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Review

Evolution of mariupolite (nepheline syenite) in the alkaline Oktiabrski Massif (Ukraine) as the host of potential Nb–Zr–REE mineralization

Magdalena Dumańska-Słowik

Department of Mineralogy, Petrography and Geochemistry, Faculty of Geology, Geophysics and Environmental Protection, AGH – University of Science and Technology, Kraków 30-059, 30 Mickiewicza Av., Poland

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ABSTRACT

Mariupolite, aegirine-albite nepheline syenite, outcropping only in the Oktiabrski massif in south-eastern Ukraine, is a potential resource of Nb, Zr and REE for future exploration and development. Some types of this rock can be also used in ceramics, glass and building industry and jewellery. Mariupolite is composed of (1) magmatic and (2) subsolidus and hydrothermal components. The magmatic assemblage includes zircon, aegirine, nepheline, albite, K-feldspar, pyrochlore, fluorapatite, fluorbritholite-(Ce) and magnetite. Alkaline-carbonate-chloride-rich fluids exsolved very early in the history of the rock, in a late stage of, or directly after, its consolidation, induced intensive high-temperature alteration of the primary mariupolite components resulted in formation of cancrinite, calcite, fluorite, REE-bearing minerals such as monazite, parasite-(Ce), bastnäsite-(Ce), as well as sodalite, natrolite and hematite. The genesis of this peculiar mineralization seems to be associated with multistage magmatic and tectonic activity of the Ukrainian Shield and fluids mediated metasomatic processes.

Contents

1. Introduction

Alkaline rocks occur rarely in nature. They usually contain significant amounts of rare metals such as Li, Be, Nb, Ta, Zr, Th, REE and volatile components, mainly F and Cl. Hence, they are the source of various rare minerals (Sørensen, 1992), and show high potential for deposits of industry-important metals (Goodenough et al., 2016). The Ukrainian Shield is a unique province of Proterozoic (1.8–2.1 Ga) alkaline magmatism and includes ca. 50 known massives and smaller occurrences of alkaline rocks, e.g. Chernigivka, Oktiabrski, Mala Tersa, Pokrovo–Kirievo, Kalchinski, Proskurovka, Antonivka and Yastrubetski, mostly of Proterozoic, rarely Palaeozoic (Devonian) in age (Krivdik, 2005; Krivdik et al., 2007; Ponomarenko et al., 2013). Only some of them are more than 1 km^2 in area (Fig. 1). The alkaline rocks from the eastern province of the Ukrainian Shield exhibit different geochemical signatures (higher contents of incompatible rare elements such as Nb, Zr, REE) than the rocks from the western part, probably because of different geodynamic conditions. The

E-mail address: dumanska@uci.agh.edu.pl.

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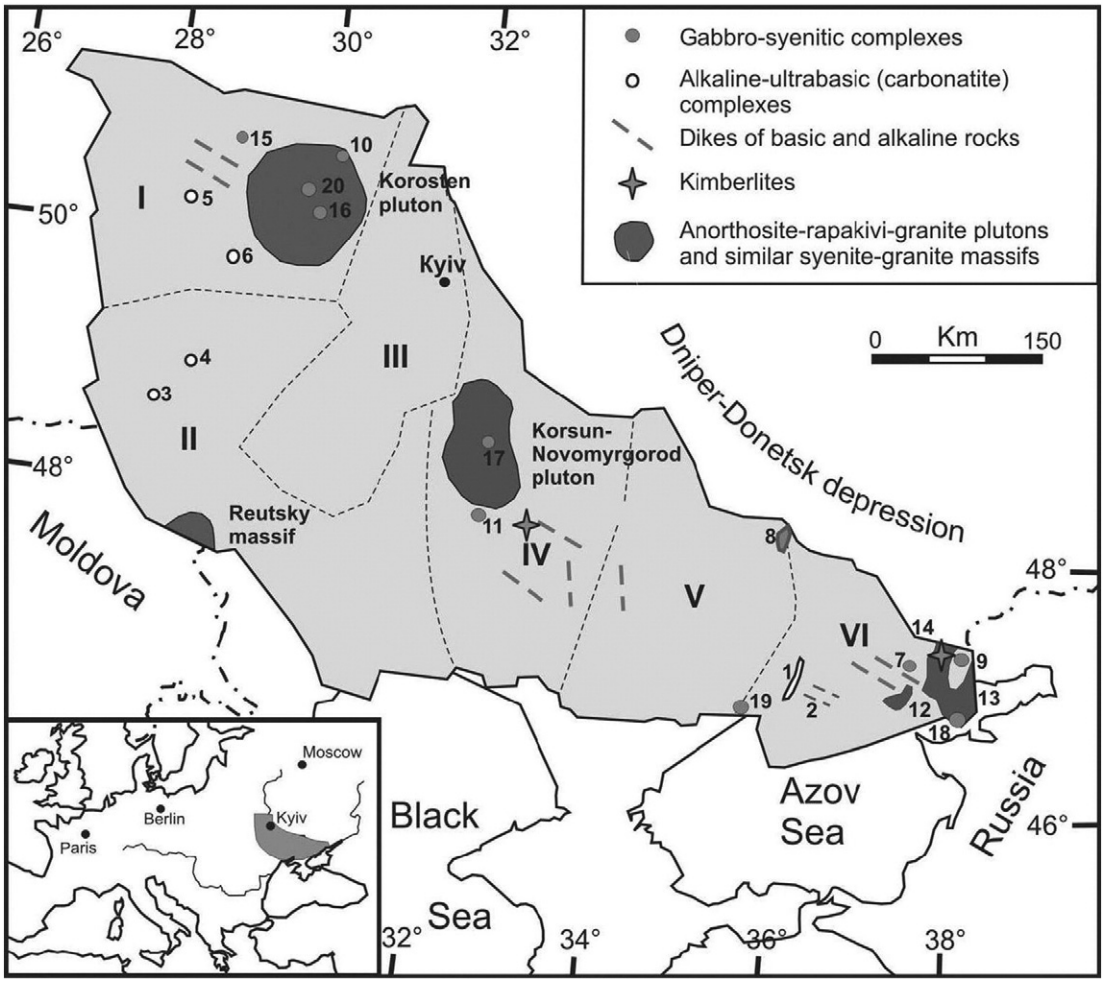

Fig. 1. Sketch map of the Ukrainian Shield with alkaline rocks occurrences (Ponomarenko et al., 2013).

rocks of the eastern part formed during the rifting, whereas the western ones are linked to compressional settings, i.e. subduction and collision (Krivdik, 2005; Ponomarenko et al., 2013).

Mariupolite is a variety of nepheline-syenite, a silica-undersaturated rock, named by Morozewicz (1902, 1929) and taking its name from Mariupol, Sea of Azov, in Ukraine. It outcrops only in the Oktiabrski Massif, which is situated in the eastern province (Azov) of the Ukrainian Shield in south-eastern Ukraine. Mariupolite is a miaskitic nepheline syenite, though melanocratic varieties of mariupolites have an agpaitic index up to 1.5 owing to the presence of aegirine (Krivdik and Tkachuk, 1998; Sharygin et al., 2009). Albite, nepheline and aegirine are the main components, whereas zircon, pyrochlore, sodalite, natrolite, cancrinite, K-feldspar, annite, fluorbritholite-(Ce), fluorapatite, fluorite, calcite, parasite-(Ce), bastnäsite-(Ce), magnetite, hematite make up the accessory phases. Generally, the main mineral composition of mariupolite is constant; however, among these rocks many types can be distinguished, which differ in composition of accessory phases and show unique and variable texture features. Morozewicz (1929) identified such types of mariupolite as: leucocratic, melanocratic, fine-grained, porphyritic, zircon-bearing gneiss-like, sodalite-cancrinite with britholite schlieren, coarse-grained, pegmatitic-like and many others.

Mariupolite is a potential source of Nb, Ta, Zr and REE since it hosts sometimes abundant zircon, pyrochlore-group minerals, monazite-(Ce), fluorapatite, fluorbritholite-(Ce) and REE-bearing carbonates [parasite-(Ce), bastnäsite-(Ce)]. In the last century Nb and Zr were economically recovered from the alkaline rocks of the Oktiabrski massif (Volkova, 2001). Mariupolites are also rich in volatile components such as Cl and F, which were trapped by sodalite, fluorapatite, fluorbritholite-(Ce), fluorite and annite. Water-rich minerals of mariupolite are mainly represented by annite, cancrinite and natrolite.

This study presents the evolution of the mariupolite along with hosted mineralization based on new data and author's previous works (Dumańska-Słowik et al., 2011a, 2011b, 2012, 2014, 2015a, 2015b, 2015c) to interpret the chemical processes involved in the magmatic and post-magmatic evolution of alkaline melt in the Oktiabrski Massif. Understanding the role of fluid assisted remobilization processes in formation of these rocks is crucial since such fluids are capable of concentrating some rare elements like Zr, Nb, Ta, REE and Th to high abundances (vide Schönenberger et al., 2006). The compositions of the main mineral phases will be presented together with the distinction made between the primary rock components and a secondary assemblage resulting from subsolidus re-equilibration during mariupolite cooling. Based on the textural characteristics and mineral composition, the origin of the mariupolite is discussed. Finally, the possible paragenetic sequence of main and accessory components of mariupolites is presented.

2. Economic importance of alkaline rocks

The occurrences of alkaline rocks are mainly found in continental rift-related settings, rarely in oceanic islands in various parts of the world (Pirajno, 2015). Most of the intrusions have a quasi-circular shape with imperfect ring and block structure (e.g. Worley and Cooper, 1995; Fall et al., 2007; Korobeinikov et al., 2000; Volkova, 2000). They were formed during a period of intra-plate alkaline