

# New data on the magmatism and the magmatic fluids of the Kožuf volcanic massif, Macedonia

## Нови данни за магматизма и магматичните флуиди на вулканскиот масив Кожуф, Македонија

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### Geology

The Kožuf volcanic massif is disposed in the frame of the Vardar zone. The volcanic and volcano-sedimentary rocks from the “complex of Pliocene sediments and pyroclasts” overlay the metamorphic (Precambrian and Paleozoic) and sedimentary (Triassic to Upper Eocene) rocks of the region (Jankovic et al. 1997; Boev & Jelenkovic, 2012). The Pliocene volcanic and volcano-sedimentary rocks occur as layers in a lacustrine basin and subvolcanic bodies crosscutting the older rocks (Triassic carbonates; Percival, Radke, 1994; Boev & Jelenkovic, 2012). The Pliocene volcanism is strongly explosive and predominating volcanic rocks are volcanoclastic (pyroclastic tuffs and breccias and epiclastic conglomerates). The radiogenic age (K-Ar method) determinations of the volcanic rocks are between 6.5 and 1.8 Ma (Boev et al., 1992). Volcanic rocks are represented by shoshonites, latites, quartz latites, dacites, trachytes, and rhyolites. Latites, and trachytes are the most widespread volcanic rocks. Subvolcanic rocks are represented by latites and dacites (Percival, Radke, 1994), trachytes (Boev & Jelenkovic, 2012) and porphyritic monzonites. They are small isometric outcrops supposed to be remnants of the magma conducting channels for the volcanism. The monzonite porphyrites outcrop southeastern of the Alshar deposit with diameter of the magmatic body about 50-70 m. The Alshar Au-As-Sb-Tl-Hg deposit is mainly hosted in Triassic carbonate rocks but the hydrothermal fluids have altered and ore contaminated the Pliocene subvolcanic and volcanoclastic rocks. Percival and Radke (1994) suppose a genetic link of the Au-As-Sb-Tl-Hg mineralization with a hypothetical shallow disposed intrusion.

### Petrography and geochemistry

All the studied volcanic and subvolcanic rocks are porphyritic with phenocrysts of plagioclase, clinopyroxene, amphibole, biotites, sanidine. Pyroclastic rock clasts have massive or vesicular structure. In volcanic rocks amphiboles and biotites are often opacitized and amphiboles are altered in most of the cases. The mineral composition is based on 88 microprobe analyses (41 this study). Pyroxene quantity decreases toward the more acidic rocks (absent in rhyolites) and is represented by diopside to augites ( $Mg\# = 0.9-0.76$ ). Sanidine ( $Or_{57.5-38}$ ,  $Ab_{36-59}$ ,  $An_{6.6-3.8}$ ) is lacking in shoshonites and increases in quantity toward trachytes. Biotites are often red-brown ( $Mg\# = 0.6-0.56$ ). The groundmass in most of the cases is recrystallized, but hyalopilitic and trachytic texture are also established. Accessory minerals are apatite, titanomagnetite and rare ilmenite and rounded zircons. The established porphyritic monzonite has phenocrysts of plagioclase ( $An_{36.6-42.3}$ ,  $Or_{2.5-8}$ ), clinopyroxene ( $Mg\# = 0.68-0.67$ ) and biotite ( $Mg\# = 0.68-0.71$ , plotting at the border line between biotites and flogopites). The groundmass is holocrystalline, hypidiomorphic, composed of, euhedral plagioclases, anhedral alkali feldspars ( $Or_{57.5}$ ,  $Ab_{36-38}$ ,  $An_{6-4}$ ) and rare isometric clinopyroxenes.

The major part of the analyses from the Kožuf volcanic area plot in the silica saturated fields (shoshonites, latites, trachytes; Le Maitre, 1989) and belong to the high-K series. Only dacites belong to the calc-alkaline rocks (low-K series). On major element Harker diagrams are established general trends of K<sub>2</sub>O, CaO, MgO, FeO, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> decreasing with silica increasing.

The chondrite normalized REE patterns show enrichment of LREE relative to HREE and in most of the cases relatively well pronounced negative Eu anomaly. All the Primordial Mantle normalized spidergrams show negative anomalies for Ta, Nb, and Ti characteristic for synsubductional magmatism (Boev, Yanev, 2001; Yanev et al., 2008).

The rock diversity could be partly ascribed to the fractionation of clinopyroxene, amphibole, biotite, magnetite, plagioclase and apatite. Some peculiarity of the zonal arrangement of the plagioclase let us suppose the possible influence of magmatic mixing to the magmatic rock diversity. The role of the contamination is suggested by Yanev et al., (2008). The pressure of crystallization of amphiboles (after the geobarometer of Johnson, Rutherford, 1979) is about 7 kbars. The estimated temperature of apatite saturation and the apatite-biotite equilibrium (Harrison, Watson, 1984; Sallet, 2000) are about 950 °C. Oxygen fugacity is estimated to 2.8 units above the QFM buffer (Spenser, Lindsley, 1981)

### Fluids in magma

The presence of fluid containing minerals even in the most basic volcanic rocks is an indication of the high fluid concentration in the magma. The estimation of the water content in the magma is based on the geohydrometer of Merzbaher and Eggler (1984). In latites and dacites the water content is determined to be about 6–7 wt. %. In subvolcanic monzonite porphyrites are established primary (magmatic) rounded sulfide inclusions (pyrrhotite and bornite) in clinopyroxenes with dimensions 10–30 microns. The chemical composition of pyrrhotite gave us the opportunity to have an estimation of the fugacity of S (after Toulmin, Barton, 1964;  $\lg f_{S_2} = 1.4$ ). Based on the chemical composition of apatite the estimated preeruptive content of Cl is 0.02 to 0.7 wt. % and the F content is about 0.15 to 0.39 wt. % (after Matez, Webster, 1994).

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