotime-(Y) grains did not contain any pretulite exsolutions or intergrowths.

PHYSICAL PROPERTIES

Pretulite grains were recovered with heavy liquid separation techniques from the <120 μm sieve fraction of sample HK1A (Höllkogel) for morphological, optical, and X-ray crystallographic studies.

Euhedral crystals of pretulite are transparent, pale pink with an adamantine luster and up to 60 × 60 × 120 μm in size. The habit is bipyramidal with the dominant form {211}, small {100}, and rounded {111}, determined with an optical two-circle reflection-goniometer (Fig. 2). Twinning was not observed. The more abundant anhedral grains appear white and translucent and may reach 200

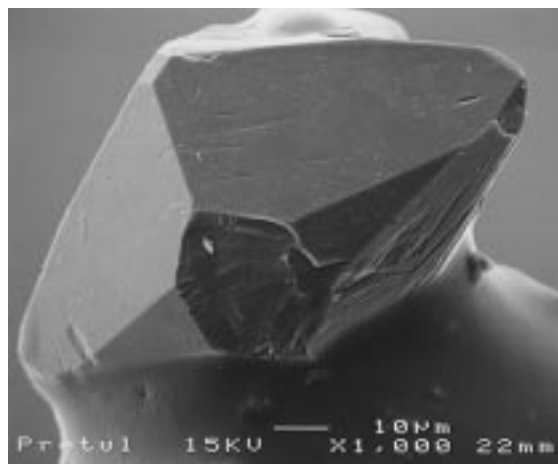


FIGURE 2. SEM-photograph of a distorted, euhedral pretulite crystal with the dominant form {211}, small {100} and rounded {111}. This crystal was used for structure refinement and is mounted with epoxy. Sample HK1A.

μm in length. The streak is white, Mohs hardness is about 5. The mineral is brittle with a splintery fracture and exhibits a perfect cleavage parallel {100}. Pretulite shows a weak orange fluorescence in short-wave UV light (254 nm) and a bright blue cathodoluminescence. Density could not be measured due to small grain size; the calculated density from unit-cell parameters is 3.71 g/cm³. Pretulite is nonpleochroic and uniaxial positive with $\omega = 1.790$ (5) and $\epsilon = 1.86$ (1), measured with the spindle stage using the λ variation method. Calculations using the Gladstone-Dale relationship with the constants of Mandarino (1981) indicate superior compatibility: $1 - (K_p/K_c) = -0.004$.

CHEMICAL COMPOSITION

Chemical analysis was carried out with an ARL-SEMQ electron microprobe equipped with four wavelength dispersive spectrometers, applying ZAF correction procedures. Operating conditions were 15 kV accelerating voltage and 20 nA sample current on brass. Synthetic ScPO₄ was used as standard for Sc and P and synthetic REE-glass for Y (Jarosewich and Boatner 1991; Drake and Weill 1972). Wavelength dispersive scans confirmed that most other elements with $Z > 8$ are below the detection limit of the electron microprobe (<0.05–0.1 wt%), in particular no Al or Fe could be detected. Only Dy, Er, and Yb reach 0.2 wt% in some Y-rich spots, but these elements are also generally below the detection limit. Analytical results are listed in Table 1.

The mean of 50 analyses on eight pretulite grains within one polished thin section from sample HK1A (Höllkogel) yields the empirical formula $(\text{Sc}_{0.98}\text{Y}_{0.02})_{1.00}\text{P}_{1.00}\text{O}_{4.00}$, or simplified ScPO₄, based on four O atoms. Totals near 100 wt% suggest that volatile components like H₂O, (OH)⁻, or (CO₃)²⁻ are insignificant. Fourier transform in-

TABLE 1. Microprobe data of pretulite in sample HK1A

	Mean*	Range	End-member†
Weight percent			
P ₂ O ₅	50.02	49.09–51.20	50.72
Sc ₂ O ₃	47.38	46.20–48.63	49.28
Y ₂ O ₃	1.45	0.39–2.49	—
Total	98.85		100.00

* n = 50.

† Theoretical composition of pure ScPO₄.

frared microspectroscopy on a crystal fragment showed no evidence of these volatiles.

However, pretulite is inhomogeneous on a micrometer scale (Fig. 3), caused by a variable Y-content ranging from 0.39–2.49 wt% (Table 1), corresponding to a xenotime-(Y) component Y/(Y + Sc) of 0.5–3.2 mol%. The simple exchange vector is YSc₋₁, as can be derived from Figure 4, but solid solution between pretulite and xenotime-(Y) appears to be limited. Chemical zoning is in most cases patchy and rarely concentric, with a tendency to higher Y-contents in the cores (Fig. 3).

X-RAY POWDER DATA AND SINGLE CRYSTAL STRUCTURE REFINEMENT

The X-ray powder diffraction pattern was obtained with a Siemens D-5000 X-ray powder diffractometer using CuK α radiation and quartz as internal standard. Least squares refinement of unit-cell parameters using 14 reflections ($13^\circ < \theta < 45^\circ$) gave $a = 6.589$ (1) Å, $c = 5.806$ (1) Å and $V = 252.1$ (1) Å³ ($Z = 4$). The data agree well with results for synthetic ScPO₄ (JCPDS 8-47), which has a zircon-type crystal structure and space group $I4_1/amd$ (Table 2; Mooney 1956). The d -spacings of pretulite have slightly higher values than for pure synthetic ScPO₄, probably due to limited substitution of larger Y ions for Sc in pretulite (Table 2). A strong preferred ori-

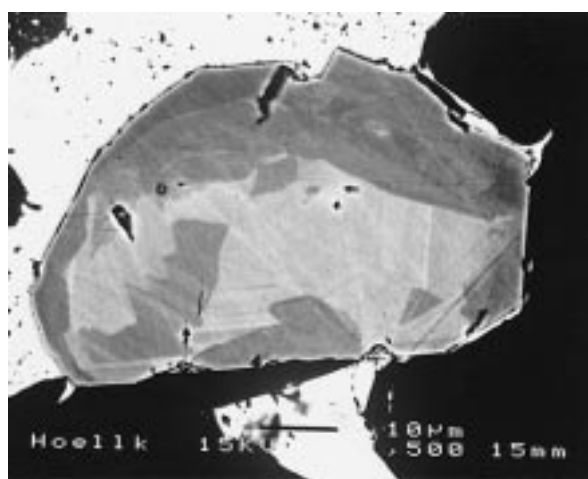


FIGURE 3. BSE-image of a sectioned pretulite grain (HK1A) showing chemical inhomogeneity. Brighter areas are enriched in Y, white areas are fluorapatite.

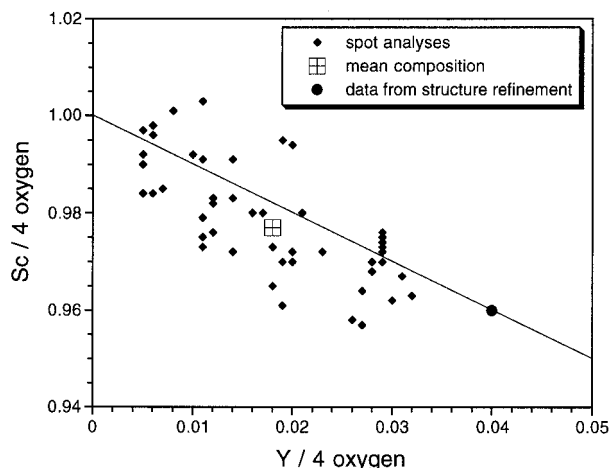


FIGURE 4. Plot of Sc-atoms vs. Y-atoms pfu of pretulite in sample HK1A. Number of atoms normalized to four O atoms.

entation effect was detected for ($h00$) reflections caused by perfect cleavage parallel to $\{100\}$.

The pretulite crystal of Figure 2 with dimensions of $60 \times 70 \times 110 \mu\text{m}$ was mounted on a Philips PW1100 four-circle diffractometer (MoK α radiation, graphite monochromator). Cell dimensions were refined from reflections $\theta < 30^\circ$, resulting in $a = 6.585$ (1) Å, $c = 5.802$ (1) Å, which are in good agreement with results from powder data. A total of 728 reflections were measured from $\theta = 4$ to 30° , $h = -9$ to 9 , $k = -9$ to 9 , $l = 0$ to 8 , recorded by 1.2° θ - 2θ scans at a scan rate of $1^\circ/\text{min}$. Data reduction included corrections for background and LP. An absorption ($\mu = 4.25 \text{ mm}^{-1}$) correction was not applied owing to the small crystal size. The observed intensities are consistent with space group $I4_1/amd$ and origin at center $2/m$ was chosen according to structure refinements of xeno-

TABLE 2. X-ray powder diffraction data of pretulite and synthetic ScPO₄

<i>hkl</i>	Pretulite, Höllkogel				Synth. ScPO ₄ JCPDS 8-47	
	d_{obs}	d_{calc}	I_{obs}^*	I_{calc}^\dagger	d_{obs}	I_{obs}
200	3.293	3.2946	524	100	3.287	100
211	2.6277	2.6277	4	2	2.624	6
112	2.4636	2.4638	42	42	2.459	40
220	2.3301	2.3296	6	6	2.325	8
202	2.1777	2.1780	20	14	2.175	18
301	2.0546	2.0543	21	14	2.052	18
103	1.8571	1.8568	5	7	1.8538	8
321	1.7432	1.7432	9	7	1.7403	12
312	1.6927	1.6927	30	45	1.6888	35
400	1.6470	1.6473	33	14	1.6445	12
420	1.4735	1.4734	5	6	1.4708	4
332	1.3697	1.3694	6	15	1.3668	10
413	1.2321	1.2323	3	<1	1.2299	10
224	1.2319	1.2319	3	8		
512	1.1804	1.1806	3	7	1.1783	6
600	1.0982	1.0982	5	5	1.0963	4

* Intensities measured with fixed soller slit and normalized to $\{112\} = 42$.

† Intensities calculated from structure refinement.

TABLE 3. Atomic coordinates, occupancy, and displacement parameters for pretulite

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Occupancy	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M	0	3/4	3/8	0.96(1) Sc 0.04(1) Y	52(3)	52(3)	37(3)	0	0	0
P	0	1/4	3/8	1.00	54(3)	54(3)	36(4)	0	0	0
O	0	0.0700(2)	0.2067(2)	1.00	108(6)	62(6)	52(6)	0	0	-8(4)

Note: Displacement factors (\AA^2) are multiplied by 10^4 and the exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$.

time-(Y). Averaging symmetry-equivalent reflections yielded 108 reflections with $R(\text{int}) = 0.019$ of which 98 had $F_o > 4\sigma(F_o)$. The structure was refined using the program SHELXL-93 (Sheldrick 1993). The coordinates of ScPO_4 (Milligan et al. 1982) were used as a starting model. The site occupancy factor for the site assigned to Sc (Wyckoff notation 4a) was allowed to vary and converged in an occupancy of 1.036 instead of 1.000. This suggests that this site cannot be occupied only by Sc, but also by an element with an atomic number >21 , consistent with microprobe analysis (Table 1). The final refinement of positional parameters for O, site populations for Sc + Y in 4a and anisotropic temperature factors for all atoms converged with 14 parameters to $R(F_o) = 0.018$ and $R_w(F^2) = 0.042$ and $S = 1.3$ for all 108 reflections. The final difference-Fourier map showed residual electron densities between 0.31 and $-0.22 \text{ e}\text{\AA}^{-3}$. Final atomic positions, site occupancy factors, and thermal parameters for pretulite are presented in Table 3. The refined site occupancies for Sc and Y are in good agreement with chemical data. Selected interatomic distances and angles are listed in Table 4. P-O bond lengths are within the normal range. The variation in bond angles (Table 4) indicates a distorted tetrahedron.

The monophosphates YPO_4 , ScPO_4 , and LuPO_4 all crystallize with the zircon-type structure. Structure details of the eightfold-coordinated metal atoms to O connected by the distorted phosphate tetrahedron were reported by Milligan et al. (1982). In pretulite, replacement of Sc by small amounts of Y is indicated by increasing the lattice parameter *a* from 6.574 (1) to 6.585 (1) to 6.8817 (5) \AA , *c* from 5.791 (1) to 5.802 (1) to 6.0177 (6) \AA , and increasing average distances M-O from 2.206 to 2.210 to 2.336 \AA for ScPO_4 , pretulite, and YPO_4 , respectively (Milligan et al. 1982).

GENETIC CONSIDERATIONS

The presence of a Sc mineral such as pretulite in every investigated phyllite-micaschist hosted lazulite specimen of the Grobgnais complex suggests an enrichment of Sc

in lazulite-quartz veins compared to normal crustal rocks. Preliminary analytical results of two samples weighing several hundred grams from Höllkogel show that a lazulite-rich domain (sample HK1A) contains 183 ppm Sc and 20 ppm Y, whereas a quartz-rich domain from the same vein (sample HK1F) contains 5 ppm Sc and 100 ppm Y, in agreement with the petrographic observation that pretulite is confined to lazulite-rich domains. The value of 183 ppm Sc is 17 times higher than the mean upper crustal abundance of 11 ppm and about four times the contents found in subalkaline basic igneous rocks (Fron del 1970). The metasedimentary rocks and the granitoid gneisses of the wider area do not show any significant Sc enrichment. A sample of a quartz-rich phyllite, taken 5 m away from the vein, contains 5 ppm Sc, and the granitoid gneisses of the wider area have a Sc content of 2–11 ppm (Schermaier et al. 1997). These values are in the normal range of such rocks.

As Sc generally substitutes at low levels for Al and Fe in rock-forming minerals (Fron del 1970), it is surprising that the 183 ppm Sc of the lazulite-rich domain are hosted, at least in part, in a separate Sc mineral (pretulite) and not totally in lazulite or sheet silicates. The only mineral with a Sc content detectable by electron microprobe is xenotime-(Y), which contains 1–2 wt% Sc_2O_3 . However, the modal amount of xenotime-(Y) in lazulite-rich domains is much too small to incorporate all Sc. In contrast, in the quartz-rich domain xenotime-(Y) is abundant, whereas the Sc content is very low (5 ppm). Thus it is likely that xenotime-(Y) contains the whole amount of Sc in the quartz-rich domain, thereby preventing the formation of a separate Sc mineral.

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TABLE 4. Selected interatomic distances (\AA) and angles ($^\circ$) in pretulite

M-O	2.160(1) \times 4	O-P-O	101.05(9) \times 2
	2.260(1) \times 4		113.84(5) \times 4
Mean	2.210	Mean	109.58
P-O	1.536(1) \times 4		

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