

GEOCHEMISTRY OF SELECTED GARNETS IN PEGMATITES FROM THE RĂZOARE FORMATION (PRELUCA MOUNTAINS, ROMANIA)

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Abstract

The Răzoare formation, part of the Preluca Mountains from NW Romania, is the host of granitic pegmatites rich in garnets. The large garnet grains of dark pink colour are associated with quartz, muscovite and albite. Generally, garnet is a common accessory mineral in granitic pegmatites associated with granite, and its composition denotes the nature of the crystallization environment. The investigated garnets display a significant spessartine content (about 30 mol %), which is typical for garnets from magmatic pegmatites. The REE pattern and the Y, Li, Nb/Ta, Zr/Hf and Sc contents support the magmatic origin of the pegmatites investigated. This sum of geochemical features points to the development of the rocks from a peraluminous melt rich in volatile components which are involved in the enhancement of trace element mobility during the differentiation processes.

Keywords: garnet, pegmatites, trace elements, Răzoare formation, Preluca Mountains.

Introduction

Garnet is a typical accessory mineral in granite pegmatites. The solid-solution of garnet belongs to the almandine-spessartine series, while the spessartine content increases along with the geochemical evolution of pegmatites. Thus, in granite pegmatites of the rare elements class

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(Černý and Hawthorne, 1982), garnet may contain up to 83 mol% spessartine in solid-solution. The progressive enrichment in the spessartine molecule is found to be typical during the process of pegmatite differentiation.

Manganese, followed by iron and magnesium, was observed as the preferential order for cation accommodation in the garnet X-site (Kleck and Ford, 1999), resulting in the crystallisation of the almandine-spessartine solid-solution, which is characteristic for magmatic pegmatite garnet (Whitworth and Feely, 1994; Habler et al., 2007). In addition, garnet can accumulate significant amounts of trace elements such as REE, Y, Zr, Hf, Sc and V. The degree of trace element concentration in garnets can be used as a geochemical tool in the determination of the pegmatite crystallisation environment (Bau, 1996; Irber, 1999).

Pegmatites from the Preluca Mountains have a granitic composition. The rock-forming minerals are quartz, K-feldspar, plagioclase (albite or oligoclase) and muscovite, while the ordinary accessory minerals are represented by tourmaline, garnet, biotite, apatite and zircon.

The pegmatites from the Răzoare formation are rich in garnets, in contrast with the pegmatites present in the other three metamorphic formations from the Preluca Mountains. Garnets have a dark pink colour, occurring either as coarse-grained garnets (up to few centimetres in diameter) or as fine-grained garnets. The large subhedral grains are associated only with quartz, feldspar and muscovite, while the small euhedral grains are found within clusters of mafic minerals such as biotite, tourmaline, and apatite with subordinate quartz, muscovite and feldspar. The present study deals with garnets associated with feldspar (Ab), quartz and muscovite.

Geological setting

The Preluca Mountains represent an isolated metamorphic block located in the NW region of Transylvania. The crystalline rocks which build up this metamorphic block belong to the Baia de Aries group (Rusu et al., 1983; Balintoni, 1996), one of the nappes from the basement of the Apuseni Mountains.

The metasedimentary rocks in the Preluca Mts have been grouped by Rusu et al. (1983) and Balintoni (1996) into four units, as follows: (1) the upper terrigenous formation of Valea Cavnicului in the NW; (2) the quartzite-amphibolite formation of Preluca Noua in the central-western part, (3) the carbonate rock formation of Măgureni in the central part; (4) the lower terrigenous formation of Răzoare in the SE (fig. 1).

The metamorphic grade decreases gradually from SE to NW, from the sillimanite zone to the garnet+biotite zone of the amphibolite facies. The Răzoare formation underwent a second metamorphic event (M_2) (Balintoni, 1996; Radu, 1997). The geobarometric data based on Grt+Rt+Als+Ilm+Qtz assemblages yielded a pressure between 6 and 8 kbar. Based on the Grt+Bt and Grt+St assemblages, the temperatures of the metamorphic peak are between 530 and 650°C (Radu, 1997). These data suggest that the M_2 metamorphic event took place in the upper amphibolite facies, close to the boundary with the granulite and eclogite facies and to the minimum (incipient) melting zone, where the anatectic melts with granitic composition are generated.

The discordant pegmatite bodies are hosted by paragneisses. The pegmatite structure comprises three main zones, and garnets are found in the intermediate zone, as well as on the border of the core zone.

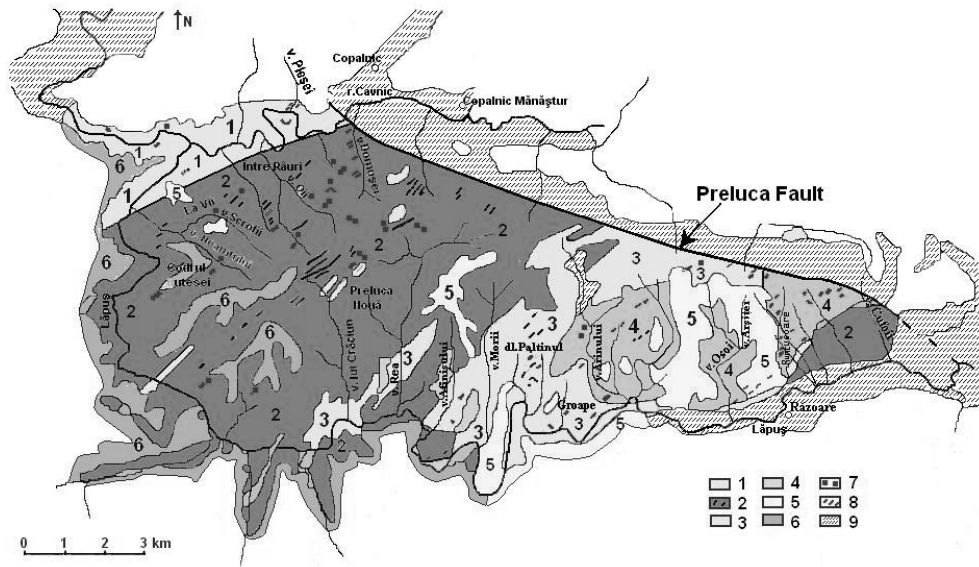


Fig.1 Geological sketch of Preluca Mountains (after Kalmár, 1973). 1-Valea Cavnicului Formation; 2-Preluca Noua Formation; 3-Măgureni Formation; 4-Răzoare Formation; 5 and 6-Eocene deposits; 7-and 8-Pegmatites; 9-Quaternary deposits.

Material and methods

Electron microprobe analyses (EMPA) were performed using a JEOL JXA-8900 instrument at an operating current of 20 nA, an accelerating voltage of 20 kV and a beam diameter of 5 μm . The X-ray intensities of the alkalis and the major elements were counted for 5 s, 40 s, and 60 s, respectively. The components were standardized using natural minerals, glasses of natural rocks and synthetic oxide compounds. Sums exceeding 100% usually occur for garnets and other Fe-rich minerals, but these results are acceptable as long as the mineral stoichiometry does not show great deviation from the ideal composition.

The optically clean garnet fragments were handpicked under a binocular microscope in order to be analysed for trace elements. The garnet samples were crushed in agate mortar and dried overnight, prior to analyses, at 105°C (dry basis). The digestion of the samples (100 mg) was carried out using a microwave digestion system (Multiwave Sample Preparation System, Perkin Elmer/Par Physica) with HF and HClO₄ at high pressure (50-60 bar) and temperature (210°C). After the evaporation of HClO₄ and two consecutive evaporation steps with HCl, the sample cakes were dissolved in HNO₃, placed in up to 50 ml volumetric flasks (finally 2% HNO₃) and stored in polyethylene bottles. The efficiency of the digestion was checked and confirmed by a different high pressure digestion system (PDS, Pressure Digestion System, Lofthield), following the steps described above. All reagents, as well as the water used, were of high purity grade.

Tab. 1 Representative microprobe analyses (wt.%) and structural formulas (a.p.f.u.) of garnets from Răzoare pegmatites

Samples	G 101a	G 101b	G 101c	Grt 602a	Grt 602b	Grt 302c	Grt 1	Grt 2	Grt 3	Grt 4	Grt 5
Oxides											
SiO ₂	35.920	35.649	35.835	35.656	35.808	35.305	36.111	36.194	36.310	36.464	36.533
TiO ₂	0.038	0.051	0.030	0.004	0.014	0.007	0.023	0.009	0.015	0.039	0.002
Al ₂ O ₃	21.953	21.983	21.684	21.395	21.511	21.316	21.499	21.144	21.215	21.031	21.243
FeO	29.576	29.846	29.322	28.890	29.002	28.782	28.807	28.848	28.755	28.931	28.945
MgO	0.611	0.681	0.617	0.426	0.354	0.399	0.573	0.591	0.608	0.595	0.582
MnO	12.697	12.724	12.649	13.891	13.638	13.695	13.354	12.864	12.938	13.028	12.332
CaO	0.208	0.200	0.203	0.259	0.251	0.260	0.192	0.194	0.193	0.223	0.202
Na ₂ O	0.013	0.089	0.046	0.010	0.079	0.056	0.009	0.034	0.066	0.058	0.062
K ₂ O	0.000	0.000	0.007	0.012	0.000	0.010	0.000	0.025	0.000	0.000	0.000
P ₂ O ₅	0.352	0.371	0.302	0.380	0.368	0.359	0.290	0.267	0.291	0.253	0.289
Cr ₂ O ₃	0.025	0.000	0.008	0.022	0.025	0.009	0.000	0.002	0.000	0.000	0.000
Sum	101.393	101.594	100.703	100.945	101.050	100.198	100.858	100.173	100.391	100.623	100.189
Crystallochemical formula											
Si	2.910	2.889	2.923	2.914	2.920	2.908	2.941	2.965	2.965	2.974	2.982
Ti	0.002	0.003	0.002	0.000	0.001	0.000	0.001	0.001	0.001	0.002	0.000
P	0.060	0.064	0.052	0.066	0.064	0.063	0.050	0.046	0.050	0.044	0.050
Al	2.096	2.100	2.085	2.061	2.067	2.069	2.064	2.041	2.042	2.022	2.043
Fe	2.004	2.023	2.000	1.974	1.978	1.983	1.962	1.976	1.964	1.973	1.975
Mg	0.074	0.082	0.075	0.052	0.043	0.049	0.070	0.072	0.074	0.072	0.071
Mn	0.871	0.873	0.874	0.962	0.942	0.955	0.921	0.892	0.895	0.900	0.852
Ca	0.018	0.017	0.018	0.023	0.022	0.023	0.017	0.017	0.017	0.019	0.018
Na	0.001	0.007	0.004	0.001	0.006	0.004	0.001	0.003	0.005	0.005	0.005
K	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.001	0.000	0.000	0.000
Cr	0.005	0.000	0.002	0.004	0.005	0.002	0.000	0.000	0.000	0.000	0.000
Mn / (Mn+Fe)	0.303	0.302	0.304	0.328	0.323	0.325	0.320	0.311	0.313	0.313	0.301
Sum Z	2.973	2.956	2.977	2.980	2.985	2.971	2.992	3.011	3.017	3.021	3.032
Sum X	2.975	3.003	2.972	3.016	2.996	3.017	2.970	2.962	2.955	2.970	2.921
End -members											
Alm	67.538	67.519	67.419	65.584	66.264	65.867	66.071	66.810	66.577	66.550	67.738
Spess	29.366	29.154	29.456	31.939	31.560	31.742	31.022	30.174	30.339	30.353	29.230
Pyr	2.488	2.747	2.527	1.724	1.442	1.630	2.342	2.441	2.511	2.441	2.427
Grs	0.609	0.580	0.597	0.753	0.735	0.761	0.565	0.575	0.573	0.656	0.605
Mn / (Mn+Fe)	0.303	0.302	0.304	0.328	0.323	0.325	0.320	0.311	0.313	0.313	0.301

Structural formulae calculated on the basis of 12 oxygen atoms per formula unit.

Alm – almandine, Spess – spessartine, Pyr – pyrope, Grs – grossular

The solutions obtained were analyzed by ICP-MS using a Perkin Elmer/Sciex ELAN 6000 ICP-MS quadrupole mass spectrometer. Measurements of element concentrations were performed using Ru-Re (10 ng/ml) as internal standards, so as to minimize the drift effect. A batch of 5-7 samples was bracketed through two calibration procedures. The accuracy and precision of the determinations were checked using certified reference materials (CRM) (Govindaraju, 1994; Dulski, 2000).

Both EMP and ICP-MS analyses were carried out within the Department of Geology and Mineralogy at the University of Cologne. Microscopic observations revealed that garnets are slightly fractured and apparently free of inclusion. Sometimes, garnet-quartz intergrowths were found, suggesting the simultaneous development of the two minerals. Submicroscopic accessory minerals such as monazite, apatite or zircon might also be present in the investigated garnet. This question is then reevaluated in agreement with the analytical results.

Results and discussion

Major elements

The garnet composition varies within a narrow range for all the major elements. The structural formula was calculated on the basis of 12 oxygen atoms per formula unit (a.p.f.u.) (tab. 1). The cation distribution on the three structural positions is close to the ideal one ($X_3Y_2Z_3O_{12}$), with some slight deviations for all positions.

A total of Al + Si + P higher than 5 a.p.f.u. (atoms per formula unit) indicates a lack or only trace amounts of Fe^{3+} in the analysed garnets (Breiter et al., 2005).

In the X-site, bivalent Fe is the dominant cation, followed by Mn and minor amounts of Mg and Ca (table 1; end-member calculated according to Deer et al., 1992). The Mn/(Fe+Mn) ratio is almost constant (0.30-0.33), and it is closely related to the ratio found in pegmatite garnets associated with muscovite, albite and quartz (Baldwin and von Knorring, 1983; Habler et al., 2007).

In the Fe – Mn – (Mg + Ca) diagram (fig. 2), garnet is placed on the edge of the almandine – spessartine solid-solution, pointing out a typical composition of garnet from peraluminous granitic rocks (Habler et al., 2007; Thöni and Miller, 2004; Zhang et al., 2001; Whitworth and Feely, 1994). In all samples, these two end-members make up about 96-98 mol% of the garnet, while pyrope is 1.44-2.75 mol% and grossular – only less than 0.76 mol%.

Garnets from metamorphic host-rocks (Radu, 1997) represented by gneisses are placed along the almandine – (pyrope + grossular) edge (fig. 2), with almandine > pyrope > grossular >> spessartine solid-solution composition (tab. 2). Thus, the compositional difference between pegmatite garnets and garnets from gneisses is obvious, and it mainly concerns the Ca and Mg contents, which are very low in pegmatite garnets (tab. 1), compared to garnets in the metamorphic host-rock.

Aluminium occupies the Y-site, with a slight excess, not higher than 0.099 a.p.f.u. In the Z-site, a slight Si deficit is noted. The charge-balance could be partly maintained by the small Al excess from the Y-site, which apparently compensates for the lower Si content in the Z-site.

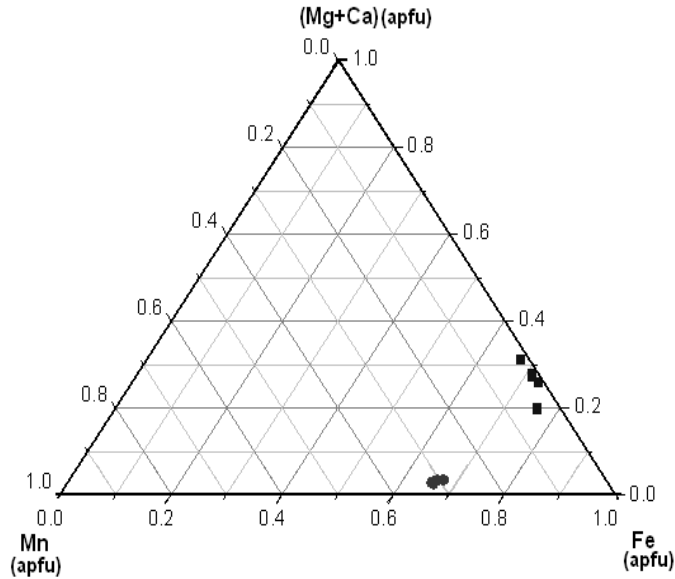


Fig. 2 Fe vs Mn vs Mg+Ca diagram for garnets from pegmatites (●) and from metamorphic host-rocks (■).

Tab. 2 The partial structural formulas (a.p.f.u.) and end-members of garnets in metamorphic host-rock (from Radu, 1997)

Sample (apfu)	PR50	PM50	PR51	PR53	PR54	PR58
Crystallochemical formula (apfu)						
Fe	2.148	2.019	2.087	2.161	2.026	2.266
Mn	0.030	0.039	0.036	0.039	0.025	0.120
Ca	0.211	0.346	0.264	0.374	0.100	0.141
Mg	0.634	0.587	0.542	0.449	0.616	0.448
End -members						
Alm	71.063	67.495	71.253	71.508	73.224	76.155
Spess	0.993	1.315	1.225	1.292	0.917	4.037
Pyr	20.979	19.636	18.511	14.843	22.258	15.060
Grs	6.965	11.555	9.012	12.358	3.602	4.748
Alm – almandine, Spess – spessartine, Pyr – pyrope, Grs – grossular						

Another remarkable feature of the garnet from Răzoare pegmatites is the presence of P as a minor cation. The phosphorous content in these garnets (tab. 1) varies within the range

detected in other occurrences for granite pegmatites, and this cation is considered to be placed in the tetrahedral Z-site of garnet (Anderson et al., 1998; Breiter et al., 2005; Burt, 1996; Haggerty et al., 1994; Zhang et al., 2001).

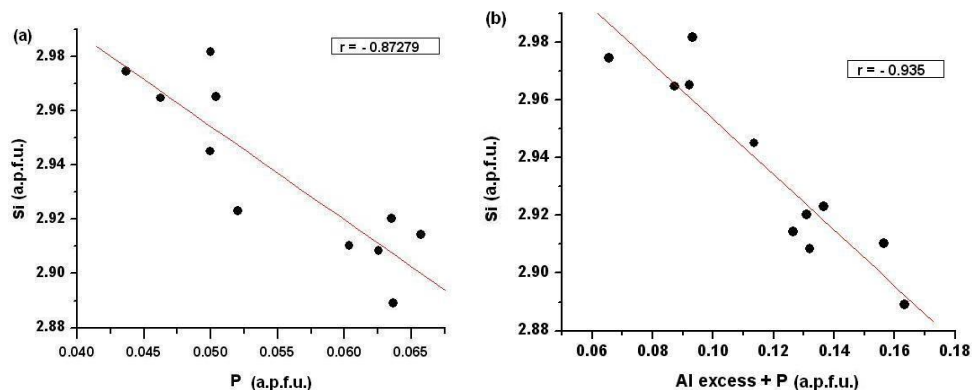


Fig. 3 (a). P vs Si (a.p.f.u.) and (b). ($Al_{ex} + P$) vs Si (a.p.f.u.) in garnets from Răzoare pegmatites.

The negative correlation between Si and P suggests the presence of P in a tetrahedral position (fig. 3a), reducing the Z-site deficit. The accommodation of P cannot come alone, and it involves a coupled substitution in order to maintain the charge-balance. The small Al excess from the Y-site was used to check the coupled substitution as $Al_{ex} P Si_{-2}$, and the relation which developed between both terms (fig. 3b) supports the accommodation of Al and P in the place of Si. Another possibility for the accommodation of P in the tetrahedral Z-site can give rise to the development of structural vacancies in the X-site and involves the substitutions as $P_2 R^{2+}_{-1} Si_{-2}$ or $Na_3 (Fe, Mn, Mg)^{2+}_{-2} Si_{-3}$ (Breiter et al., 2005). In the garnets investigated there are some vacancies in the X-site (tab. 1), but a relation between P and Na, Mn or Fe as cations implied in the substitution was not found.

Therefore, the affinity of P to sinking in the structure of Răzoare garnet does not rely on coupled substitution with cation depletion in the X-site, and it is not disturbed by the Mn/(Mn+Fe) ratio in the crystallising environment. As long as the primary phosphates of Li, Mn and Fe are missing or very rare and apatite is scarce, the P content in the melt seems to show a high affinity for garnet structure (Breiter et al., 2005).

Trace elements

Accessory minerals such as monazite, xenotime, apatite, sphene, allanite, or zircon control the REE budget of granitic rocks (Gromet and Silver, 1983; Montel, 1993; Irber, 1999). During the major or minor phases, garnet can also concentrate REE, with a high affinity for HREE over LREE.

Garnets from Răzoare pegmatites display typical concentration trends for REE, with a content higher in HREE and lower in LREE (tab. 3). Among the four samples analyzed, two (Gr X, Gr X bis) are rich in LREE. In order to state the nature of this content, the Sm/Nd ratio was correlated with the Nd content. Thus, when the Nd content is high, the

Sm/Nd ratio is low (Thöni and Miller, 2004), and this might be explained through the presence of LREE-bearing minerals as microinclusions (undetected inclusions, extremely fine-grained, $<5 \mu\text{m}$). Other potential causes for such a misleading effect on the Sm/Nd ratio of pegmatite garnets are apatite, monazite and zircon (Hoinkes et al., 1997; Rakovan et al., 1997; Whitehouse and Platt, 2003; Villaseca et al., 2003).

In both samples, the lanthanum and cerium content is also higher (Gr X, Gr X bis; tab. 3), and this gain could also be related to undetected inclusions of monazite and apatite.

The total amount of LREE for G101 and G602 garnets is obviously lower when compared to that of the first two samples. For both of these samples, the presence of microinclusions is not supported by the value of the Sm/Nd ratio, which is around 2. At the same time, for sample G1.01, the zirconium and hafnium contents could suggest the presence of zircon, another accessory mineral which could be found in garnet as microinclusions. Thus, zircon, which is able to accommodate LREE, can determine an additional LREE input in garnet.

Usually, garnet may accommodate Zr on the Y-site, but the content of Zr in garnets Gr.X, Gr X. bis and G6.02 is relatively low (tab. 3), making it difficult to determine if there are zircon microinclusions. Moreover, Zr ranges within the same interval attributed to other pegmatite garnets (Thöni and Miller, 2004; Habler et al., 2007; Thöni et al., 2008), suggesting the presence of Zr as trace element, and not as zircon mineral inclusion. A new method, such as XPS, is recommended for the elucidation of the existence of microinclusions of REE minerals which can contribute to the REE budget of garnet.

All garnets display a strong enrichment in HREE over LREE ($\text{Yb}_N/\text{Ce}_N = 88\text{-}2859$), with an almost flat irregular LREE pattern (fig. 4). The chondrite-normalized pattern (fig. 4) also emphasizes a strong progressive increase of HREE and a small Eu/Eu^* , features which are characteristic for spessartine-rich garnets crystallised from a peraluminous anatectic melt (Bea et al., 1994; Villaseca et al., 2003).

The yttrium behavior is similar to that of HREE. It is positioned exclusively in the X-site (Van Westrenen et al., 1999) and it generally has a higher concentration than HREE (Gramaccioli and Pezzotta, 2000). The concentration of Y varies within a narrow range (tab. 3) for all the samples, reaching values similar to those found in other pegmatite spessartine-rich garnets (Habler et al., 2007; Zhang et al., 2001). The charge-balance required by the partition of Y^{3+} and REE^{3+} into the garnet X-site could be achieved through coupled substitution as $(\text{Y,REE})\text{Al}(\text{Fe,Mg,Ca})_{-1}\text{Si}_{-1}$. The ability of Y^{3+} and REE^{3+} to compete with Mn^{2+} in the X-site has already been documented (e.g. Pyle and Spear, 2000), and a negative correlation between Mn and Y could suggest this kind of substitution.

The scarcity of data does not allow us to characterize the relation between Mn and Y, but pegmatite garnet is the typical mineral of Mn accommodation, considering the fact that Y usually develops its own minerals (e.g. xenotime) under crystallisation conditions.

The use of geochemical parameters such as Y/Gd and Y/Dy (Gramaccioli and Pezzotta, 2000), with higher values than those corresponding to the upper crust (Y/Gd = 5.8 and Y/Dy = 6.3), suggests the development of garnet from a fluid (melt) with a significant concentration of complexing agents (fluxing components), such as F, B and P. The complex compounds of volatile elements with REE and Y have increased mobility and, thus, REE and Y have the tendency to concentrate during a later crystallisation stage of felsic rocks, including granite pegmatites (Bau, 1996; Gramaccioli and Pezzotta, 2000).

Tab. 3 ICM-MS analyses ($\mu\text{g/g}$) of selected garnet from Răzoare pegmatites

Trace elements	Gr X	Gr X bis	G6-02	G1-01
Li	-	-	80.62	139.59
Sc	19.1	14.8	17.01	7.40
Rb	15	7	11.68	2.61
Sr	3.1	2.5	1.43	1.28
Y	369	589	456.61	126.23
Zr	26.0	21.3	13.76	56.09
Nb	0.55	0.44	0.41	0.87
Cs	0.22	0.20	0.43	0.23
Ba	20.74	23.15	5.81	12.49
La	1.68	1.63	0.08	0.16
Ce	3.16	3.39	0.18	0.24
Pr	0.33	0.38	0.03	0.04
Nd	1.14	1.39	0.15	0.20
Sm	0.45	1.04	0.33	0.44
Eu	0.10	0.13	0.09	0.07
Gd	2.64	10.75	2.95	3.43
Tb	1.41	4.11	2.32	2.34
Dy	26.25	57.78	39.42	19.17
Ho	8.31	14.49	13.40	3.14
Er	36.06	55.44	61.25	8.23
Tm	7.91	11.47	14.35	1.33
Yb	71.73	103.48	133.13	9.19
Lu	10.58	16.25	19.41	1.20
Hf	1.49	1.81	0.93	3.32
Ta	0.36	0.71	0.38	0.63
Pb	1.50	1.58	11.54	3.48
Th	0.89	0.93	0.04	0.61
U	2.92	0.58	0.87	1.08
Yb _N /Ce _N	87.698	117.874	2859.444	151.137
LREE	6.874	7.964	0.854	1.149
HREE	164.885	273.784	286.22	48.027
Y/Dy	14.047	10.201	11.583	6.585
Y/Gd	139.934	54.823	154.783	36.770
Sr/Eu	29.865	19.586	16.295	17.722

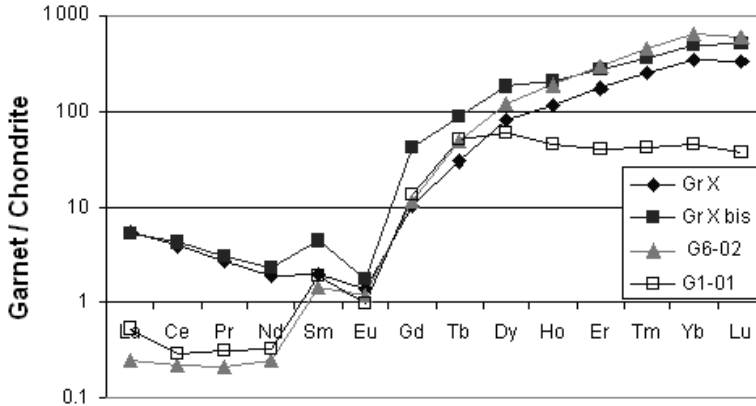


Fig. 4 Chondrite-normalized REE patterns of garnet.

Lithium also shows affinity for garnet, reaching significant concentrations (tab. 3). The Li^+ content in garnet can rise along with the entrance of REE^{3+} into the X-site. Thus, Li^+ is involved in the maintenance of the charge-balance of the X-site, while REE^{3+} substitutes for Mg or Ca, as follows: $\text{LiREE}^{3+}\text{Mg}_2$ $\text{LiREE}^{3+}\text{Mg}_1\text{Ca}_1$ (Freeman et al., 2005).

Scandium is another trace element with an increased ability to accommodate in the structure of garnet. Usually, Sc has been found in significant concentrations in Ca-rich garnets, which are not typical of the pegmatite domain. Sc^{3+} enters in the Y-site and substitutes for Al^{3+} (Raade et al., 2002; Van Westrenen et al., 1999). The almandine-spessartine garnet from Răzoare pegmatites has a low Sc content (tab. 3), typical of granite pegmatite garnets.

Some unusual geochemical features are noted and they refer to the Nb–Ta and Sr–Ba pairs. Thus, the Nb and Ta contents are low, but not under ICP-MS detection limits, with Ta concentration close to that of Nb or slightly higher, a feature which denotes a loss of coherence for this geochemical pair due to the development of complex compounds with volatile elements (Bau, 1996; Irber, 1999). As far as Sr and Ba are concerned, Ba reaches higher concentration than Sr (tab. 3), this being uncommon geochemical behaviour for spessartine-rich garnets. The higher solubility of Ba is found in the $\text{Py}_{50}\text{Gr}_{50}$ solid-solution, when the lattice energy allows this kind of accumulation (Freeman et al., 2005).

Conclusions

Commonly, the lack of any connection with granite bodies raises questions regarding the origin of pegmatites. The geochemical studies of rock-forming and accessory minerals contribute with valuable information to the solving of this problem. The pegmatites from the Răzoare formation within the Preluca Mountains belong to this category, and herein the garnet geochemistry reveals the development of the pegmatites from melts rich in volatile components which contribute to the concentration of trace elements such as Li, REE, Y, Zr, Hf, Nb and Ta in garnets of late mineral association. The manganese content provides about

30 mol% of spessartine in the garnet solid-solution, which is characteristic for magmatic pegmatite garnets (Baldwin and von Knorring, 1983; Habler et al., 2007; Whitworth and Feely, 1994). Mn-enriched garnet develops from progressively differentiating melts and occurs due to a high Mn content in the presence of Al excess (Du Bray, 1988). In addition, Mn stabilizes garnet at shallow depth (Green, 1977). Consequently, in pegmatites showing no visible relation with granite bodies the high content of spessartine can be used as an argument for garnet crystallisation from an evolved granitic melt and against the idea of derivation from allochthonous sources or metamorphic growth.

The garnets with higher HREE content and moderate negative Eu anomaly that were investigated are typical of garnet from granite pegmatites. In addition, the values obtained for the Y/Dy and Y/Gd ratios denote the growth of garnets from melts rich in volatile components. The abundance of fluxing components (F, B, P) in the crystallizing melt could also be reflected by the high P concentration in garnet from Răzoare pegmatites. Among the fluxing components, F and P were found to have a strong affinity to associate with Na and Al in the melt (Wolf and London, 1994; London et al., 1999). We consider that, through their association with albite, muscovite and quartz, the investigated garnets are in agreement with the experimental data and support the evolution of pegmatites from a peraluminous melt rich in fluxing components. The evolving nature of the melt is also denoted by the loss of geochemical coherence between the Nb–Ta and Zr–Hf pairs, which indicates a gradual increasing role of volatiles in the crystallisation of minerals, including that of garnet (Bau, 1996).

The present data related to previous results on apatite from the same location (Rădăşanu et al., 2003) indicate the derivation of pegmatites from melts of crustal anatexis.

The origin of pegmatites from an anatectic melt is also supported by geobarothermometric data regarding metamorphic host-rocks, which reveal the conditions required for the development of minimum granitic melts (Balintoni, 1996; Radu, 1997).

References

- Anderson, S.D., Černý, P., Halden, N.M., Chapman, R., Uherm, P., 1998. The Yitt-B pegmatite swarm at Bernic Lake, southeastern Manitoba: a geochemical and paragenetic anomaly. *Can. Mineral.*, **36**, 283–301.
- Baldwin, J.R., von Knorring, O., 1983. Compositional range of Mn-garnet in zoned granitic pegmatites. *Can. Mineral.*, **21**, 683–688.
- Balintoni, I., 1996. Geotectonics of the metamorphic terrains from Romania. Ed. Univ. Babeş-Bolyai, Cluj-Napoca, 241p. (In Romanian).
- Bau, M., 1996. Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contrib. Mineral. Petrol.*, **123**, 323–333.
- Bea, F., Pereira, M.D., Stroh, A., 1994. Mineral/leucosome trace-element partitioning in a peraluminous migmatite (a laser ablation-ICP-MS study). *Chem. Geol.*, **117**, 291–312.
- Breiter, K., Novak, M., Koller, F., Cempirek, J., 2005. Phosphorus – an omnipresent minor element in garnet of diverse textural types from leucocratic granitic rocks. *Mineral. Petrol.*, **85**, 205–221.
- Burt, D.M., 1996. Compositional limits of phosphorus substitution in garnet in pegmatites and in the mantle. *Geol. Assoc. Can. – Mineral. Assoc. Can., Abstr. 2*, A–15.
- Černý, P., Hawthorne, F.C., 1982. Selected peraluminous minerals; In: Černý, P. (Ed.). (1982). *Granitic pegmatites in sciences and industry*. Mineral. Assoc. Can., Short Course Handbook, **8**, 63–98.
- Deer, W.A., Howie, R.A., Zussman, J., 1992. *An introduction to the rock forming minerals*, 2nd Edition. Ed. Prentice Hall, 696p.

- Du Bray, E.A., 1988. Garnet compositions and their use as indicators of granitoid petrogenesis – Southeastern Arabian Shield. *Contrib. Mineral. Petrol.*, **100**, 205–212.
- Dulski, P., 2000. Reference materials for geochemical studies: New analytical data by ICP-MS and critical discussion of reference values. *Geostandards Newsletter*, **25**, 87–125.
- Freeman, C.L., Lavrentiev, M., Allan, N.L., Purton, J.A., van Westrenen, W., 2005. Similarity in silicate chemistry: trace elements in garnet solid solutions. *Journal of Molecular Structure: Theochem.*, **727**, 199–204.
- Govindaraju, K., 1994. Compilation of working values and sample description for 383 Geostandards. *Geostandards Newsletter*, **18**, Special Issue, 1–158.
- Gramaccioli, C.M., Pezzotta, F., 2000. Geochemistry of yttrium with respect to the rare-earth elements in pegmatites. *Memorie della Società Italiana di Scienze naturali e del Museo Civico di Storia Naturale di Milano*, **XXX**, 111–115.
- Green, T.H., 1977. Garnet in silicic liquid and its possible use as P–T indicator. *Contrib. Mineral. Petrol.*, **65**, 59–67.
- Gromet, L.P., Silver, L.T., 1983. Rare earth element distribution among minerals in a granodiorite and their petrogenetic implications. *Geochim. Cosmochim. Acta*, **47**, 925–939.
- Habler, G., Thöni, M., Miller, C., 2007. Major and trace element chemistry and Sm–Nd age correlation of magmatic pegmatite garnet overprinted by eclogite-facies metamorphism. *Chem. Geol.*, **241**, 4–22.
- Haggerty, S.E., Fung, A.T., Burt, D.M., 1994. Apatite, phosphorus and titanium in eclogitic garnet from the upper mantle. *Geophys. Res. Lett.*, **21**, 1699–1702.
- Hoinkes, G., Thöni, M., Lichem, Ch., Bernhard, F., Kaindl, R., Schweigl, J., Tropper, P., Cosca, M., 1997. Metagranitoids and associated metasediments as indicators for the pre-Alpine magmatic and metamorphic evolution of the western Ötztal Basement (Kaunertal, Tirol). *Schweiz. Mineral. Petrogr. Mitt.*, **77**, 299–314.
- Irber, W., 1999. The lanthanide tetrad effect and its correlation with K/Rb, Eu/Eu*, Sr/Eu, Y/Ho, and Zr/Hf of evolving peraluminous granite suites. *Geochim. Cosmochim. Acta*, **63**, 489–508.
- Kalmár, I., 1973. Pegmatites from Preluca Mountains. *D. S. Inst. Geol.*, **LIX**, 1, 231–249. (In Romanian).
- Kleck, W.D., Ford, E.E., 1999. The chemistry, mineralogy, and petrology of the George Ashley Block pegmatite body. *Am. Min.*, **84**, 695–707.
- London, D., Wolf, M., Morgan VI, G.B., Garrido, M.G., 1999. Experimental silicate–phosphate equilibria in peraluminous granitic magmas, with a case study of the Albuquerque batholith at Tres Arroyos, Badajoz, Spain. *J. Petrol.*, **40**, 215–240.
- Montel, J.-M., 1993. A model for monazite/melt equilibrium and application to the generation of granitic magmas. *Chem. Geol.*, **110**, 127–146.
- Pyle, J.M., Spear, F.S., 2000. An empirical garnet (YAG)-xenotime thermometer. *Contrib. Mineral. Petrol.*, **138**, 51–58.
- Raade, G., Ferraris, G., Gula, A., Ivaldi, G., Bernhard, F., 2002. Kristiansenite, a new calcium-scandium-tin sorosilicate from a granite pegmatite in Tordal, Telemark, Norway. *Mineral. Petrol.*, **75**, 89–99.
- Rădăşanu, S., Murariu, T., Kasper, H.U., Schoenbeck, T., 2003. The geochemistry of apatite from Răzoare pegmatites. *Studia Univ. "Babeş Bolyai"*, Special Issue, 98–102.
- Radu, D.M., 1997. Geothermometry of metapelitic rocks from the western part of Preluca crystalline complex, Maramureş. *Rom. J. Mineral.*, **78**, 21–30.
- Rakovan, J., McDaniel, D.K., Reeder, R.J., 1997. Use of surface controlled REE sectoral zoning in apatite from Llallagua, Bolivia, to determine a single-crystal Sm–Nd age. *Earth Planet Sci. Lett.*, **146**, 329–336.
- Rusu, A., Balintoni, I., Bombiţă, G., Popescu, G., 1983. Geological Map of the Preluca zone, 1: 50.000, sheet 18c, L-34-24-C. Institutul de Geologie şi Geofizică, Bucureşti. (In Romanian).
- Thöni, M., Miller, C., 2004. Ordovician meta-pegmatite garnet (N–W Ötztal basement, Tyrol, Eastern Alps): preservation of magmatic garnet chemistry and Sm–Nd age during mylonitization. *Chem. Geol.*, **209**, 1–26.
- Thöni, M., Miller, Ch., Zanetti, A., Habler, G., Goessler, W., 2008. Sm–Nd isotope systematics of high-REE accessory minerals and major phases: ID-TIMS, LA-ICP-MS and EPMA data constrain multiple Permian–Triassic pegmatite emplacement in the Koralpe, Eastern Alps. *Chem. Geol.*, **254**, 216–237.
- Van Westrenen, W., Blundy, J., Wood, B., 1999. Crystal-chemical controls on trace element partitioning between garnet and anhydrous silicate melt. *Amer. Mineral.*, **84**, 838–847.
- Villaseca, C., Martín Romera, C., De la Rosa, J., Barbero, L., 2003. Residence and redistribution of REE, Y, Zr, Th and U during granulite-facies metamorphism: behaviour of accessory and major phases in peraluminous granulites of central Spain. *Chem. Geol.*, **200**, 293–323.
- Whitehouse, M.J., Platt, J.P., 2003. Dating high-grade metamorphism constraints from rare-earth elements in zircon and garnet. *Contrib. Mineral. Petrol.*, **145**, 61–74.
- Whitworth, M.P., Feely, M., 1994. The compositional range of magmatic Mn-garnets in the Galway Granite, Connemara, Ireland. *Mineral. Mag.*, **58**, 163–168.

- Wolf, M.B., London, D., 1994. Apatite dissolution into peraluminous haplogranitic melts: in experimental study of solubilities and mechanisms. *Geochim. Cosmochim. Acta*, **58**, 4127–4145.
- Zhang, C., Gieré, R., Stuenkel, H., Brack, P., Ulmer, P., 2001. Garnet–quartz intergrowths in granitic pegmatites from Bergell and Adamello, Italy. *Schweizerische Mineralogische und Petrographische Mitteilungen*, **81**, 1, 89–113.

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