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COMPOSITIONAL EVOLUTION OF METASOMATIC GARNET IN MELILITIC ROCKS OF THE OSEČNÁ COMPLEX, BOHEMIA

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Abstract

Zoned garnet occurs in melilitic rocks of the subvolcanic alkaline Osečná complex, in northern Bohemia, Czech Republic. The first generation of garnet (I) consists of dark brown spots of Zr-bearing melanite grading into brown melanite. The second generation (II), a pale yellow (OH,F)-bearing titanian andradite, forms overgrowths on garnet I, locally replaces it, or crystallizes in independent grains. It shows oscillatory zoning of colorless (OH,F)-bearing Ti-poor aluminous andradite, yellow Ti-enriched (OH,F)-bearing andradite, and brown melanite. Garnet I is primarily dispersed in only slightly metasomatized melilitolite, micromelilitolite and polzenite, and in relics in all rocks of the Osečná complex. Garnet II predominates in metasomatic derivatives of the melilitolite, *i.e.*, phlogopitite, melilitolitic pegmatite and ijolite, in association with perovskite, titanian magnetite, calzirtite, apatite, carbonate, zeolites, pectolite and other minerals. Melanite contains 9.0 – 12.7 wt.% TiO_2, and Zr-bearing melanite has between 1.3 and 9.1 wt.% ZrO_2. Titanian (OH,F)-bearing andradite contains 0.1–0.6 wt.% F and 0.9 – 1.8 wt.% H_2O^+. Both generations of garnet crystallized from fluids with low a(Si) and initially rather low but increasing $f(O_2)$ and F, in a metasomatic reaction at the expense of melilite, phlogopite and probably monticellite. An essentially two-phase assemblage of phlogopite + garnet (± titanian magnetite, perovskite) was formed in phlogopitite, whereas a nepheline + calcite + aegirine-augite (± garnet, phlogopite) assemblage was generated in ijolite; the melilitolitic pegmatites consist of nepheline + phlogopite + garnet (± melilite, apatite, perovskite and calzirtite). The occurrence of the Zr-bearing melanite, Mn-enriched ilmenite and primary magmatic carbonates with $\delta^{13}C$ of −3.9 to −7.4‰ link the Osečná complex to mantle-derived carbonated alkaline ultramafic intrusions of the Maimecha–Kotui province, Magnet Cove and Marathon Dikes kindred.

Keywords: garnet, melanite, andradite, zirconium, melilitolite, polzenite, Osečná, Bohemia, Czech Republic.

Sommaire

On trouve des cristaux zonés de grenat dans des roches mélilitiques du complexe alcalin subvolcanique de Osečná, dans le nord de la Bohème, en République Tchèque. La première génération de grenat (I) paraît sous forme de taches brun foncé de mélanite riche en Zr, zonée vers une mélanite brune. Une seconde génération (II), faite d'andradite titanifère jaune pâle contenant OH et F, forme une surcroissance sur le grenat I, et le remplace localement, ou encore cristallise en grains séparés. Cette génération montre une zonation oscillatoire impliquant andradite alumineuse incolore, pauvre en Ti et contenant OH et F, andradite jaune, enrichie en Ti et contenant OH et F, et mélanite brune. Le grenat I est surtout disséminé dans la mélilitolite faiblement métasomatisée, la micromélilitolite et la polzénite, et se présente sous forme de reliques dans toutes les roches du complexe de Osečná. Le grenat II prédomine dans les dérivés métasomatiques de la suite mélilitolite, c'est-à-dire phlogopitite, les facies pegmatitiques et l'ijolite, en association avec pérovskite, magnétite titanifère, calzirtite, apatite, carbonate, zéolites, et pectolite, entre autres. La mélanite contient entre 9.0 et 12.7% de TiO_2 par poids, et la mélanite riche en Zr contient entre 1.3 et 9.1% de ZrO_2. L'andradite titanifère contient entre 0.1 et 0.6% de F, et entre 0.9 et 1.8% de H_2O^+. Les deux générations de grenat ont cristallisé à partir d'une phase fluide ayant une faible activité de Si et, au départ, une faible fugacité d'oxygène et de fluor, suite à une réaction métasomatique aux dépens de mélilite, phlogopite et, tout probablement, monticellite. Un assemblage essentiellement à deux phases, phlogopite + grenat (± magnétite titanifère, pérovskite) en a résulté dans la phlogopitite, tandis que l'assemblage néphéline + calcite + augite aegyrinique (± grenat, phlogopite) est apparue dans l'ijolite. Les facies pegmatitiques contiennent l'assemblage néphéline + phlogopite + grenat (± mélilite, apatite, perovskite et calzirtite). La présence de mélanite enrichie en Zr, d'ilménite enrichie en Mn, et de carbonates primaires ayant une valeur de $\delta^{13}C$ de −3.9 à −7.4‰ établit une affiliation entre le complexe de Osečná et les massifs intrusifs ultramafiques, alcalins, carbonatés, et d'origine mantellique de la province de Maimecha – Kozui, de la suite de Magnet Cove, et des filons de Marathon.

(Traduit par la Rédaction)

Mots-clés: grenat, mélanite, andradite, zirconium, mélilitolite, polzénite, Osečná, Bohème, République Tchèque.

Introduction

The Osečná complex of melilite-bearing subvolcanic rocks in northern Bohemia, Czech Republic, is an exceptional feature within the young European (Upper Cretaceous to Quaternary) alkaline volcanic province, which stretches from central Spain through France and western Germany to the Czech Republic (Wimmenauer 1974). The Osečná complex forms an integral part of a bimodal melilitite – phonolite suite in northern Bohemia; it approaches the constitution of the composite, carbonatite-bearing and melilite- and nepheline-rich complexes of the Oka, Gardiner and Maimecha–Kotui type. These complexes are generally scarce in the worldwide population of alkaline igneous rocks.

Effects of late postmagmatic, low-temperature metasomatic processes are widespread in the Osečná complex, and lead to concentration of a broad spectrum of large-ion incompatible elements and volatile components. Zirconium is of particular interest because of its mobility in low-temperature conditions and its incorporation in a number of minerals such as calzirtite, hainite and fluorian eudialyte (Ulrych *et al.* 1992).

Garnet also concentrates significant quantities of Zr in the Osečná complex, as is typical of garnet from alkaline ultramafic rocks and carbonatites, and recognized at all of the seven localities identified to date (Platt & Mitchell 1979). A high Ti content of garnet also is typical of silica-undersaturated alkaline igneous rocks (*e.g.*, Gomes 1969, Sørensen 1974, Meagher 1982, Keller 1984, Dingwell & Brearley 1985), and it was identified in numerous exposures of phonolite and associated rocks of the České Středohoří Mountains (Cornu 1911, Reinisch 1914, Wurm 1914, Kavka 1958) and Kaiserstuhl (Keller 1984).

Besides its chemistry, the garnet of the alkaline igneous suites also is interesting from a paragenetic viewpoint. Sørensen (1974) and Flohr & Ross (1989) reported that the garnet could be either magmatic or metasomatic in origin. Shand (1943) and Kavka (1958) claimed a magmatic crystallization for garnet, whereas Larsen & Goranson (1932), Borodin & Pavlenko (1974), Egorov (1969) and Ulrych *et al.* (1988b) considered the garnet to be a late, deuteric or metasomatic phase.

The worldwide scarcity of garnet-bearing alkaline igneous rocks, the compositional complexity of garnet in this environment, and the controversial position of garnet in the crystallization sequences of alkaline rocks prompted us to initiate a thorough study of garnet in the Osečná complex. The results presented here show that this occurrence of garnet is eminently suited to contribute to an understanding of its role in the evolution of the alkaline rocks.

The Osečná Complex

The Osečná complex is located in the region of the upper Ploučnice river in the Cretaceous basin of northern Bohemia (Fig. 1) (Pivec *et al.* 1987, Ulrych *et al.* 1988b). It comprises the largest of the swarms of alkaline rocks penetrating Upper Cretaceous sediments of

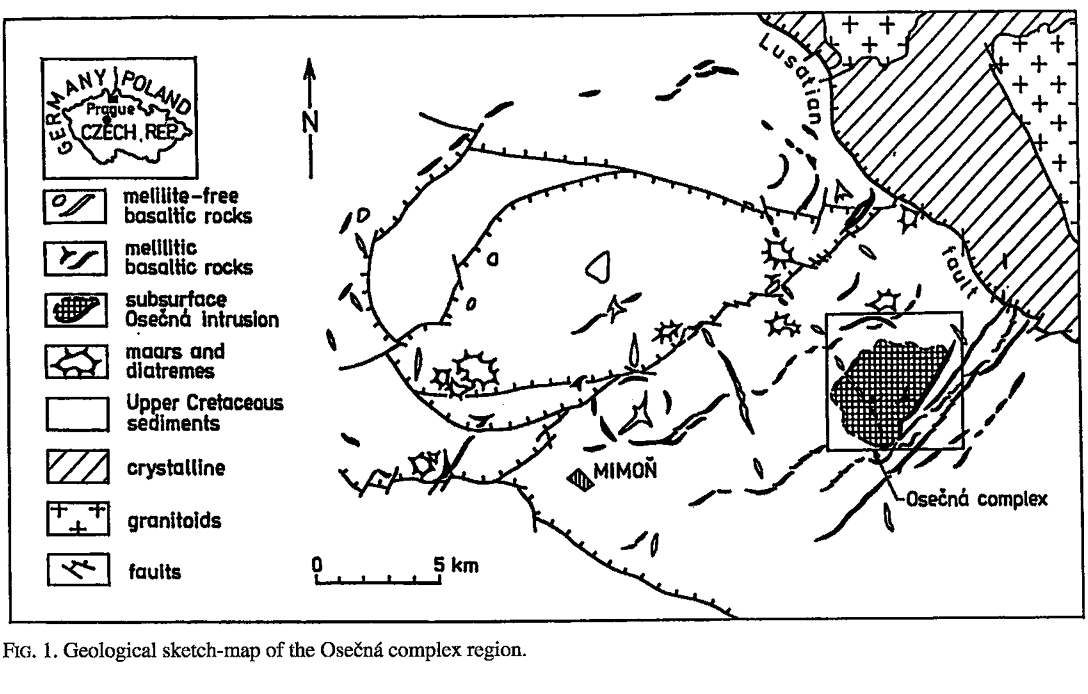

FIG. 1. Geological sketch-map of the Osečná complex region.

this area and, in part, adjacent Germany.

A lopolith-like body of melilitolite forms the central part of the complex, intruded into Cenomanian–Turonian sandstones (Fig. 2). This intrusion is exposed on the surface only in its marginal facies of fine-grained micromelilitolite. The hidden part has an areal extent of about 12.5 km^2 and an apparent thickness of 23 to 66 m, as revealed by drilling. Cone sheets of polzenite and subordinate micromelilitolite, and radial dykes of tephrite to basanite, both several cm to a few m in thickness, accompany the lopolith-like body of melilitolite in a centrosymmetric pattern typical of ring complexes. Volcanic breccia pipes also are present, with a basaltic pyroclastic groundmass carrying melilite and occasional fragments of eclogite and garnet peridotite. Independent dikes of micromelilitolite, polzenite and especially of the melilite-bearing nephelinite to olivine melilitite form the characteristic NE–SW-trending system of the so-called Devil's Wall. More felsic rocks, such as phonolite, are rare in the immediate vicinity of the Osečná complex. The crystallization of olivine,

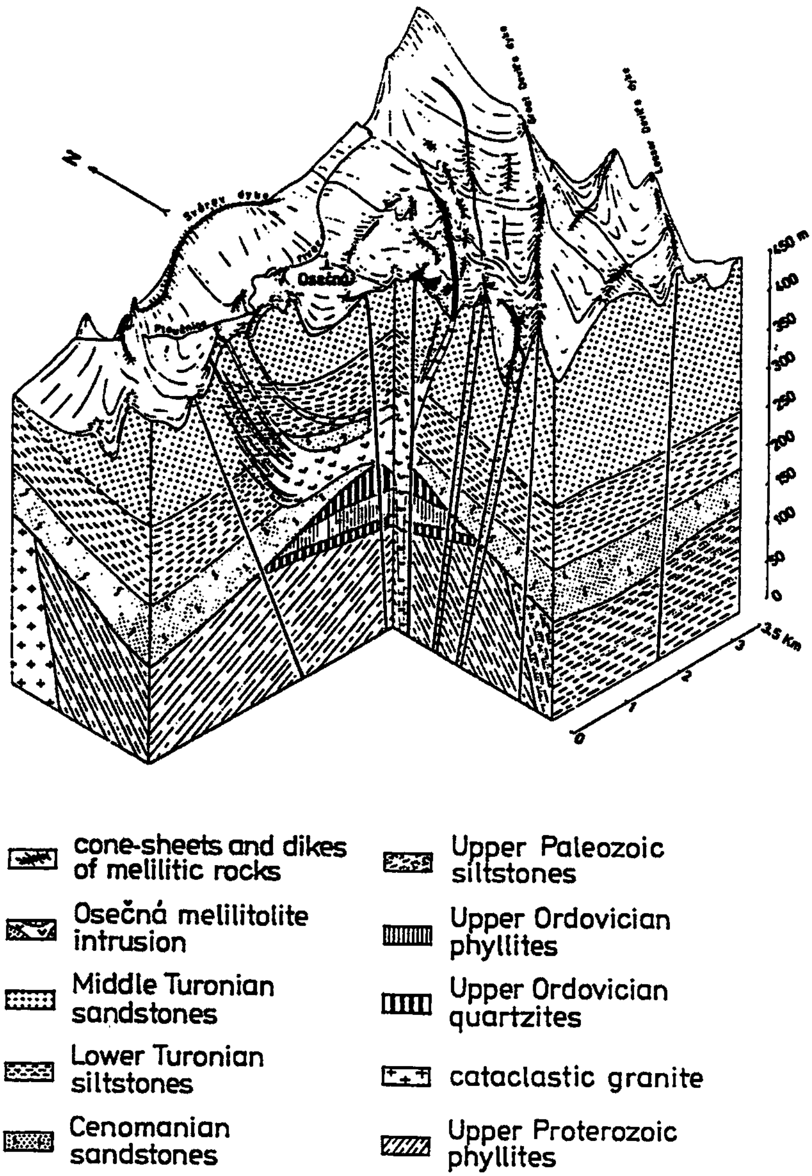

FIG. 2. Block diagram of the Osečná complex.

pyroxene and melilite is responsible for the origin of the (micro)melilitite – polzenite – melilitite – nephelinite – basanite–tephrite differentiation series.

Metasomatic derivatives of the above-mentioned melilitic rocks are found locally, mainly in the central lopolithic intrusion. Metasomatic products are widely dispersed, formed mainly at the expense of olivine, melilite and possibly also clinopyroxene. Local structurally controlled concentrations of the metasomatic assemblages are represented by secondary phlogopitites (phlogopite + garnet >> titanian magnetite, perovskite), ijolites (nepheline + calcite + aegirine-augite > garnet, phlogopite) and melilitolitic pegmatites (coarse-grained nepheline + phlogopite + garnet, ± melilite in relics) with late apatite, perovskite, titanian magnetite and numerous other minerals, as characterized by Borodin & Pavlenko (1974). Postmagmatic fluids rich in K, Ca, Al, Fe^{3+} and Ti, and carrying Sr, Ba, the *REE*, Th, U, Zr, Hf, Nb, Ta, P, F and other minor elements, are held responsible for the replacement phenomena (Ulrych *et al.* 1988b).

Distribution of Garnet

Garnet is a minor constituent (0.5–2.0 vol.%) of the melilitolite that makes up the central lopolithic body. However, much greater concentrations of garnet are found in the metasomatic derivatives: phlogopitites (18–40 vol%), melilitolitic pegmatites (8–21 vol.%) and ijolites (3–8 vol.%). Minor amounts of garnet also are present in the cone-sheet dikes of polzenite and

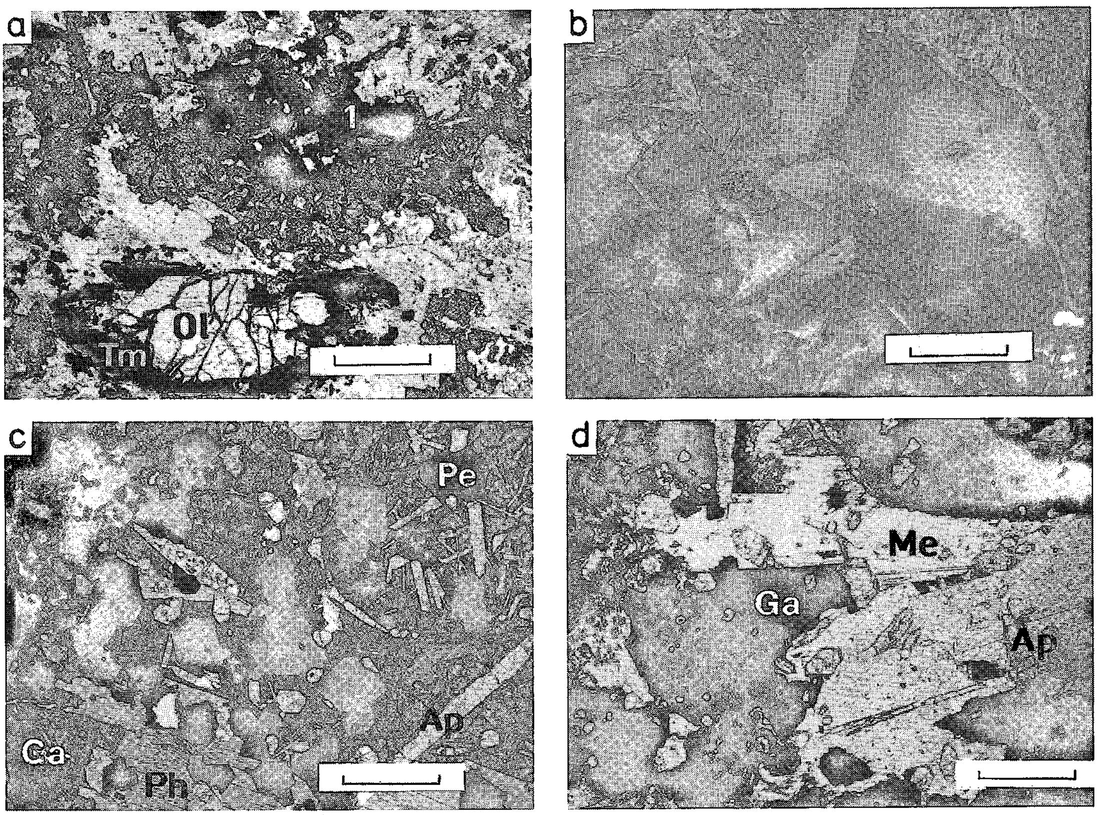

FIG. 3. Features of garnet from the Osečná intrusion. a. Photomicrograph of subhedral core (1) of melanite (Ib generation) with anhedral rim (2) of (OH,F)-bearing titanian andradite (IIa generation) in melilite–phlogopite matrix. Anhedral olivine (Ol) relic rimmed by titanian magnetite (Tm) is present in the lower part of the figure. Phlogopitite, Osečná (sample 3), plane-polarized light, scale bar 0.2 mm. b. Secondary electron image of striated crystal of (OH,F)-bearing titanian andradite (generation II) in miarolitic cavity. Melilitolitic pegmatite, Osečná (sample 31), JEOL JXA–50 A, scale bar 0.33 mm. c. Photomicrograph of garnet (Ga) aggregate (melanite of generation Ib) replacing phlogopite (Ph) laths, with abundant euhedral crystals of perovskite (Pe) and needles of apatite (Ap). Melilitolitic pegmatite, Osečná (sample 31), plane-polarized light, scale bar 0.33 mm. d. Photomicrograph of subhedral garnet (Ga) grains of melanite composition (Ib generation) replacing melilite (Me). Abundant euhedral crystals of apatite (Ap) are present in decomposed melilite. Melilitolitic pegmatite, Osečná (sample 31), plane-polarized light, scale bar 0.2 mm.

micromelilitolite. The grain size of garnet is somewhat variable among the different rock-types: 0.05–0.3 mm in melilitolite, micromelilitolite and polzenite, 0.05–1.0 mm in phlogopitite, 0.3–2.6 mm in melilitolitic pegmatite, and 0.1–0.5 mm in ijolite. In all of its occurrences, garnet is associated with secondary minerals of metasomatic origin, such as phlogopite, perovskite, titanian magnetite, calzirtite, apatite, monticellite, pectolite, zeolites and carbonates (Figs. 3a, b, c, d, 4a, b). This applies equally to the sparsely disseminated as well as highly concentrated metasomatic assemblages. Textural relationships locally indicate direct replacement of primary minerals (*e.g.*, melilite, phlogopite, monticellite and clinopyroxene) by garnet (Figs. 3c, d).

Specimens and Experimental Methods

The garnet was examined in detail in fifteen rock samples: six of melilitolite (samples 2, 6, 7, 10, 15, 11), two each of melilitolitic pegmatite (16, 31), phlogopitite (3, 71a), micromelilitolite (1, 34) and polzenite (4, 9), and one of ijolite (71).

Garnet of an overall composition of andradite, with between 5 and 15 wt.% TiO_2, is termed melanite, following the classification of Deer *et al.* (1982). Compositions with between 1 and 5 wt.% TiO_2 are designated Ti-bearing andradite (Kukharenko & Bagdasarov 1962). Electron-microprobe analyses were performed using a JEOL JXA – 50 A instrument, under conditions given by Ulrych *et al.* (1986); synthetic ZrO_2 (JEOL) was used for determination of Zr, and topaz for F. FeO and Fe_2O_3 were determined in garnet separates by wet-chemical analysis (volumetrically) and by Mössbauer spectrometry. A standard KFKI (Hungary) spectrometer with constant acceleration source was used, with ^{57}Co in a Rh matrix as source of radiation, and with a scintillation detector. The spectra were evaluated using the data and procedures of Stevens (1983). The contents of the *REE* and other trace elements were determined by instrumental neutron-activation analysis (INAA) by V. Moučka (Geoindustria, Praha), V by K. Absolon (Geological Institute, Czechoslovak Academy of Sciences, Praha) using optical emision spectroscopy (OES), and F by R. Rychlý (State Glass-Research Institute, Hradec Králové) using a Cam Scan S4–DV electron microprobe.

Granular separates of garnet (distinguished according to density and color) were used for the determination of physical properties. The index of refraction was determined by the immersion method, in Na light. The mid-infrared spectra were recorded using a Zeiss UR–20 spectrometer using KBr pellets. Density was measured by the suspension method in Clerici solution, using a Mohr–Westphal balance.

The cell edge of different density-fractions of eight samples of garnet was calculated from X-ray (C.I.S.) diffractograms, under conditions quoted by Ulrych *et al.* (1988a) and using the program of Weiss (1972).

Mineralogy of the Garnet

Zoning and chemical composition

Two types of garnet, brown and pale yellow, are

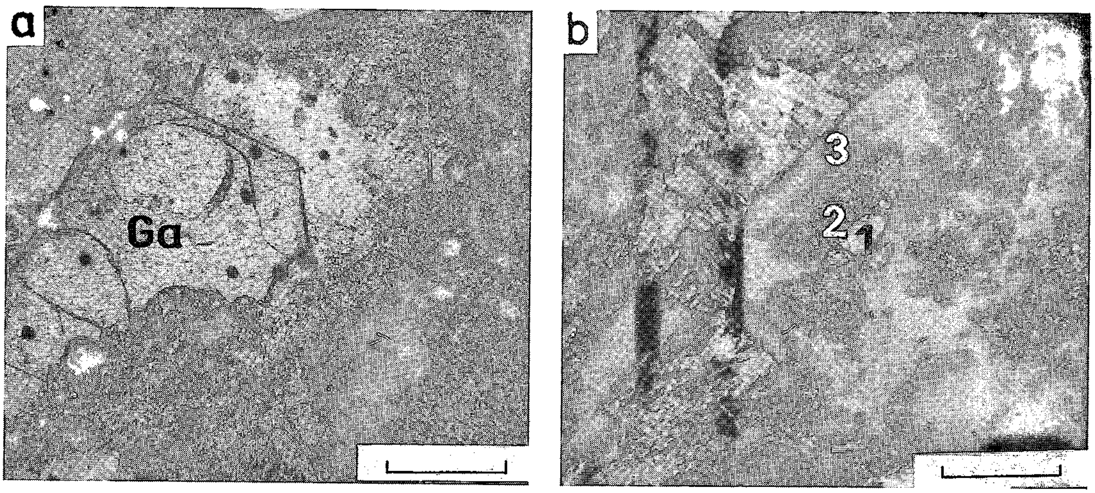

FIG. 4. Photomicrographs of garnet from the Osečná intrusion. a. Subhedral to euhedral (OH,F)-bearing, Ti-poor aluminous andradite (Ga; IIb generation) growing into a miarolitic cavity filled by thomsonite–pectolite aggregates, with black grains of perovskite. Melilitolitic pegmatite, Osečná (sample 16), plane-polarized light, scale bar 0.4 mm. b. Subhedral to euhedral crystal of garnet with central part (1) formed by (OH,F)-bearing Ti-poor aluminous andradite (generation IIb, white) rimmed (2) by (OH,F)-bearing titanian andradite (generation IIa, light grey) with a growth zone of composition similar to that of the central part (1), and by (3) Ti-rich andradite to Ti-poor melanite (generation IIc, dark grey to black) with growth zones compositionally similar to the intermediate zone (2). Melilitolite, Osečná (sample 2). Plane-polarized light, scale bar 0.4 mm.

TABLE 1. REPRESENTATIVE ELECTRON-MICROPROBE DATA ON ZONED GARNET FROM THE OSEČNÁ COMPLEX

Rock Type	melilitolite				pegmatite		ijolite		phlogopit	polzenite	micromelilitolite	
No.	15/Ia	15/Ib	2/Ia	2/IIc	31/Ia	31/IIc	71/Ia	71/Ib	3/Ib	9/Ib	34/IIc	34/IIc
SiO_2 wt.%	28.61	33.31	31.10	35.25	32.66	35.50	30.95	33.43	30.76	34.16	34.89	35.33
TiO_2	12.33	10.30	10.83	4.03	10.27	4.93	11.63	10.38	11.86	12.67	3.40	1.53
ZrO_2	9.10	0.49	1.25	0.05	4.11	0.05	0.70	0.23	0.27	0.00	0.00	0.00
Al_2O_3	0.03	0.77	0.43	1.86	0.17	3.03	0.40	1.95	0.12	5.28	6.82	4.18
Cr_2O_3	0.21	0.11	0.28	0.03	0.15	0.00	0.08	0.05	0.19	0.30	0.02	0.00
$Fe_2O_3^x$	17.56	22.13	23.68	25.09	19.32	22.44	23.63	21.22	22.74	15.09	20.91	26.65
MnO	0.05	0.09	0.04	0.05	0.03	0.05	0.10	0.17	0.20	0.06	0.18	0.20
MgO	0.12	1.56	1.21	1.59	1.11	1.04	1.36	0.30	1.43	1.13	1.17	0.56
CaO	31.51	31.16	31.03	31.56	32.03	32.18	31.22	32.14	32.27	30.90	32.02	31.65
Na_2O	0.08	0.03	0.15	0.06	0.20	0.03	0.11	0.05	0.11	0.14	0.03	0.02
K_2O	0.03	0.01	0.02	0.03	0.03	0.01	0.03	0.01	0.03	0.03	0.00	0.00
Total	99.63	99.96	100.02	99.60	100.08	99.26	100.21	99.93	99.98	99.76	99.44	100.12
Number of ions calculated on the basis of 8 cations and 12 oxygen atoms												
Si	2.546	2.811	2.652	2.944	2.799	2.965	2.634	2.824	2.614	2.828	2.863	2.935
Al	0.003	0.077	0.043	0.056	0.017	0.035	0.040	0.176	0.012	0.172	0.137	0.065
Fe^{3+}	0.451	0.112	0.305	-	0.184	-	0.326	-	0.374	-	-	-
Octahedral sites												
Al	-	-	-	0.127	-	0.263	-	0.018	-	0.343	0.523	0.335
Cr	0.015	0.007	0.019	0.002	0.010	-	0.005	0.003	0.013	0.020	0.001	-
Ti	0.825	0.654	0.695	0.253	0.662	0.310	0.744	0.659	0.724	0.789	0.210	0.096
Zr	0.395	0.020	0.052	0.002	0.172	0.002	0.029	0.009	0.011	-	-	-
Fe^{3+}	-	0.842	0.862	1.430	0.533	1.151	0.825	0.822	0.890	0.258	1.196	1.525
Fe^{2+}	0.741	0.281	0.218	-	0.418	0.145	0.224	0.451	0.163	0.451	-	-
Mg	0.016	0.196	0.154	0.186	0.142	0.129	0.173	0.038	0.181	0.139	0.070	0.044
Dodecahedral sites												
Mg	-	-	-	0.012	-	-	-	-	-	-	0.073	0.025
Fe^{2+}	-	0.170	0.135	0.147	0.048	0.114	0.138	0.076	0.027	0.230	0.095	0.141
Mn	0.004	0.006	0.003	0.004	0.002	0.004	0.007	0.012	0.014	0.004	0.013	0.014
Ca	3.004	2.817	2.835	2.824	2.941	2.879	2.846	2.909	2.937	2.740	2.815	2.817
Na	0.014	0.006	0.025	0.010	0.005	0.002	0.005	0.002	0.018	0.022	0.005	0.003
K	0.003	0.001	0.002	0.003	0.003	0.001	0.003	0.001	0.003	0.003	-	-

No. of rock sample/code of garnet type: I: first-generation garnet; a (nucleus): Zr-bearing melanite, b (core): melanite; II: second-generation garnet (rim); a: predominant (OH,F)-bearing titanian andradite, b: growth zone of (OH,F)-bearing Ti-poor aluminous andradite, c: growth zone of (OH,F)-poor Ti-rich andradite to melanite; ^{x} all Fe expressed as Fe_2O_3. Phlogopit stands for phlogopitite, and pegmatite stands for melilitolitic pegmatite.

found in the Osečná complex. The brown variety is typical of micromelilitolite and polzenite. Grains of garnet with a brown core and a yellow outer zone are characteristic of melilitolite (core:margin 1:3), melilitolitic pegmatite, phlogopitite and ijolite (core:margin up to 1:6). Yellow garnet lacking a brown core is found mainly in the phlogopitite and melilitolitic pegmatite. This distribution indicates that the growth of garnet proceeded in two stages: the brown garnet characterizes the products of incipient metasomatism, whereas the yellow variety develops in advanced stages of this process. The later yellow garnet commonly forms a simple overgrowth on a brown core in the zoned crystals, but replacement of the cores also is widespread; the brown garnet is locally reduced to anhedral relics enclosed within the yellow crystals.

The brown garnet of the first generation (I) forms isolated grains in polzenite, a subhedral core of garnet replacing melilite or clinopyroxene in micromelilitolite and polzenite, and an anhedral core of garnet grains lining miarolitic cavities in melilitolite and melilitolitic pegmatite (Fig. 3). Compositionally, the brown garnet (I) corresponds to melanite with 9.0–12.7 (average 10.4) wt.% TiO_2. The content of Zr also is high, but its distribution is irregular. Dark brown spots (Ia) in the central parts of brown garnet from melilitolite and melilitolitic pegmatite samples contain 1.1–9.1 (average 3.2) wt.% ZrO_2, but the remainder of this garnet (Ib) has only 0.3–0.5 (average 0.4) wt.% ZrO_2. In other types of rocks, the ZrO_2 content of garnet is generally low: 0.1–0.3 wt.% in phlogopitite and 0.1–0.7 wt.% in ijolite. Typical compositions of the brown garnet (Ia, b) are shown in Table 1.

The yellow garnet of the second generation (II) replaces the brown cores (I) or forms zonal overgrowths on them, and it also constitutes subhedral to euhedral crystals in cavities (Fig. 3d). The yellow garnet is commonly heterogeneous, consisting of three varieties alternating in oscillatory zonal arrangement:

type IIa (predominant): distinct pale yellow zones of titanian andradite are (OH,F)-bearing, with 3.7–4.2 (average 4.0) wt.% TiO_2, 3.0–4.7 (average 4.0) wt.% Al_2O_3, 0.1–0.2 wt.% ZrO_2, 0.1–0.5 wt.% F and 1.2–1.3 wt.% H_2O (Table 2, IIa); type IIb (poorly defined): nearly colorless zones of (OH,F)-bearing, Ti-poor aluminous andradite contain only 1.5–2.1 (average 1.8) wt.% TiO_2, but the Al_2O_3 content is as high as 4.1–6.5 (average 5.9) wt.% (Table 2, IIb); type IIc: yellow–brown zones of Ti-rich andradite to Ti-poor melanite have 4.8–6.8 (average 5.6) wt.% TiO_2, 0.2–0.3 wt.% ZrO_2, and no detectable (OH, F) (Table 2, IIc).

The presence of compositional zoning of garnet (II) was confirmed by linear electron-microprobe scans of Fe, Ti and Al, and the (OH, F) content of the titanian andradite was verified in samples from melilitolitic pegmatite (31, 2), in the density fraction 3.5–3.7 g/cm^3 by gravimetric determination (1.47–1.63 wt.% H_2O^+), and by the photometric method (0.11–0.16 wt.% F).

TABLE 2. REPRESENTATIVE COMPOSITIONS OF (OH,F)-GRANDITE GARNET

Rock type	melilitolite	pegmatoid			ijolite	phlogopitite	
No.	2/IIa	31/IIa	31/IIb	31/B	71/IIa	3/IIa	3/IIb
SiO_2 wt.%	34.26	33.52	33.09	34.70	33.31	34.50	34.61
TiO_2	2.10	3.70	1.40	2.55	5.59	4.18	2.12
ZrO_2	0.00	0.12	0.05	0.14	0.00	0.08	0.05
Al_2O_3	4.12	3.91	6.47	5.80	1.51	3.68	4.76
Cr_2O_3	0.03	0.02	0.00	-	0.01	0.02	0.00
Fe_2O_3	23.98	20.88	22.17	19.88	24.43	20.60	22.66
FeO	-	-	-	0.36	-	-	-
MnO	0.09	0.08	0.10	0.04	0.21	0.20	0.17
MgO	0.80	0.95	0.24	0.81	0.91	1.18	0.79
CaO	33.50	34.81	34.40	33.61	32.79	34.50	33.81
Na_2O	0.04	0.09	0.03	0.07	0.05	0.02	0.03
K_2O	0.01	0.03	0.00	0.05	0.02	0.00	0.01
F	0.09	0.38	0.47	0.11	0.12	0.09	0.16
H_2O+	-	-	-	1.47	-	-	-
Subtotal	99.02	98.49	98.42	99.59	98.95	99.05	99.17
F≡O	-0.04	-0.16	-0.20	-0.05	-0.05	-0.04	-0.07
corr. total	98.98	98.33	98.22	99.54	98.90	99.01	99.10
H_2O calc.	1.02	1.67	1.78	-	1.10	0.99	0.90
Number of ions							
			Tetrahedral sites				
Si	2.800	2.713	2.669	2.799	2.784	2.807	2.820
OH/4	0.139	0.225	0.239	0.198	0.151	0.134	0.122
F/4	0.006	0.024	0.030	0.007	0.008	0.006	0.010
Al	0.055	0.038	0.062	-	0.093	0.053	0.048
	3.000	3.000	3.000	3.004	3.000	3.000	3.000
			Octahedral sites				
Al	0.342	0.335	0.553	0.551	0.053	0.300	0.409
Cr	0.002	0.001	-	-	0.001	0.001	-
Ti	0.129	0.225	0.084	0.155	0.346	0.256	0.130
Zr	-	0.005	0.002	0.006	-	0.003	0.002
Fe^{3+}	1.475	1.271	1.345	1.206	1.512	1.261	1.398
Mg	0.052	0.115	0.016	0.082	0.088	0.143	0.070
Ca	-	0.048	-	-	-	0.036	-
	2.000	2.000	2.000	2.000	2.000	2.000	2.000
			Dodecahedral sites				
Mg	0.045	-	0.013	0.015	0.024	-	0.026
Fe^{2+}	-	-	-	0.024	-	-	-
Mn	0.006	0.005	0.007	0.003	0.015	0.014	0.012
Ca	2.934	2.970	2.972	2.904	2.890	2.971	2.951
Na	0.006	0.014	0.005	0.011	0.008	0.003	0.005
K	0.001	0.003	0.000	0.005	0.002	0.000	0.001
	2.992	2.992	2.997	2.962	2.939	2.988	2.995
F	0.023	0.097	0.120	0.028	0.031	0.023	0.041
OH	0.556	0.901	0.957	0.791	0.604	0.537	0.489
O	11.421	11.001	10.923	11.181	11.365	11.440	11.470
	12.000	11.999	12.000	12.000	12.000	12.000	12.000

For explanations, see Table 1.

TABLE 3. CONCENTRATION OF REE AND OTHER TRACE ELEMENTS IN (OH,F)-BEARING TITANIAN ANDRADITE*

La	Ce	Sm	Eu	Tb	Yb	Lu	Co	Ni	Zn
45	86	8.7	3.0	1.2	2.2	0.15	6	17	126
Sc	**Zr**	**Hf**	**Th**	**U**	**V§**	**Ta**	**As**	**Cr**	**W**
48	1410	20	2.6	2.8	380	4	10	21	2

Analyst: V Moučka, INAA; §K. Absolon, OES. All data are reported in ppm. * Sample number 31.

In general, the compositions of the brown garnet I and of the zonal components of the yellow garnet (II) are rather uniform in all rock types. The only significant exceptions are shown by the garnet in polzenite, which is consistently enriched in Al (4.2–6.8 wt.% Al_2O_3) and by the yellow garnet (II) from melilitolitic pegmatite and phlogopitite, which shows somewhat elevated contents of (OH, F).

The *REE* contents of the (OH,F)-bearing titanian andradite (sample 31) are given in Table 3, together with the concentrations of some other minor elements. The chondrite-normalized pattern of the *REE* in this sample of andradite is shown in Figure 5, compared to those of perovskite, apatite and phlogopite from the same sample, and of monticellite from sample 1. The andradite is enriched in the *LREE*, in contrast to the usual *HREE* enrichment in this mineral (*e.g.*, Schnetzler & Philpotts 1970, Flohr & Ross 1989).

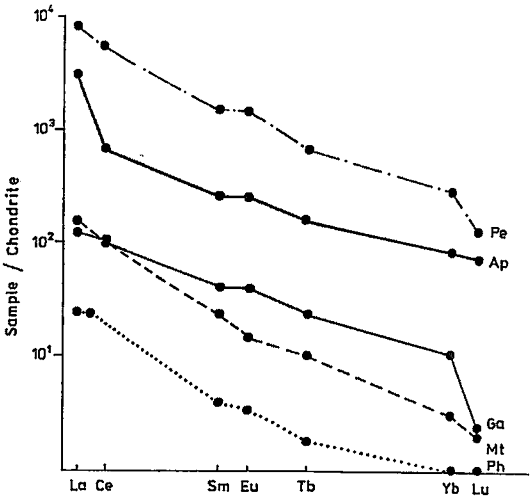

FIG. 5. Chondrite-normalized abundances of the *REE* for (OH,F)-bearing titanian andradite (Ga), perovskite (Pe), apatite (Ap), phlogopite (Ph) from a melilitolitic pegmatite at Osečná (sample 31) and monticellite from micromelilitolite, Ocasov near Osečná (sample 1).

This may be a consequence of the metasomatic origin of this garnet, affected by the composition of postmagmatic fluids concentrating the *LREE* preferentially, rather than crystal–melt partitioning. The elevated contents of other incompatible elements in this garnet also are remarkable, as are the high ratios of Zr/Hf (70), Nb/Ta (75) and the low value of Th/U (0.9).

Crystal chemistry

The calculation of structural formulas from analytical results obtained by the electron microprobe is complicated by two unknown quantities, Fe_2O_3 and H_2O. For (OH,F)-free garnet, the ratio of Fe^{3+} to Fe^{2+} was calculated by assuming ideal stoichiometry, *i.e.*, 8 cations per 12 atoms of oxygen. The method of Flohr & Ross (1989) was applied to the recalculation of the (OH,F)-bearing compositions.

Assignment of cations to individual structural sites in the garnet structure is complicated by the distribution of Fe^{3+}–Fe^{2+} and Ti^{4+}–Ti^{3+}, which can be directly determined only by specialized methods, and cannot be derived from the results of chemical analysis alone (Huggins *et al.* 1977a, b, Dingwell & Brearley 1985). The physical nature of the material examined was not suitable for systematic application of critical tests, and the calculation of formulas had to be constrained by several assumptions. The formulas given in Tables 1 and 2 are based on all Ti in the tetravalent state, all (OH, F) in tetrahedra, and the preferential entry of cations substituting for Si in the sequence Al > Fe^{3+} > Ti (as established by Huggins *et al.* 1977a, b).

The above treatment of the atomic contents indicates a highly variable but rather substantial incorporation of Al, and in part Fe^{3+}, into the tetrahedral site of the (OH,F)-free garnet (up to 6 and 16 atomic %, respectively, of the available positions; Table 1). In contrast, the population of Si-deficient tetrahedra of the hydrogarnet is accommodated by (OH,F) and Al (up to 7 and 3 atomic %, respectively); all Fe^{3+} must be assigned to the octahedral site (Table 2).

The anhydrous and (OH,F)-bearing garnets also show an apparently systematic difference in the calculated content of Fe^{2+}. The anhydrous compositions have a broadly fluctuating but substantial proportion of $^{VI}Fe^{2+}$, occasionally dominant over Fe^{3+}. Such fluctuations are caused by numerous relics of anhydrous garnet contaminating the separates of hydrogarnet.

The results of a Mössbauer study of sample 31 reveal yet another discrepancy, which is potentially more significant but which cannot be realistically assessed or experimentally verified. Deconvolution of the Mössbauer spectrum shows 8% (0.096 atoms per formula unit, apfu) of Fe^{3+} in the tetrahedral site, and the remaining 92% (1.116 apfu) in octahedral positions. However, recalculation of the analytical results suggests that the population of Si-deficient tetrahedra is accommodated by (OH,F) alone (Table 2, col. 31–B).

TABLE 4. SELECTED PHYSICAL PROPERTIES OF GARNET FROM THE OSEČNÁ COMPLEX

	Zr-bearing melanite n = 3	(OH,F)-bearing andradite n = 5
Color	dark brown	light yellow
birefringence	none	anomalous
density (g.cm^{-3})	3.76 - 3.81 (1)	3.51 - 3.69 (1)
index of refraction	1.916 - 1.939 (2)	1.861 - 1.884 (2)
unit cell *a* (Å)	12.075 - 12.109 (4)	12.040 - 12.057 (4)

In general, the preferred sequence of substitutions into the tetrahedral site used in our study suggests total exclusion of Ti and its restriction to the octahedral site. This is in conspicuous contrast to the role usually attributed to Ti in melanite. Huggins *et al.* (1977a, b) and Dingwell & Brearley (1985) found Ti to be the predominant substituent in tetrahedra, and the results of Gomes (1969) also support this conclusion.

Physical properties

Selected physical properties of the examined samples of garnet are listed in Table 4, as measured on concentrates purified to 96–99%.

Both generations of garnet show appreciable scatter of the index of refraction and density, which reflects the broad variation in their chemical composition. A weak anomalous birefingence (<0.003) is typical of the pale yellow outer zones of the (OH,F)-bearing titanian andradite (generation II).

Unit-cell edges of the individual types of garnet are consistent with the data on zoned garnet spanning the range of schorlomite – melanite – fluorohydrograndite – Ti-poor melanite, as published by Flohr & Ross (1989). The relatively large unit-cell dimension of the Zr-bearing melanite (up to 12.109 Å) probably results from the substantial content of Zr (Milton *et al.* 1961, Borodin & Bykova 1961), or from that of (OH, F) (Flohr & Ross 1989), or from the combined effects of both components.

Discussion

The role of garnet in the Osečná complex

The textural and paragenetic relationships of garnet in the melilite-rich rocks of the Osečná complex indicate that this mineral is a late phase, formed by metasomatic replacement of the assemblage of igneous minerals. Garnet is closely associated with late phlogopite, and also is accompanied by perovskite, titanian magnetite, apatite, calzirtite, carbonates, zeolites, pectolite and other phases. The replacement was promoted by a postmagmatic fluid phase bearing K, Ca, Al, Fe^{3+} and Ti, as well as Sr, Ba, the *REE*, Th, U, Zr, Hf, Nb, Ta, P and F among others.

The garnet replaced mainly melilite, penetrating along its cleavages. Monticellite is rarely attacked, but symplectites of garnet + secondary phlogopite II seem to replace locally late magmatic phlogopite I. In advanced stages of replacement, granular clusters of garnet do not show textural evidence of a metasomatic origin; the process is indicated only by widespread clouding and incipient decomposition of primary minerals close to the metasomatic aggregates.

The composition of garnet has evolved during the progress of replacement. In early stages, anhydrous Zr-enriched melanite formed, dispersed in the magmatic substrate. The late-stage garnet, particularly abundant in the metasomatic melilitolitic pegmatite, phlogopitite and ijolite, shows oscillatory zoning of compositions that are generally poorer in Zr and Ti, enriched in Al and (OH, F), and more oxidized.

Comparison with related occurrences

The Zr-bearing melanite from Osečná can be added as number eight to the list of occurrences of zirconium-rich garnet (Platt & Mitchell 1979). Rare as its localities are, most of them show close similarities, particularly when the full compositional range of garnet is considered. Zoning of the garnet at Osečná is not as extensive as that in the melilitic rocks of Maimecha–Kotui province (Egorov 1969: schorlomite – melanite – andradite – grossular) or in the metasomatized ijolitic rocks from Magnet Cove (Flohr & Ross 1989: schorlomite – melanite – fluorohydrograndite – Ti-poor melanite), but it is rather close in its physical and compositional character. More significantly, the restricted trend of compositional evolution at Osečná is closely comparable to that established for garnet from related occurrences, such as the lamprophyric Marathon Dikes of Ontario (Platt & Mitchell 1979). The garnet-bearing mineral assemblages also show remarkable similarities. The Osečná phlogopitites and ijolites match the products of the second and third stages of metasomatism in the alkaline rocks of the Maimecha–Kotui and Karelia–Kola provinces, as described by Borodin & Pavlenko (1974).

Compositional analogies also are evident with garnet from other but genetically related environments. The early garnet (I) at Osečná shows distinct similarities to the Zr-bearing schorlomite described by Borodin & Bykova (1961) from carbonatitic rocks of the Vuorijärvi complex, and particularly of the Guli complex, in the Maimecha–Kotui province of Russia (Egorov 1969).

Conditions of garnet evolution

Platt & Mitchell (1979) concluded that crystallization of zirconian garnet generally proceeds under subvolcanic postmagmatic conditions at low a(Si), increasing $f(O_2)$, and rising participation of H_2O and F. These conditions are in agreement with precipitation of phlogopite, apatite, and fluorite, and with the appearance of late fluorohydrograndite.

Crystallization of the early garnet (I), Zr-bearing melanite, requires a low a(Si) and $f(O_2)$. Nash & Wilkinson (1970) found such a garnet composition coexisting with perovskite and aegirine-poor clinopyroxene in the Shonkin Sag laccolith. However, progression to the (OH,F)-bearing titanian andradite of the second generation necessitates an increase in the above parameters. The increased Fe^{3+}/Fe^{2+} ratio corresponds to such a change, and also to the experimental results of Huckenholz *et al.* (1976). However, it must be noted that the above trends in conditions and the resulting compositions of garnet, fitting the observations at Maimecha–Kotui, Magnet Cove and Osečná, are apparently reversed in the nephelinic lamprophyres of the Gardiner complex (Hansen 1980).

In general, the mineral assemblages carrying Zr-bearing melanite are associated with carbonatites and carbonated ultramafic rocks (Platt & Mitchell 1979). This environment also is characterized by Mn-enriched members of the spinel group. At Osečná, Mn is not particularly enriched in magnetite (0.09–1.14 wt.% MnO), but it is enriched in sporadic ilmenite (5.63 wt.%: Ulrych *et al.* 1986). The presence of primary magmatic carbonate with isotopic values typical of a mantle derivation ($\delta^{13}C$ of –3.9 to –7.4‰: Pivec *et al.* 1991) provides a further argument in support of a carbonatite connection, as do the primitive Zr/Hf and Nb/Ta values in the garnet. Thus the occurrence of the Zr-bearing melanite strengthens the evidence collected to date that links the Osečná complex to mantle-derived, carbonated alkaline ultramafic rocks (Ulrych *et al.* 1988a), and suggests the presence of hidden carbonatites (Strnad 1965, Kopecký 1978, 1988), as documented by Kresten & Morogan (1986) in the Fen region.

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