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PETROGENESIS OF LAMPROPHYRES FROM THE DITRĂU ALKALINE MASSIF

Theses of PhD dissertation

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I. INTRODUCTION

The Ditrău Alkaline Massif [DAM] is situated in the S-SW part of the Giurgeu Alps belonging to the Eastern Carpathians (Romania). In the first part of the XX century the DAM was one of the best studied, and at the same time regarding its generation, the most controversial geological formation of Europe. During the last one and a half century the DAM has been studied by excellent geologists such as Ferenc Herbich, Alajos Fellner, Antal Koch, Gyula Szádeczky, Béla Mauritz, Miklós Vendl, Aladár Földvári, Gábor Pantó, Alexandru Codarcea, Emil Constantinescu, Gyula Jakab, Brian Upton, Godfrey Fitton, Albert Streckeisen and Elemér Pál-Molnár.

The DAM is the locus typicus of several magmatic rock types and rock names which have become generally accepted in national and international literature such as ditroite (sodalitic nepheline syenite), orotvite (alkali gabbro-alkali diorite), ditroessexite (alkali monzogabbro-alkali monzodiorite) (Pál-Molnár, 1994, 2008).

While several scientific studies concerning the mineralogy, petrology, structure, way and time of origin of the DAM, as well as economic potential of its rock and ores have been made, the lamprophyres intersecting the different rock types have slightly been discussed (Mauritz, 1912; Mauritz et al., 1925; Streckeisen, 1954; Anastasiu, Contantinescu, 1982).

Since the occurrence of lamprophyres can be studied the best at the northern part of the DAM, and the contacts of lamprophyres with the most rock type in natural outcrops can be found at this part as well, the Orotva Creek and its northern affluents (Tarnica, Tászok, Fülöp, Gudu, Török and Nagyág Creeks) have been chosen as the studied area.

The aim of my dissertation to summarize the petrography, mineralogy, geochemistry and petrogenesis of lamprophyres occurring in the northern part of the DAM, to determine the relationship between lamprophyres and the DAM, and to identify co-magmatic and co-genetic sequences regarding petrographical, mineralogical and geochemical results.

II. ANALYTICAL METHODS

The studied lamprophyres (85 thin sections of 55 samples) were collected from thirteen natural outcrops of Orotva, Tarnica, Tászok, Fülöp, Gudu, Török and Nagyág Creeks. The optical analyses were performed by Olympus SX-9 binocular microscope, Nikon Microphot FXA and Olympus BX-41 polarizing microscope at the Department of Mineralogy, Geochemistry and Petrology, University of Szeged.

Mineral compositions were determined by Cameca SX-50 electron microprobe under probe current of 15 nA and acceleration voltage of 20 kV operating conditions at the Department of Earth Sciences, University of Uppsala. Spectra and element mapping were made by Horiba Jobin-Yvon XGT-5000 X-Ray fluorescent (XRF) spectrometer, equipped with an Rh X-Ray source at the Department of Mineralogy, Geochemistry and Petrology, University of Szeged. 30 kV excitation voltage and 0.8 mA anode current was used. Cathodluminescence studies were carried out by Reliotron cold cathode luminoscope and Eclipse 600 polarizing microscope at the Institute for Geochemical Research, Hungarian Academy of Sciences, Budapest.

Major oxide compositions (26) were analysed on a Finnigan MAT Element spectrometer by HR-ICP-MS, and trace elements were determined by ICP-AES using a Varian Vista AX spectrometer at the Department of Geology and Geochemistry, University of Stockholm.

Sr and Nd isotopic data were obtained on 4 lamprophyres, a hornblendite and a syenite by a Finnigan MAT 261 TIMS at the Laboratory for Isotope Geology, Swedish Museum of Natural History.

III. NEW RESULTS

1. Based on field work, and petrographical and mineralogical studies of the collected samples, lamprophyres occurring in the northern part of the DAM can be divided into three groups. They separate on field as well as they differ in mineral composition:

- **I. group:** pyroxenic, kaersutite-bearing lamprophyres – Orotva, Tarnica, Tászok, Fülöp and Gudu Creeks (area of Tarnica Complex). They have contact with Ladinian-Karnian hornblendite and nepheline syenite.
- **II. group:** pyroxene free, magnesiohastingsite-bearing lamprophyres – Fülöp Török and Nagyág Creeks. They have contact with Ladinian-Karnian nepheline syenite and Karnian-Raethian granite.
- **III. group:** pyroxenic, ferrorichterite-bearing lamprophyres – upper part of Nagyág Creek. They appear as xenoliths within tinguaite dykes, so their possible contact with host intrusive bodies is not known.

The contacts of pyroxenic, kaersutite-bearing and pyroxenic, ferrorichterite-bearing lamprophyres with hornblendite, nepheline syenite and granite, and the Aptian-Albian alkali feldspar syenite veins penetrating these lamprophyres mean that the I. and II. groups of lamprophyres emplaced in the DAM in the interval of Upper Triassic (Karnian-Raethian) – Lower Cretaceous (Aptian). Furthermore the emplacement of lamprophyres is not the latest stage in the magmatic process of the DAM.

2. During the lamprophyre research in the DAM this is the first determination of the composition of rock-forming and secondary minerals of lamprophyres based on geochemical analyses of the different mineral phases. In the course of identification of mineral phases a new mineral, the lisetite, unknown in the DAM till now, has been determined as well.

2.1. *The clinopyroxene of pyroxenic, kaersutite-bearing lamprophyres is subsilicic aluminian ferroan diopside* $[(Ca_{0.89}Na_{0.05\text{-}0.07}Fe^{2+}_{0.04\text{-}0.06})(Mg_{0.70\text{-}0.73}Fe^{2+}_{0.02\text{-}0.03}Fe^{3+}_{0.14\text{-}0.16}Ti_{0.06}\,Al_{0.05})(Al_{0.26\text{-}0.27}Si_{1.73\text{-}1.74})O_6]$. *The main pyroxene component of pyroxenic, ferrorichterite-bearing lamprophyres is aluminian ferroan diopside*

$[(Ca_{0.89}Na_{0.04}\ Fe^{2+}_{0.07})(Mg_{0.73}Fe^{2+}_{0.05}Fe^{3+}_{0.13}Ti_{0.06}Al_{0.04})(Al_{0.24}Si_{1.76})O_6$. *In minor amount they have sodian aluminian ferroan diopside* $[(Ca_{0.86}Na_{0.13})(Mg_{0.48}Fe^{2+}_{0.19}Fe^{3+}_{0.25}Ti_{0.04}Al_{0.02})\ (Al_{0.23}Si_{1.77})O_6]$ *and aegirine-augite* $[(Ca_{0.5}Na_{0.5})(Fe^{3+}_{0.47}Fe^{2+}_{0.25}Mg_{0.16}Mn_{0.04}Ti_{0.04}Al_{0.03})(Al_{0.07}Si_{1.93})O_6]$.

2.2. *The main rock-forming mineral of pyroxenic, kaersutite-bearing lamprophyres is hornblende with kaersutite core* $[(Na_{0.6\text{-}0.7}K_{0.2})_A(Ca_{1.9}Na_{0.1})_B(Mg_{2.6\text{-}2.7}Fe^{2+}_{1.3\text{-}1.6}Ti_{0.6\text{-}0.8}Al_{0.1\text{-}0.3})_C(Al_{2.0\text{-}2.2}Si_{5.8\text{-}6.0})O_{23}]$ *and magnesiohastingsite rim* $[(Na_{0.5\text{-}0.6}K_{0.0\text{-}0.4})_A(Ca_{1.8}Na_{0.2})_B(Mg_{1.9\text{-}2.5}Fe^{2+}_{1.4\text{-}1.9}Ti_{0.1\text{-}0.3}Fe^{3+}_{0.3\text{-}0.9}Al_{0.1\text{-}0.2})_C(Al_{1.7\text{-}1.9}Si_{6.1\text{-}6.3})O_{23}]$. *The hornblende of pyroxene free, magnesiohastingsite-bearing lamprophyres is hastingsite-magnesiohastingsite with composition of* $(Na_{0.4\text{-}0.6}K_{0.2\text{-}0.3})_A(Ca_{1.9}Na_{0.1})_B(Mg_{1.8\text{-}2.2}Fe^{2+}_{1.8\text{-}2.0}Fe^{3+}_{0.5\text{-}0.7}Ti_{0.2\text{-}0.4}Al_{0.2\text{-}0.4})_C(Al_{1.8\text{-}2.2}Si_{5.8\text{-}6.2})O_{23}$. *The pyroxenic, ferrorichterite-bearing lamprophyres have Na-rich ferrorichterite* $[(Na_{1.0})_A(Ca_{1.7\text{-}2.0}Na_{0.8\text{-}1.4})_B(Fe^{2+}_{2.6\text{-}2.7}Mg_{0.9\text{-}1.1}Al_{0.2\text{-}0.3})_C(Al_{0.0\text{-}0.1}Si_{7.9\text{-}8.0})\ O_{23}]$.

In the pyroxenic, kaersutite-bearing lamprophyres secondary Ca-amphiboles occur after pyroxenes. These are tremolite $[(Ca_{1.8\text{-}2.0})_B(Mg_{4.0\text{-}4.8}Fe^{2+}_{0.0\text{-}0.4}Fe^{3+}_{0.0\text{-}0.5}Al_{0.0\text{-}0.1})_C(Fe^{3+}_{0.0\text{-}0.2}Al_{0.0\text{-}0.5}Si_{7.5\text{-}8.0})O_{23}]$, *actinolite* $[(Ca_{1.9}Na_{0.1})_B(Mg_{4.0}Fe^{2+}_{0.7}Fe^{3+}_{0.3})_C(Al_{0.2}Si_{7.8})O_{23}]$ *and magnesiohornblende* $[(Na_{0.0\text{-}0.2})_A(Ca_{1.7\text{-}1.9}Na_{0.0\text{-}0.1})_B(Mg_{3.3\text{-}4.4}Fe^{2+}_{0.0\text{-}1.3}Fe^{3+}_{0.3\text{-}0.6}Al_{0.0\text{-}0.1})_C(Fe^{3+}_{0.0\text{-}0.2}Al_{0.3\text{-}0.7}Si_{7.3\text{-}7.5})O_{23}]$.

2.3. *The primary and secondary micas of pyroxenic, kaersutite-bearing and pyroxenic, ferrorichterite-bearing lamprophyres are Mg-biotites (mg#=0.60–0.65) and phlogopites (mg#=0.67–0.73). While micas of pyroxene free, magnesiohastingsite-bearing lamprophyres are Fe-Mg-biotite (mg#=0.47–0.50).*

2.4. *Interstitial plagioclases of pyroxenic, kaersutite-bearing lamprophyres are albite-oligoclase (An=5.3-16.0). Pyroxene free, magnesiohastingsite-bearing lamprophyres have albite-andesine (An=3.9-34.0) in the groundmass. Feldspars of pyroxenic, ferrorichterite-bearing lamprophyres are pure albites (Ab=99.6). In the core and at zone boundaries of sodian aluminian ferroan diopside of pyroxenic, ferrorichterite-bearing lamprophyres secondary K-feldspar (Or=96.0-96.6) occurs.*

2.5. *The lisetite appears in felsic globular sturctures and in the groundmass of pyroxenic, ferrorichterite-bearing lamprophyres. Determination of lisetite is the* *first time both in lamprophyres of the DAM and in the mineralogy of the whole massif. The composition of lisetite is* $Ca_{0.90-0.92}Na_{2.01-2.21}Al_{3.84-3.90}Si_{4.07-4.11}O_{16}$.

2.6. *In some of the felsic globular structures of pyroxenic, kaersutite-bearing lamprophyres allanite-(Ce,La) occurs in cores of plagioclases. This is characteristic at kaersutite and plagioclase intergrowth.*

2.7. *The subsilicic aluminian ferroan diopside of the pyroxenic kaersutite-bearing lamprophyres formed under approx. 800-1000 °C and 9-17 kbar (Nimis, 1999). The aluminian ferroan diopside and sodian aluminian ferroan diopside of pyroxenic, ferrorichterite-bearing lamprophyres formed under very similar mantle conditions as the previous one, approx. 800-1000 °C, 7-16 kbar and 6-19 kbar, respectively (Nimis, 1999). The aegirine-augite occurring at the rim of the aluminian ferroan diopside was generated under low pressure conditions based on its Ti- and Al-content. The pyroxenes are anorogenic and derive from an alkaline magma based on their Ti+Cr/Ca and Ti/Ca+Na ratios, respectively.*

2.8. *In the pyroxenic kaersutite-bearing lamprophyres kaersutite formed under 7-9 kbar, magnesiohastingsite formed under 5.4-6.9 kbar, while hastingsite-magnesiohastingsite of pyroxene free, magnesiohastingsite-bearing lamprophyres formed under 6-9 kbar (Hammarstrom, Zen, 1986; Hollister et al., 1987; Schmidt, 1992). These hornblendes were crystallized in the early stage of magmatism under mantle conditions based on their Ti- and Al-content and Ca+Al vs. Si+Na+K distribution. In the pyroxenic, ferrorichterite-bearing lamprophyres the ferrorichterite is estimated to have crystallized above 7 kbar in the groundmass and around 6 kbar in felsic globular structures (Brown, 1977)*

2.9. *In felsic globular structures of pyroxenic, ferrorichterite-bearing lamprophyres the lisetite containing ferrorichterite laths could have formed around 6 kbar. This formation pressure of lisetite agrees with its stability field (400 °C, 10±4 kbar) suggested by Smith et al. (1986).*

3. On the basis of major oxide and trace element geochemical analyses the pyroxenic, kaersutite-bearing and the pyroxene free, magnesiohastingsite-bearing lamprophyres are silica- and alumina-undersaturated alkaline basic rocks and

basanitic in composition. Furthermore they are secondary fractionates of primary melts.

Based on the low SiO_2 *and high alkali,* TiO_2*, LILE and LREE content, high Yb/Nb, Ti/V,* $(La/Yb)_N$ *ratios,* Zr/TiO_2 *vs. Nb/Y distribution, nepheline and olivine normative composition of the pyroxenic, kaersutite-bearing and the pyroxene free, magnesiohastingsite-bearing lamprophyres of the DAM they are silica-undersaturated, alkaline basic rocks and basanitic in composition. Their alumina-undersaturated or metaluminious character and their primitive mantle-normalized trace element patterns agree well with average alkaline lamprophyres.*

The mg#, Cr, Ni, Co and Sc concentration of the pyroxenic kaersutite-bearing lamprophyres indicate that they derive from a more primitive melt than the pyroxene free, magnesiohastingsite-bearing lamprophyres. Only a few pyroxenic kaersutite-bearing lamprophyre samples represent primitive melt composition. The majority of lamprophyres derive from a differentiated melt. The studied lamprophyres lack mantle xenoliths, do not have modal olivine, and most of them show whole-rock mg# 44-60 supposing that they could be secondary fractionates of primary melts.

4. Based on the Sr-Nd isotopic and strongly incompatible composition, the LILE/HFSE and LREE/HFSE ratios, the pyroxenic, kaersutite-bearing and the pyroxene free, magnesiohastingsite-bearing lamprophyres derive from an OIB mantle source containing HIMU and EM I mantle components. The intraplate origin of the lamprophyres is confirmed by their Ti/100 *vs.* Zr *vs.* Y*3 distribution.

The $^{87}Sr/^{86}Sr=0.70334\text{-}0.70371$, $^{143}Nd/^{144}Nd=0.51273\text{-}0.51283$, *negative* ε_{Sr} *(–11.2-–16.5) and positive* ε_{Nd} *(1.8-3.8) values of the pyroxenic kaersutite-bearing and the pyroxene free, magnesiohastingsite-bearing lamprophyres of the DAM show obviously their mantle origin. The La/Nb, Zr/Nb, Ba/Nb, Ba/La, Rb/Nb and K/Nb ratios of the lamprophyres corresponding with their Sr-Nd isotopic composition indicates the presence of HIMU and EM I mantle components in the source region of the DAM lamprophyres. The OIB-normalized REE patterns and the Ti/100 vs. Zr vs. Y*3 distribution of the lamprophyres show that they are related to an intraplate magmatic activity.*

5. The pyroxenic, kaersutite-bearing and the pyroxene free, magnesiohastingsite-bearing lamprophyres are enriched in LREE and depleted in HREE (La/Yb=15-26) indicating that the lamprophyre magma derived from a garnet lherzolite mantle source by very low degrees (~1-2 %) of partial melting. In this case the lamprophyre magma must have originated at a great depth, around 60-80 km (Watson, McKenzie, 1991).

While the pyroxenic, kaersutite-bearing and the pyroxene free, magnesiohastingsite-bearing lamprophyres have just 5- to 9-fold higher HREE content, they have 50- to 100-fold higher LREE content than the primitive mantle. Such fractionation of the LREE and HREE (La/Yb=15-26) show that during partial melting the lamprophyric magma is enriched in LREE much more than in HREE. The low HREE content of the lamprophyres indicate the presence of residual garnet in the source region. The enrichment in LREE of the lamprophyres suggests very low degrees (~1-2 %) of partial melting of garnet lherzolite.

6. The REE and the Sr-Nd isotopic composition of pyroxenic, kaersutite-bearing lamprophyres, the pyroxene free, magnesiohastingsite-bearing lamprophyres and the hornblendite of the DAM indicate that they were generated from the same magma, and originated in the same petrotectonic setting. Thus the generation of lamprophyres took place during the first magmatic event of the DAM (Middle Triassic – Upper Triassic).

6.1. *Both the pyroxenic, kaersutite-bearing and the pyroxene free, magnesiohastingsite-bearing lamprophyres have the same primitive mantle- and OIB-normalized REE patterns and Sr-Nd isotopic composition which mean that they are co-magmatic and co-genetic.*

6.2. *The DAM hornblendite-normalized REE patterns of the pyroxenic kaersutite-bearing and the pyroxene free, magnesiohastingsite-bearing lamprophyres prove that the lamprophyres are co-magmatic with the hornblendite. Their Sr-Nd isotopic characteristics point to a co-genetic origin. Based upon petrographical, mineralogical and geochemical evidences the generation of lamprophyres took place during the first magmatic event of the DAM (Middle Triassic – Upper Triassic) in intraplate tectonic setting as late-stage dykes of the ultrabasic body.*

IV. PUBLICATIONS IN THE TOPIC OF THE DISSERTATION

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V. OTHER PUBLICATIONS

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