Major and trace element compositions of clinopyroxenes from Zvezdel palaeovolcano (Eastern Rhodope): petrogenetic implications

Главни елементи и елементи-следи в клинопироксените от Звезделския палеовулкан (Източни Родопи): петрогенетични изводи

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Introduction

Clinopyroxene is a major mafic rock-forming mineral, which is present in all volcanic varieties of Zvezdel palaeovolcano. The mineral is one of the major carriers of incompatible trace elements, which can be easily and precisely measured by LA-ICP-MS. Therefore, a careful study of the compositional variations within strongly zoned clinopyroxene can provide valuable information about the parental magma and complicated processes in the magma chambers. Here we present an extensive data set of major and trace element contents of clinopyroxene phenocrysts of Zvezdel lavas.

Geological setting and petrography of Zvezdel lavas

The Zvezdel palaeovolcano is located in the Eastern Rhodope volcanic area which represents a part of the Macedonian-Rhodope-North Aegean volcanic zone (Harkovska et al., 1989). The volcanic structure is composed of lava flows intercalated with epiclastictic and rare pyroclastic rocks, and cut by domes and dykes. The central part of the volcano is intruded by a co-magmatic differentiated intrusive body of monzogabbro, monzonite, quartzmonzonite and granite-aplite rocks (Nedialkov, 1986).

The Zvezdel volcanic rocks are predominantly high-K calc-alkaline with subordinate calk-alkaline and shoshonitic varieties ranging in composition from basalts to andesites and dacites (Nedialkov, Pe-Piper, 1998; Raicheva, Marchev, 2006; Raicheva et al., 2007). Trace element spiderdiagrams show typical patterns of orogenic rocks with negative anomalies of Nb and Ta and positive Rb and Th anomalies. Two evolutionary series (Upper and Lower) have been determined on the basis of their stratigraphic position, and the mineral and chemical compositions of the lavas (Raicheva et al., 2007).

Plagioclase and clinopyroxene phenocrysts are typical for all lava types. Olivine was found in the basalts, basaltic andesites and some andesites. Amphibole and biotite are represented in the most evolved lavas. Accessory mineral are oxides, apatite and sulphides. Zircon is present in the most evolved lavas.

The volcanic rocks from Zvezdel volcano show evidence of magma mingling and mixing, which include magmatic inclusions in andesites, banded lavas and disequilibrium phenocryst associations (Nedyalkov, 1986; Nedialkov, Pe-Piper, 1998; Raicheva, Marchev, 2006). Petrographically the magma mixing events are recognized by the appearance in the same sample of clear normally zoned and sieved textured reversely zoned plagioclases; normally and reversely zoned clinopyroxenes with differing core compositions; resorbed orthopyroxenes with high-Mg clinopyroxene mantles; plagioclase and clinopyroxene microlites with unusually high An and Mg# content respectively.

Analytical methods

Major elements of clinopyroxenes were determined using a JEOL 870 SUPERPROBE at the University of Florence. Trace elements of clinopyroxenes were determined at ETH Zurich, Switzerland and Geological Institute of BAS (Sofia, Bulgaria). LA-ICP-MS analyses of minerals in ETH were determined using an ArF excimer UV (193 nm) laser source coupled with an ELAN 6100 ICP quadrupole mass spectrometer. The system at GI consists of a 193 nm ArF excimer laser source (ATLEX-SI) coupled with a quadrupole ICP mass spectrometer ELAN DRC-e.

Clinopyroxene composition

Clinopyroxene phenocrysts are roughly classified into two major types: high-Mg (type 1) and low Mg (type 2). Type 1 phenocrysts are usually normally zoned or slightly reversely zoned in terms of Mg# zoning from core to rim. Mg-values of the cores are in the range 77.1–85.2 ($Wo_{40.0–45.1}$ $En_{39.4–46.1}$). Sometimes the outer rims are similar to cores of type 2. Type 2 cores have Mg# 77–68 ($Wo_{37.9–43.6}$ $En_{39.4–46.1}$). Their zonation could be normal, reverse and complex in the different lava flows. The composition of the rims often reaches type 1 cores. The most Fe-rich (type 2a) clinopyroxene cores are resorbed with Mg# 63.3–66.4 ($Wo_{35.7–39.7}$ $En_{38.9–41.4}$). They are usually reversely zoned with abrupt increase of Mg# in the outer rims (up to 85). Type 2a clinopyroxenes are found in the Upper series only.

Compared to type 2, type 1 clinopyroxenes have lower concentration of incompatible trace and rare earth elements and higher Cr and Sr, which are compatible in clinopyroxene and plagioclase respectively. All clinopyroxenes display a concave-down REE pattern, with the middle REEs slightly enriched over both LREE and HREE. The Eu/Eu* of type 1 is 0.60–1.09 and much deeper in type 2 (0.24–0.59). Primitive mantle normalized trace element patterns of clinopyroxene display negative Ba, Nb, Sr, Zr and Ti troughs and positive peaks of Th, La–Ce, Pr, Nd and Sm. The low Mg outer rims of the type 1 clinopyroxenes are enriched in trace elements, while Mg rich outer rims of type 2 clinopyroxenes have lower contents of trace elements, suggestive of derivation from more evolved and more basic magmas respectively.

Discussion and conclusions

Clinopyroxene – melt equilibria, using Fe-Mg exchange between core composition and whole rock analyses, indicate that type 1 clinopyroxenes are in equilibrium with basalt to basaltic andesite melts. Their more primitive nature is reflected in the higher contents of Cr and Sr and lower concentrations in incompatible trace elements. Type 2 clinopyroxenes are in equilibrium with basaltic andesites to andesites. The most Fe rich clinopyroxenes (type 2a) require low-Mg# liquids which are more evolved than any erupted magma composition. In accordance with major elements type 2 and 2a clinopyroxenes are enriched in incompatible trace elements.

Parallel trends in the REE and primitive mantle normalized trace elements indicate crystallization from co-genetic magmas. The inverse correlation between negative Eu/Eu* and Mg# suggests an early crystallization of feldspar and increasing role of plagioclase fractionation. This proposition is confirmed by the positive correlation of Sr and Eu/Eu* in clinopyroxenes.

The results obtained for major and trace element composition confirm our previous conclusions about large operation of the process of magma mixing and fractional crystallization in the genesis of the Zvezdel lavas. Mixing and mingling in the Lower series was between basaltic to basaltic andesite and andesite magmas. It is supposed that mixing in the Upper series was a result of basaltic input in a low pressure magma mush composed of high-Fe clino- and orthopyroxenes and Na-rich plagioclase. The mush was formed after prolonged fractionation of pyroxene and plagioclase. This led to formation of high Fe clinopyroxenes (type 2a), mantled with abrupt high-Mg rims with lower concentration of incompatible trace elements.

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