Locality No. 8

Vlastějovice near Ledeč nad Sázavou

Fe-skarn, barren fluorite pegmatite

Minerals of interest: garnet (F,OH), hastingsite (F), titanite (F,OH), fluorite

Vladimír ŽÁČEK, Milan NOVÁK, Louis RAIMBOULT, Jiří ZACHARIÁŠ & Lukáš ACKERMAN

1. General geology

Several lenticular bodies of Fe-skarns at Vlastějovice, up to several tens m thick and several hundreds m long, occur in the NE-SW-trending synclinal structure (Fig. 8-1; Koutek 1950). They are associated with a large body of two-mica tourmaline-bearing orthogneiss (cf. Klečka et al. 1992) and minor and much smaller bodies of amphibolite, quartzite and rare eclogite. These rocks are hosted in two-mica paragneiss of the Ledeč-Chýnov belt of Variegated Group, Moldanubian Zone. Regional foliation trends NE-SW and dips at moderate to steep angles to NW.

The skarn bodies are highly heterogeneous consisting of massive garnetites, garnetpyroxene, garnet-pyroxene-epidote and magnetite rocks. They are cut by a variety of dikes, pods, veins and lenses originated in various stages of the geological evolution (magmatic, metamorphic to late hydrothermal). Dikes of hedenbergite and epidote, up to several dm thick, consisting of masses and crystals of Mg-hedenbergite, epidote, grossular-andradite, fluorapatite, calcite and minor quartz are quite common. Pegmatite dikes, commonly 30 cm thick but exceptionally up to 3-5 m, are abundant in skarn but very rare in host rocks (see Vavřín 1962, Novák & Hyršl 1992). They commonly exhibit homogeneous internal structure only highly evolved elbaite pegmatite found in the beginning of eighties and consisting of Kfeldspar, quartz, albite and tourmaline (schorl and elbaite) is zoned. Three types of the pegmatites were distinguished based on their mineral assemblages and internal structure (Vavřín 1962); however, they probably represent a single pegmatite population with a various degree of differentiation and assimilation. Calcite - apophyllite or quartz - prehnite apophyllite veins and pods, up to several cm thick, are scarce (Tvrdý 2000, Žáček & Fišera 2001). Rare quartz-calcite veins with antimony mineralization are mostly bound to steep S-Ntrending mylonite zones and contain dominant berthierite (Koutek & Žák 1953).

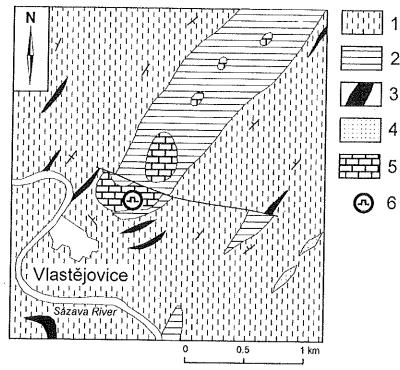


Fig. 8-1. Geological map of the Vlastějovice area. 1 – paragneiss; 2 – orthogneiss; 3 – amphibolite; 4 – quartzite; 5 – skarn; 6 – locality (modified Koutek 1950).

The Fe-skarn bodies were periodically exploited for iron-ore (magnetite) from the beginning of 16th century till 1965. Large stone-quarry situated at the Holý vrch hill, about 0.5 km northeast from Vlastějovice, provides recently an excellent section of the southernmost and largest skarn body and associated rocks.

2. Petrology

The skarn rocks are composed (in descending order of abundance) of Ca-Fe garnets (grandites), diopside-hedenbergite, magnetite and epidote; the minor to accessory minerals include amphibole, biotite, calcite, quartz, feldspars, scapolite, hematite, titanite, apatite, allanite and fluorite. The skarn is highly heterogeneous and the following rock types were distinguished: (i) the most abundant skarn s.s. - monomineral massive garnetites and banded garnet-clinopyroxene; (ii) clinopyroxene-garnet-epidote rock; (iii) lenses of massive magnetite, up to several m thick; (iv) hybrid rock (hastingsite + almandine + biotite + quartz + K-feldspar + plagioclase) forming zone, few decimetres to several metres thick, located between skarn and surrounding gneisses. The Fe-skarn is regionally metamorphosed at the conditions T ~ 590-680 °C and P ~ 4.5-6.5 kb corresponding to the main Variscan metamorphic event (Žáček 1997a).

The dike rocks are represented by: (v) coarse-grained pegmatite dikes (quartz + oligoclase + K-feldspar ± fluorite). They are less or more contaminated and contain abundant hastingsite and less frequently biotite occurring either as rims at contact with host rock (up to several tens cm thick) or as large phenocrysts in the pegmatite dike. Monomineralic grey quartz forms locally irregular masses and veins located along the contact with host skarn and enclosing its fragments. Allanite-(Ce), titanite, zircon and apatite are typical accessory minerals. Hedenbergite, garnet, epidote, calcite, magnetite, chlorite, prehnite, apophyllite and pyrite occur in minor amounts in marginal parts of pegmatite dikes or as products of late hydrothermal processes and/or contamination (Vavřín 1962, Žáček & Povondra 1991, Novák & Hyršl 1992). The most differentiated and fractionated dikes contain albite (clevelandite), accessory pyrochlore, uraninite and thorite (Rezek & Kryst 1985); schorl, elbaite, very rare annite and fluorite occur in highly evolved elbaite pegmatite (Novák & Hyršl 1992).

3. Mineralogy

The skarn bodies with associated pegmatites and various hydrothermal veins from Vlastějovice contain a very wide spectrum of minerals of a distinct origin. They were studied by many authors, see e.g., (Koutek & Žák 1953, Vavřín 1962, Povondra et. al. 1985, Žáček & Povondra 1991, Staněk & Schnorrer 1993, Žáček 1997a,b, Tvrdý 2000, Žáček & Fišera 2001, Goliáš 2002).

Garnet

Description: The skarn rocks (i) are formed by three successive garnet generations, garnet I, II and III, garnet IV is associated with epidote, and garnet V is restricted to the hybrid rock between skarn and surrounding gneisses (Table 8-1). Very rare garnet I is colourless, homogeneous, typically found as microscopic relics in garnets II and III. Garnet II is a dominant type of massive garnetites, but it also occurs on the fractures of skarn as red to redbrown crystals. Garnet II is pale-orange under the microscope, some crystals display discontinuous oscillatory zoning and a distinct birefringence. Garnet III is deep red-brown in hand-specimen, orange under the microscope, birefringence is very low and zoning is not pronounced. It frequently forms well-developed crystals. Garnet IV forms small but numerous 0.1-1 mm sized subhedral to euhedral pale orange porphyroblasts growing in fine-grained sugary epidote (ii). Garnet V forms rounded to euhedral porphyroblasts associated with other minerals - hornblende, biotite, plagioclase, quartz and minor muscovite and ilmenite in hybrid rock (iv).

Chemical composition: Compositional ranges found in the individual garnet types from Vlastějovice are (Žáček 1997a; see Fig. 8-2, Table 8-1):

Garnet I	Grs ₇₉₋₈₇	Adr_{12-18}	$Alm_{0.3-2}$	$Sps_{0.1-0.6}$	$Pyr_{<0.2}$
Garnet II	Grs ₂₆₋₆₀	Adr ₃₄₋₆₅	$Alm_{0.5-12}$	Sps _{0.4-3.7}	$Pyr_{0.0-0.8}$
Garnet III	Grs ₈₋₁₂	Adr _{71.84}	Alm ₇₋₁₄	$Sps_{0.4-0.8}$	Pyr _{0.2-0.6}
Garnet IV	Grs ₂₇₋₅₆	Adr ₇₋₂₇	Alm ₂₂₋₅₀	$Sps_{1\text{-}8.5}$	Pyr _{0.0-2.5}
Garnet V	Grs ₁₋₃₉	Adr _{0.0-19}	Alm ₃₆₋₉₅	Sps _{0.5-25}	Pyr _{0.7-7}

The garnet I, II and III yielded low MgO (0.06 to 0.35 wt.%), MnO (0.05 to 0.85 wt.%), TiO₂ (0.15 to 1.38 wt.%) and increased Sn (300 to 1000 ppm). Garnet IV (grossular - almandine) shows a weak continuous progressive zoning, low TiO₂ (0.0 to 0.3 wt.%), MgO (0.0 to 0.7 wt.%) and variable MnO (0.4 to 1.2 (3.7) wt.%). Garnet V (almandine) from hybrid rock (iv) displays strong continuous "bell-shaped" progressive zoning with a significant enrichment of Mn + Ca in cores.

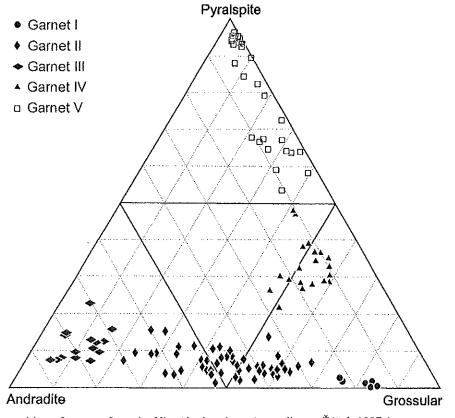


Fig. 8-2. Composition of garnets from the Vlastějovice skarn (according to Žáček 1997a)

Light elements: The garnet I, II and III are slightly Si-deficient with tetrahedral vacancy up to 0.18 pfu (Table 8-1). Garnet I contains 0.82 to 1.18 wt.% F, up to 0.22 apfu (average 0.94 wt.%) and 0.6 to 1.2 wt.% H₂O (up to 0.49 apfu OH), garnets II and III contain 0.0 to 0.50 wt.% F and 0.07 to 0.93 wt.% H₂O, respectively.

Hastingsite

Description: Black to green-black very coarse-grained hastingsite I occurs mainly in marginal parts of barren pegmatites (v). It forms euhedral to subhedral phenocrysts, up to ~10 cm in size, or massive, nearly monomineral coarse-grained aggregates. Hastingsite I is strongly pleochroic in thin section enclosing frequent titanite and accessory apatite. Hastingsite II occurs in hybrid rock (iv).

Chemical composition: Amphibole from pegmatite (v) is characterized by $Fe^{3+} > {}^{VI}Al$ ($Fe^{3+} = 0.70$ to 1.07 apfu, ${}^{VI}Al = 0.18$ to 0.30 apfu), high X_{Fe} (0.84 to 0.72), and low A-site vacancies (0.09 to 0.25 (0.45) pfu). Due to highly variable K (0.23 to 0.66 apfu), it corresponds to potassic hastingsite, potassian hastingsite and rarely to hastingsite (Table 8-2). Other atomic abundances: Si (5.89 to 6.11), ${}^{IV}Al$ (1.89 to 2.11), Fe^{2+} (2.71 to 3.20), Mg (0.59 to 1.05), Ca (1.85 to 1.99), ${}^{A}Na$ (0.22 to 0.41) (all in apfu). The Ti and Mn are low \leq 0.10 and \leq 0.09 apfu, respectively. Hastingsite II from hybrid rock (iv) is hastingsite to potassian hastingsite, exceptionally magnesiohastingsite, with the composition: Si (6.08 to 6.42 apfu), X_{Fe} (0.93 to 0.48), and with somewhat larger A-site vacancy (0.29 to 0.41 pfu).

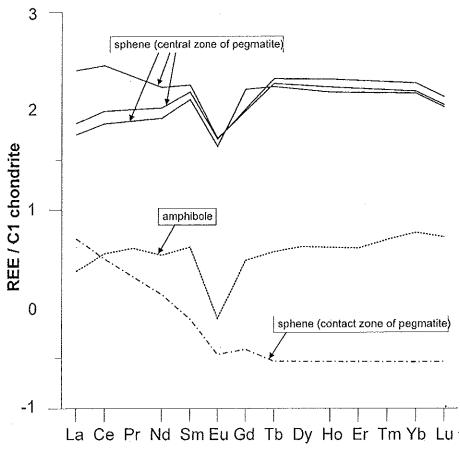


Fig. 8-3. Chondrite-normalized REE pattern of titanite and amphibole.

Light elements: Besides numerous microprobe data, two wet analyses of hastingsite I yielded 0.69 to 0.72 wt.% F (0.35 to 0.37 apfu) and 1.61 to 1.72 wt.% H₂O (1.74 to 1.85 apfu OH); (Žáček & Povondra 1991).

Titanite

Description: Abundant inclusions of yellowish-brown titanite occur in black hastingsite I and fluorite from reaction zones between pegmatite and skarn. <u>Subhedral</u> to <u>euhedral</u> crystals, up to about 3 mm long, are slightly rounded and exhibit characteristic "letter envelope-type" habit.

Chemical composition: Titanite is Al-rich (7.81 to 8.39 wt.% Al_2O_3 , ≤ 0.31 apfu) and contains also elevated Fe up to 1.71 wt.% of FeO (Vrána & Mrázek 1985; see Table 8-2). High Al in titanite enclosed in hastingsite I was confirmed by new EMP study by Žáček (9.26 to 9.75 wt.% Al_2O_3). Titanite exhibits 137 to 2025 ppm Th, 246 to 331 ppm U and ~3000 ppm Ta. Chondrite normalized REE pattern show lower concentrations of REE_{tot} and LREE enrichment for titanite from contact relative to titanite from central part of pegmatite dikes (Fig. 8-3).

Light elements: Titanite from fluorite-bearing pegmatite contains 1.59 wt.% F (0.16 apfu) and 0.74 wt.% H₂O (0.16 apfu OH) (Vrána & Mrázek 1985; see Table 8-2).

Fluorite

Description: Abundant dark violet, purple to rare, almost colorless fluorite forms coarse-grained aggregates in pegmatite or in exocontact zone, up to several dm in size. Fluorite locally predominates over quartz and feldspars. It is closely associated with allanite with deep violet to black rims around allanite grains.

Chemical composition: Fluorite from pegmatite and from contact zones differ in their minor elements, pegmatite fluorite is enriched in Na (38 to 114 ppm), W (69 to 35 ppm), Sc (0.1 to 0.147 ppm) and namely REE, whereas fluorite from contact is enriched in Sr (147 to 177 ppm). Chondrite normalized REE pattern show lower concentrations of REE_{tot} and HREE depletion for fluorite from contact relative to fluorite from central part of pegmatite dikes (Fig. 8-4).

Light elements: None of the light elements was determined; however, F is a dominant constituent of fluorite.

Fluid inclusions: No ambiguous primary fluid inclusions (FI) were identified in fluorite from graphic-like intergrowns with magmatic quartz and feldspars. Identified secondary aqueous FI include: 1) polyphase liquid-rich FI (5-20 μm large) containing several solid phases; 2) liquid-rich FI (5-50 μm) with sparse solid phases and 3) two-phase liquid-rich FI (5-30 μm) with no

solids. These types are further abbreviated as S1, S2 and S3 types. The solid phases in S1 (1 to 5 phases) and in S2 (1 to 2 phases) inclusions are usually anhedral, less frequently hexagonal-, square-shaped, or tabular. They are colorless, transparent, and one, or two of them are always anisotropic. Rare opaque phases (wire-like or circular) were identified in some S1 inclusions. Microthermometric data of S1-S3 types: eutectic (-35 to -46 °C), melting of ice (-5.6 °C to -0.1 °C, most frequent range: -5.6 to -3.0 °C), salinity 8.7 to 0.3 wt.% eq. NaCl, homogenization (L+V to L): 230 to 170 °C (S1), 180 to 150 °C (S2) and 150 to 110 °C (S3). Above 240 °C inclusions start to decrepitate. No dissolution of solid phases was observed (in S1 and S2) before inclusions decrepitation; consequently, the solids represent most probably accidentally trapped phases.

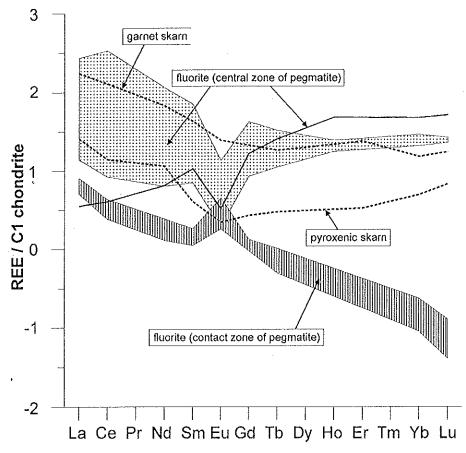


Fig. 8-4. Chondrite-normalized REE pattern of fluorite and various kind of skarns.

4. Discussion

The presence of F-enriched hydrous grossular - andradite indicates magmatic source of F in early garnet generations I, II and III in the skarn (high F up to 0.84 wt.% F was recently found in garnet from Fe-skarn Rešice near Moravský Krumlov – S. Houzar – personal communication 2003). This supports formation of the Fe-skarn from Vlastějovice by

contact metasomatism of carbonate rocks caused by granitic rock (Žáček 1997a, cf. also Koutek 1950, Němec 1991).

Assuming F-enriched garnets had represented a substantial component of the early skarn, the superimposed geological processes (metamorphism) released a large amount of F. It explains remarkable features of the Vlastějovice skarn body: the abundance of fluorite in pegmatite dikes and their contact zones, because such a high concentration of F in primitive granitic rock (locally ~30 vol.% fluorite) is unlikely of a direct magmatic origin; high concentrations of F in some minerals of magmatic to late hydrothermal stage (titanite, hastingsite, fluorapophyllite, secondary fluorcarbonates after allanite). The mineral assemblages, zoning and structural criteria provided evidence that garnet IV and V crystallized under conditions of decreasing oxygen activity during superimposed, regional amphibolite-grade metamorphism (see Němec 1971).

Titanite exhibits high contents of Al and F via the substitution AlF Ti.₁O.₁. It suggests high activity of F in the parent medium, nevertheless, high Al and F in titanite as an indicator of high-pressure conditions should be used with caution (cf. Castelli & Rubatto 2002).

Tab. 8-1. Chemical composition of garnets from Vlastějovice (from Žáček 1997a)

garnet	I	II	II	II	III	III	IV	٧
sample	Z31	Z31	Z-15	Z-6	V1-2	V1-9	VI-5	Z-1
method	EMPA /2	EMPA/16	wet	wet	wet	wet	EMPA /7	wet
SiO_2	37.65	37.20	37.60	36.90	34.18	35.13	36.85	35.91
TiO ₂	0.19	0.53	0.35	0.34	0.19	0.26	< 0.05	**0.43
Al_2O_3	19.51	12.50	13.90	11.60	3.55	6.81	19.61	20.94
Fe ₂ O ₃	*5.12	*16.32	12,60	17.84	26.73	22.54		0.11
FeO	-	-	3.90	0.16	4.69	6.27	×19.9	38.48
MgO	< 0.05	0.12	0.35	0.26	0.23	0.24	0.41	0.74
MnO	0.05	0.58	0.48	0.32	0.37	0.50	0.43	0.33
CaO	36.98	32.68	30.80	31.28	28.94	27.73	21.35	2.51
H_2O^{\dagger}	°0.97	°0.39	0.90	0.93	0.26	0.58	-	-
F	0.94	< 0.10	0.20	0.24	0.50	0.25	-	-
H ₂ O ⁻	-	-	0.21	0.13	0.01	0.01	-	0.08
O=F	-0.39		-0.08	-0.10	-0.21	-0.10	_	*
total	101.07	100.42	101.21	99.90	99.44	100.22	98.60	99.10
	ق							
Si	2.821	2.948	2.922	2.913	2.912	2.898	2.972	2.954
OH/4	0.123	0.052	0.117	0.122	0.037	0.080	-	-
F/4	0.056	< 0.006	0.012	0.015	0.034	0.016	-	-
Al^{IV}	0.000	0.000	0.000	0.000	0.017	0.006	0.028	0.046
ΣZ	3.000	3.000	3.051	3.050	3.000	3.000	3.000	3.000
Ti	0.011	0.032	0.020	0.020	0.012	0.016	< 0.003	0.027
Al ^{VI}	1.723	1.167	1.273	1.079	0.357	0.662	1.836	2.030
Fe ³⁺	0.266	0.801	0.737	1.060	1.714	1.399	0.198	0.007
Fe ²⁺	0.023	1.173	0.253	0.011	0.334	0,432	1.144	2.647
Mg	< 0.006	0.014	0.041	0.031	0.029	0.030	0.049	0.091
Mn	0.003	0.039	0.032	0.021	0.027	0.035	0.029	0.023
Ca	2.969	2,775	2,565	2.646	2.642	2.451	1.834	0.221
$\Sigma X,Y$	5.001	5.001	4.921	4.868	5.115	5.025	5.093	5.046
ОН	°0.493	°0.210	0.467	0.489	0.148	0.319	•	-
F	0.223	< 0.023	0.049	0.059	0.134	0,065	•	_

[°] calculated

^{*} All Fe as Fe₂O₃^{tot} or FeO^{tot},

^{**} TiO_2 is increased due to ilmenite inclusions, microprobe yielded $TiO_2 \le 0.05$ wt.%

Tab. 8-2. Representative chemical composition of hastingsite and titanite from Vlastějovice (from Žáček & Povondra 1991 and Mrázek & Vrána 1984).

	hastingsite	titanite
SiO_2	38.85	32.66
TiO_2	0.39	27.82
Al_2O_3	12.06	8.39
Fe ₂ O ₃	6.96	_
FeO	21.87	1.71
MgO	2.44	0.11
MnO	0.50	0.13
CaO	10.45	28.49
Na ₂ O	1.48	0.02
K ₂ O	1.92	n.d.
H_2O^{\dagger}	1.61	0.74
F	0.72	1.59
H_2O^*	0.17	-
O=F	-0.30	-0.67
total	99.12	100.99
Si	6.209	1.026
Al	1.791	7.020
ΣΤ	8.000	~
Al	0.480	0.311
Ti	0.047	0.657
Fe ³⁺	0.837	-
Fe ²⁺	2.923	0.045
Mg	0.581	0.005
Mn	0.068	0.003
ΣС	4.936	-
Ca	1.789	0.959
Na	0.211	0.001
ΣΒ	2.000	-
Na	0.248	-
K	0.391	*
ΣΑ	0.639	-
Σ cat,	15.575	3.007
F	0.364	0.158
OH	1.716	0.155
O	23.636	4.842