APATITE COMPOSITION AND ESTIMATION OF INITIAL FLUORINE CONCENTRATION IN THE WEST–CARPATHIAN GRANITES

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Abstract: Apatites reflects the granite composition. From the S-type, they are richer in Mn and Fe in comparison with apatites of the I-types, REE patterns show a stronger negative Eu-anomaly in S-type apatites than in I-type; the apatite from the I-.types are richer in chlorine. The A-type granites and their apatites are enriched in Fe and HREE. Generally, according to apatite composition, fluorine contents is 10 times lower in the volatile phases than in the melts. The S-type granitic melts had more fluorine than I-type ones, fluorine is more then twice time richer in the specialized and A-type granites.

Key words: apatite, granite, volatiles, Western Carpathians

Introduction

Apatite was characterised as an abundant accessory mineral for the more basic granite varieties in the Western Carpathians and less common for the paragenesis with monazite(e.g. Veselský & Gbelský, 1978). Up to now, the most important information extracted from apatite in the Western Carpathians was their fission track dating from the various granitic types and the using of this data for solving of granite uplift in Tatric and Veporic units (Kráľ, 1977). Important was also the identification of carboniferous impurities as graphite, carbides and hydrocarbons in the apatites which were recognised from some Tribeč and Malá Fatra Mts. granitic rocks (Broska et al., 1992) and this phenomenon was interpreted as the assimilation of black shales during granite emplacement and one of the reason of the black pigmentation of apatite. The graphite incorporated in apatite indicated the reduction regime in the granites with S-type affinity where is this apatite sometimes common. The objective of this work was to gather together an information about the composition of apatite in various granite types of the Western Carpathians and using of this mineral for the modelling of the fluorine concentration in the initial melts.

Apatite has been investigated in all principal West-Carpathian granites which basically could be divided into several geotectonic groups: (1) Lower Carboniferous orogenic granites with S-type affinity (2) the orogenic granites with I-type granite affinity (3) the Permian A-type post-orogenic granites (4) post-orogenic specialized S-type granites - Permian-Triassic in age (e.g. Petrík & Kohút, 1997, Broska and Uher, 2001 and reverences therein). The phosphorus geochemistry is specific for all this granite suites as well as the apatite compositions due to their derivation from the different sources (Petrík 2000). The apatite composition show strong dependence on the host bulk rock chemistry or granite suite. Apatite composition basically has measured by microprobe.

Results

Phosphorus geochemistry: The content of P_2O_5 vs. SiO_2 show tendency of P_2O_5 decrease with increasing of SiO_2 during differentiation more basic members - tonalites, granodiorites - of the S-type granitoids. In contrast of it, both P_2O_5 and SiO_2 contents increase in the late granites, a trend also be seen in the ASI against P_2O_5 diagram. This is connected with general increase of phosphorus solubility with increasing of magma alkalinity (Pichavant et al., 1992). The K-feldspar are slightly enriched in P in these granites.

Granites with the I-type affinity generally show strong decrease in P resulted by apatite fractionation. However, also in the I-type group, late-magmatic interstitial K-feldspar originated from Al-rich residual melts is slightly enriched in phosphorus. The late - magmatic feldspars are similar in P content to those of the S-type granites.

The A-type granites form a distinctive group containing the very low concentration of bulk-rock P, and it is joined also with low modal proportion of apatite, in comparison to the I, S- and specialized S-type granites. The P_2O_5 content in alkali feldspars of the A-type granites was always under detection limit of microprobe.

Alkali feldspar is the host phase for P in the specialized S-type granites, especially in their topaz-bearing facies. The P_2O_5 content in the K-feldspar is variable up to 0.3 wt.%, whereas albite contains only 0.01- 0.1 wt.% P_2O_5. The majority of alkali feldspar in the highly evolved granites, show much higher concentrations of P, up to 0.4 wt % P_2O_5.

Apatite distribution and composition

Primary early-magmatic apatite: Apatite is the most abundant in the I-type granites, and less common in the S-, specialized S- and A-type granites. Apatite from the I-type granites contains significantly lower concentrations of Mn and Fe, than apatite from S-type granites. The highest contents of MnO in apatite were observed in the specialized S-type granites with concentration often above 1.5 wt. % MnO. On the other hand apatite from the I-type granitoids is slightly enriched in sulphur and also by Cl. Apatite from the granites is generally light-REE rich, but apatite from the A- and specialized S-type granites is relatively enriched in heavy-REE including Y, because of, the higher primary HREE`s of these granites. . The A-type granites and their apatites are enriched in Fe and HREE.

The concentration of REEs were measured in two concentrations of apatites by ICP MS method (T-18; S-type granitoid and T-22; I-type granitoid; Broska & Uher, 1998). When we compare the quantity and normalised pattern of the REE`s in apatites from these two different granite types and the REE in apatites from the Lachland fold belt - a classical region for the division of the S- and I- granite typology (Sha & Chappel, 1999), no important differences were observed (Fig. 2). Both groups show for the S-type granite a higher content of LREE, their fractionation, pronounced negative Eu-anomaly and flat pattern of HREE`s part. On the other hand the I-type show lower LREE`s and less pronounced Eu-negative anomaly, even no anomaly in the Western Carpathian specimen (T-22). The low oxygen fugacity and the high peraluminosity of the S-type granitoids melts enhance the Eu^{2+}/Eu^{3+} ratios while this ratio is lower in oxidised, metaluminous I-type melts (Sha & Chappell, 1999). So a higher Eu^{2+}/Eu^{3+} mean a lower content of Eu^{3+} in the melt, which means a lower amount of Eu in apatite since the crystal structure of apatite shows a strong preference for Eu^{3+}. Stronger negative Eu-anomaly (lower ratio) indicate a higher Eu^{3+} formed in the oxidised content in apatites which will increase the concentration of Eu in apatite. This fact is in accord with the knowledge that Western Carpathian S-type granitoids have lower content of water in comparison with I-type (Petrík & Broska, 1994).

Late-magmatic or secondary apatite: Abundance of the tiny scattered crystals of apatites (typically <10 μm in diameter) were observed inside of alkali feldspar (mainly albite) of the specialized West-Carpathian S-type granites. These fluorapatite crystals probably were formed as a result of subsolidus exsolutions (or post-magmatic alteration) of P which released from P-bearing alkali feldspar during decreasing temperature and intensive fluid activity. Consequently, the albite grains hosting the exsolved apatites have very low P contents (under microprobe detection limit). In contrast to primary late-magmatic fluorapatite in these granites, the post-magmatic fluorapatite have significantly lower Mn, Fe and REE contents.

Fluorine contents

The apatite was used to determine the amount of fluorine in the melt using the following equations (Piccoli & Candela, 1994) :

$$C_F^l = \frac{\dfrac{X_{FAp}^{Ap}}{X_{HAp}^{Ap}} \cdot \dfrac{1.90\times 10^7}{18} \cdot \dfrac{1}{10^{\left[0.18219+\frac{5301.1}{T}-\frac{0.00360\cdot(P-1)}{T}\right]}}}{D_F^{aq/l}}$$

and

$$D_F^{aq/l} = -0.56 + 0.00093 \cdot T(°C)$$

$$\mathrm{T} = \frac{[26400 * C^l{}_{SiO_2} - 4800]}{[12.4 * C^l{}_{SiO_2} - \ln\{C^l{}_{P_2O_5}\} - 3.97]}$$

where the terms used are :

X_i^ϕ	mole fraction of phase component i in phase ϕ
C_i^l	concentration of i in melt
$D_i^{aq/l}$	partition coefficient of i between the magmatic volatile phase and melt
T	temperature in Kelvin, unless specified
P	pressure in bars

The temperature used for the calculation was the AST (apatite saturation temperature) (Harisson & Watson, 1984) as suggested by Piccoli & Candela (1994), although these are quite non-realistically high. As for the pressure for better comparison, all the samples were calculated on the basis of a 3 kbar pressure.

The results, which are presented in Tab. 1, show some differences in fluorine concentrations in the melt between the different kind of granitoid rocks (I-, S-, specialized S-type, A-type). If we compare the granitic suites, it follows that the S- and I-type granite melts show similar fluorine content but the richest melt in fluorine represent the A- and the specialized S-type granites. The higher fluorine contents in these granitoids is emphases also by their late fluorine mineralization connected with these melts in the Spiš-Gemer region.

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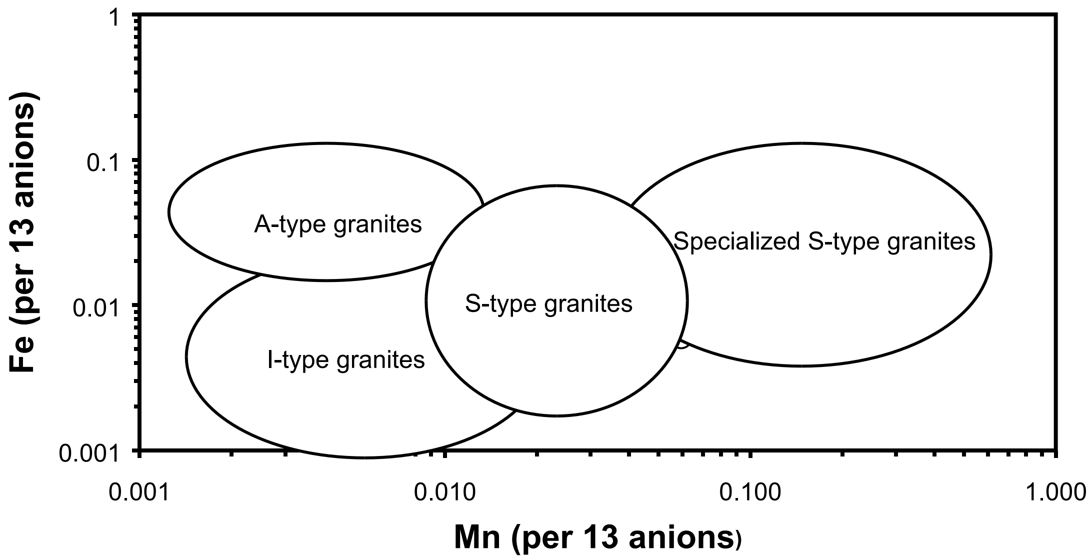
Table 1. The initial fluorine contents in the melt derived from the volatile contents in apatites calculated according to Picolli and Candela, (1994). Only late or secondary apatite composition for the specialized S-type granites has been used for the C^{l}_{F} calculations. The all apatite composition, including primary ones, provide slightly lower fluorine contents in the melt (cca 130 ppm).

Figure 1: Mn vs Fe in the apatites from the granitic rocks from the Western Carpathians (based on the EMP analyses).

Figure 2:Apatite REE composition patterns. The full triangles and the full circles represent apatite from S and I type granitoids from Lachlan Fold Belt, Australia (Sha & Chappell, 1999). For comparison, the open triangles and open circles represent respectively the composition of apatite from S and I type granitoids from the Tribeč Mts. (Western Carpathians) (Broska & Uher, 1998).

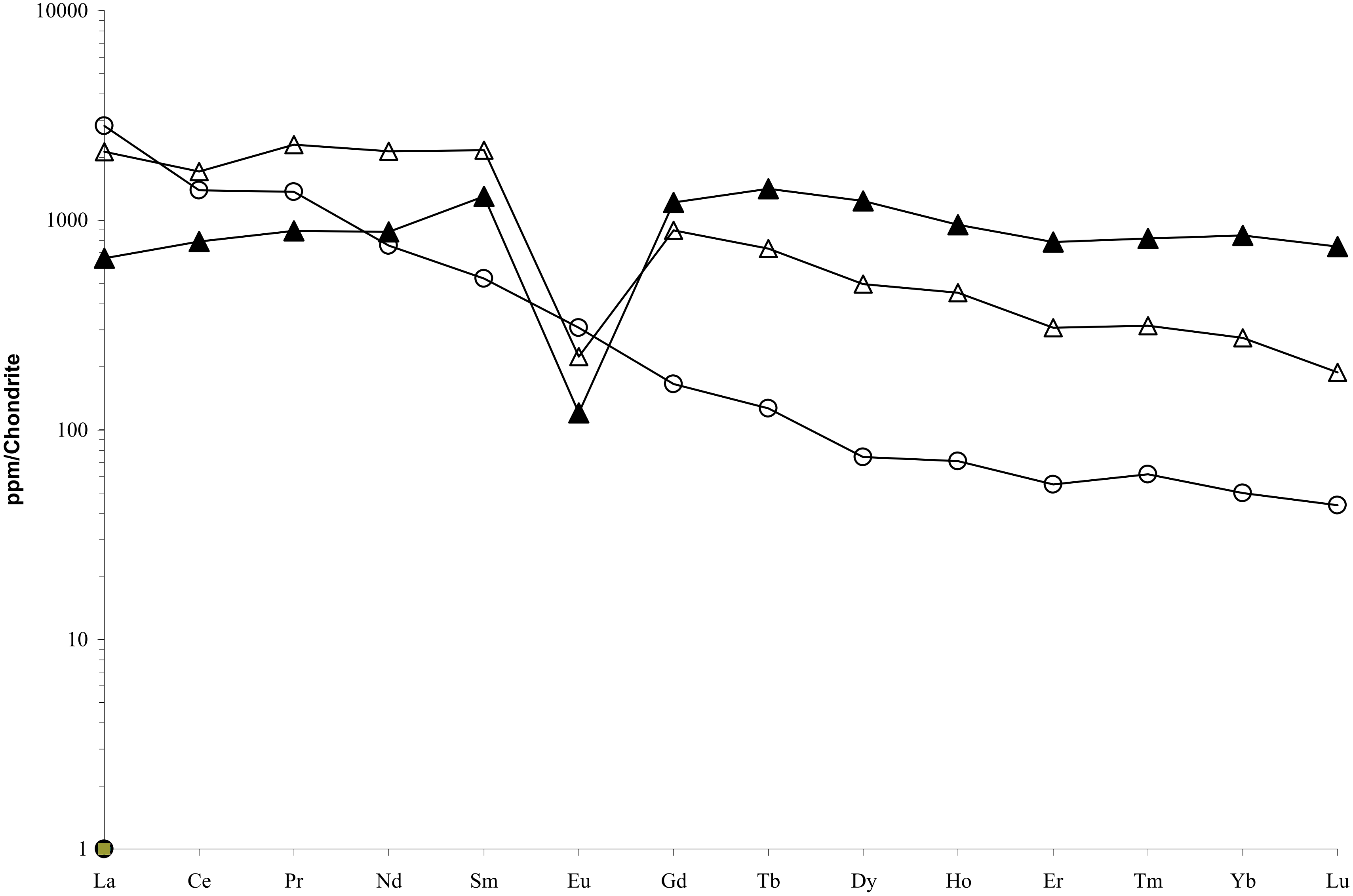
Table 1

granite suite	I-type	S-type	spec.S-type	A-type
T (cels)	700	650	650	700
P (bars)	3000	3000	3000	3000
X^{Ap}_{FAp}	0.688	0.644	0.841	0.832
X^{Ap}_{HAp}	0.305	0.352	0.150	0.167
C^{l}_{F}	63	53	162	139



1
0.1
0.01
0.001
Fe (per 13 anions)
A-type granites
I-type granites
S-type granites
Specialized S-type granites
0.001
0.010
0.100
1.000
Mn (per 13 anions)

Graf1



10000
1000
100
10
1
ppm/Chondrite
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu