Spinel accessories in ultramafic and mafic rocks from Gega ophiolite mélange in Ograzhden Mountain, Southwestern Bulgaria

Акцесорни шпинели в ултрамафични и мафични скали от Гегенския офиолитов меланж в Огражден планина, Югозападна България

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Spinels are often used as reliable “petrogenetic indicators” because they crystallize at a wide range of conditions present in mafic and ultramafic magmas, and often they are among the first phases to crystallize.

Relicts of accessory spinels from spinel ($MgAl_2O_4$) – hercynite ($FeAl_2O_4$) series are observed in the mafic and ultramafic rocks belonging to the Gega mélange body (GMB), cropping out near the Western border of Bulgaria at the village of Gega in the southern part of Ograzhden Mountain (Zidarov, Nenova, 1995).

The aim of this communication is to present newly acquired data about the chemical composition of these spinels and to discuss is significance for reconstructing the petrogenesis of the their mother rocks.

Geological setting

Blocks of unaltered or amphibolitized to various degrees mafic and ultramafic rocks are included in the cores of the amphibolitic boudines constituting a tectonically reworked metabazite body (GMB) cropping out on an area of 0.7 km^2. They are pyroxene megacrysts – bearing spinel pyroxenites together with coarse grained olivine gabbro-norites, intercepted by aphyric gabbro-norite dykes, coarse to medium grained leucocratic pyroxene gabbro, serpentinized peridotites and/or harzburgites. They form a fragment of a boudinated ophiolitic complex preserved in the axial part of recumbent fold of two-mica gneisses with ± kyanite and garnet. The magmatic protoliths are cumulates of toleitic magma with MORB affinity formed at T ^oC = 1260–960, P_{kbar} = 10–18 at 1004 ± 67 Ma (Rb-Sr analyses) (Zidarov, Nenova, 1995; 1996).

Mineralogical data

The relicts of accessory spinels are established in the spinel pyroxenites with the clinopyroxen megacrysts (clynopyroxenites and websterites), in the olivine gabbro-norites and in the aphyric gabbro-noritic dykes.

The spinels are green and their individuals (up to 0.5 mm) have irregular to crescent form or V-shaped outlines. In the clinopyroxenites they are located in and around orthopyroxene grains or intergrow simplectitely with exolved orthopyroxene together with magnetite. The associated minerals are:

- in clinopyroxenites – clinopyroxene, enstatite, chromite, ilmenite, magnetite ± plagioclase ± olivine;
- in olivine gabbro-norites – olivine, clinopyroxene, enstatite, plagioclase, ilmenite, magnetite;
- in gabbro-norites – diopside, enstatite, plagioclase, ilmenite, magnetite.

Microprobe analyses of spinels (Philips SEM 515 with WEDAX – 3A, 5–10 nA, 15–18 kV) are performed on clinopyroxenites (5 samples), olivine gabbro-norites (10 samples) and gabbro-norites (7 samples). The empirical formulae, in which Fe_{tot}, is subdivided to Fe^{2+} and Fe^{3+} by the method of Nenova (1997) are calculated and the following ratios are obtained:

- clinopyroxenites:

$(Fe^{2+}_{4.93\text{-}6.11}Mg_{2.77\text{-}3.55}Na_{0\text{-}0.48}Ca_{0\text{-}0.18}Mn_{0\text{-}0.2}Zn_{0\text{-}0.21})_{7.7\text{-}10.55}$ $(V_{0\text{-}0.03}Ti_{0\text{-}0.3}Fe^{3+}_{0\text{-}0.1}Cr_{0.06\text{-}0.43}Al_{13.97\text{-}15.32}Si_{0\text{-}0.7})_{14.03\text{-}16.52}O_{32}$; $Fe^{2+}/(Mg+Fe^{2+})$ = 0.59–0.69; Cr/(Cr+Al) = 0.004–0.03; Mg*100/(Mg+Al) = 31.19–41.26.

- olivine gabbro-norites:

$(Mg_{4.17\text{-}5.02}Fe^{2+}_{3.51\text{-}4.24}Ca_{0\text{-}0.06}Mn_{0\text{-}0.2}Zn_{0\text{-}0.26})_{7.68\text{-}9.64}$ $(Fe^{3+}_{0\text{-}0.03}Cr_{0\text{-}0.4}Al_{14.93\text{-}15.64}Si_{0\text{-}0.28})_{14.93\text{-}16.36}O_{32}$; $Fe^{2+}/(Mg+Fe^{2+})$ = 0.43–0.51; Cr/(Cr+Al) = 0–0.026; Mg* 100/(Mg+Al) = 49.47–57.50.

- gabbro-norites:

$(Fe^{2+}_{4.08\text{-}6.11}Mg_{2.39\text{-}4.04}Na_{0\text{-}0.14}Mn_{0\text{-}0.06}Zn_{0\text{-}0.05})_{6.47\text{–}10.04}$ $(V_{0\text{-}0.14}Ti_{0\text{-}0.55}Fe^{3+}_{0\text{-}0.02}Cr_{0.03\text{-}0.25}Al_{14.26\text{-}15.91}Si_{0\text{-}0.23})_{14.29\text{-}17.10}O_{32}$; $Fe^{2+}/(Mg+Fe^{2+})$ = 0.46–0.71; Cr/(Cr+Al) = 0.0019–0.016; Mg*100/(Mg+Al) = 28.60–49.50.

The minor elements in the investigated spinels are Zn, Mn, Ca, Na, V, Si.

Discussion

The compositions of the spinels are indicative for the conditions of their crystallization, tectonic environment and the origin of the magmas, which formed the rock association in GMB. Most important in this respect are the ratios $Fe^{2+}/(Mg+Fe^{2+})$, $Cr/(Cr+Al)$, $Mg*100/(Mg+Al)$, and Al partitioning between olivine and spinel.

The increasing Fe^{3+} and $Fe^{2+}/(Mg+Fe^{2+})$ ratio can be attributed to the evolution of spinel compositions during fractional crystallization of olivine or pyroxene from the host magma. This increases the Fe/Mg ratio of the melt. Presumptively, in our case, this is emphasized by the reaction between spinels in orthocumulate rocks and evolving trapped intercumulus magma. The variation in $Fe^{2+}/(Mg+Fe^{2+})$ ratio, has two ways: evolving melt composition during crystallization, and the Fe^{2+}/Mg exchange between in the spinels and coexisting silicates (usually olivine), which favours increasing $Fe^{2+}/(Mg+Fe^{2+})$ ratio in the spinels with falling environmental temperature. This effect (Barnes, Roeder, 2001) is most highlighted in slowly cooled rocks (like megacrystic spinel pyroxenites of GMB).

Mg-Al compositions are characteristic for high pressure conditions, where spinel compositions are being controlled by Al exchange with coexisting pyroxenes. The low $Cr/(Cr+Al)$ ratio might result from clinopyroxene-spinel subsolidus equilibration where a significant amount of Al is exolved from clinopyroxene in order to form aluminous spinel (Barnes, Roeder, 2001).

It can be assumed that spinels in olivine gabbronorite correspond to spinels in equilibrium with olivine of constant composition at constant temperature ~ 1353 °C. This value is calculated using the olivine-spinel geothermometer based on Al partitioning between olivine and spinel (Wan et al., 2008).

The principal constituents in spinels behave very differently during fractional crystallization or partial melting, with Cr and Mg strongly partitioned into the solid, and Al strongly partitioned into the melt. Partitioning of Mg and Fe^{2+} between spinel and silicate melts and minerals is strongly dependent on temperature and the ratio of Fe^{2+}/Fe^{3+} is sensitive to variations in fO_2 (Dick, Bullen, 1984).

The grain to grain variation of spinel's composition is most likely caused by reequilibration with adjacent silicates during cooling process (Jan et al., 1992).

The investigated spinels from GMB fall in the category of plutonic ultramafic and some mafic cumulate rocks of oceanic affinity, following classification scheme for spinel composition in mafic and ultramafic rocks (Barns, Roeder, 2001) This category includes tectonically emplaced high-pressure and high-temperature "Alpine" ultramafic bodies of probably ophiolitic affinities in orogenic belts. For these rocks the triangle Fe^{3+}–Cr–Al diagram points to the Al-rich spinels of high-pressure spinel lherzolite bodies, which are characterized by lower values of $Fe^{2+}/(Mg+Fe^{2+})$ ratio, reflecting the high-temperature of equilibration with olivine. For GMB pyroxenites, olivine gabbronorites and gabbro-norites this ratio is between 0.042 and 0.72 and the $Fe^{3+}/(Fe^{3+} + Cr+Al)$ ratio is between 0.005 and 0.002.

Conclusion

The newly acquired data for the chemical composition of these spinels confirm our formerly expressed opinion (Zidarov, Nenova, 1995) based on petrochemistry and petrography of the rocks, that GMB represents tectonically dismembered ophiolite body formed under high pressure – high temperature conditions of the Upper Mantle.

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