PERIODICO di MINERALOGIA established in 1930 An International Journal of MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY, ORE DEPOSITS, PETROLOGY, VOLCANOLOGY and applied topics on Environment, Archaeometry and Cultural Heritage

# New mineralogical and geochemical data on the Vuorijarvi ultramafic, alkaline and carbonatitic complex (Kola Region, NW Russia)

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ABSTRACT. — The Vuorijarvi massif belongs to the famous Devonian (380-360 Ma) alkaline and carbonatitic province of Kola (NW Russia). It is a complex polyphase intrusion made of ultramafic rocks, ijolites-melteigites, carbonatites and related phoscorites. Ultramafic rocks (mainly clinopyroxenites) have been interpreted as cumulates, with variable amounts of trapped interstitial liquid. Ijolites are quite complex : some are aegirine-augite and nepheline cumulates, others are partly recrystallised rocks. Carbonatites and phoscorites (apatite-forsterite-magnetite rocks) are genetically linked; the latter correspond to cumulates of silicate and oxide minerals crystallised from a carbonatitic magma. Two generations of carbonatite have been recognized, calcitic varieties and dolomitic varieties. The three groups of rocks (ultramafic rocks, alkaline silicate rocks and carbonatites) have similar initial Nd-Sr isotopic compositions which suggest their cogenetic character. Apatite is a liquidus phase in the three main lithologies; it presents a continuous chemical evolution trend interpreted in terms of isomorphous substitution  $2Ca^{2+} = REE^{3+} + Na^+$ , which is compatible with a fractional crystallisation model.

RIASSUNTO. — Il massiccio di Vuorijarvi appartiene alla famosa provincia devoniana (380-360 Ma), alcalino-carbonatitica della penisola di Kola (NW Russia). Questa è una complessa intrusione polifasica composta da rocce ultrafemiche, ijoliti-melteigiti, carbonatiti e correlate foscoriti. Le rocce ultrafemiche (principalmente clinopirosseniti) sono state interpretate come cumulati con una quantità variabile di liquido interstiziale intrappolato. Le ijoliti sono abbastanza complicate: alcune sono cumulati formati da aegerina-augite e nefelina, altre sono parzialmente ricristallizzate. Le carbonatiti e le foscoriti (rocce composte essenzialmente da apatite-forsteritemagnetite) sono legate geneticamente; quest'ultime rappresentano a cumulati di fasi silicatiche e ossidi cristallizzati da un magma carbonatitico. Due generazioni di carbonatiti sono state riconosciute, una caratterizzata da varietà calcitica ed una da varietà dolomitica. I tre gruppi di rocce (ultrafemiche, alcaline silicatiche e carbonatiti) hanno una composizione isotopica Nd-Sr iniziale simile, che suggerisce che siano cogenetiche. L' apatite è una fase nel liquido di tutte e tre le litologie principali; essa è caratterizzata da un evoluzione chimica continua interpretabile come sostituzione isomorfa di  $2Ca^{2+} = REE^{3+} + Na^{+}$ , che risulta compatibile con un modello di cristallizazione frazionata.

KEY WORDS: Vuorijarvi, carbonatite, fractional crystallisation, Kola, Russia.

## INTRODUCTION. GEOLOGICAL SETTING OF THE VUORIJARVI MASSIF.

The Vuorijarvi massif (Fig. 1) is a small elliptical  $(3.5 \times 5.5 \text{ km})$  ultramafic, alkaline and carbonatitic complex that forms part of the famous Kola Alkaline Carbonatite Province

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(Kukharenko *et al.*, 1965; Kogarko, 1987; Kogarko *et al.*, 1995) in the NE part of the Baltic Shield. It was emplaced at ~380 Ma (Gogol *et al.*, 1999; Bayanova *et al.*, 2001) into Archaean gneisses of the Belomorian Terrane. The central part of the massif consists of ultramafic rocks, while alkaline rocks of the ijolite-melteigite series are found at its periphery and as veins. Two multistage stockworks with several generations of dykes and veins of phoscorite and carbonatite crosscut the ultramafic rocks in the SE part of the complex

### The ultramafic rocks

The ultramafic rocks of the central zone are essentially clinopyroxenites which locally grade towards the border to nepheline clinopyroxenites that also contain cancrinite and apatite. The ultramafic rocks contain blocks and rare lenses of dunite and wehrlite. They are interpreted as ortho- to mesocumulates with cumulus diopside and minor olivine (Fo87); perovskite and magnetite are locally concentrated up to 50 vol.%. The interstitial liquid crystallized as phlogopite (Mg#:88-85), amphibole (pargasitetschermakite), nepheline, Sr-poor (<0.5% SrO) calcite and locally apatite. The cumulus clinopyroxene is a diopside showing a range of compositions: the Mg# of the core of cumulus grains varies widely from sample to sample, from 91 (VJA60) to 70 (VJA74). The Na content systematically increases from 0.017 to 0.073 Na p.f.u., with decreasing Mg#. The diopside can be strongly zoned (orthocumulus growth) with Mg# varying from 84 to 71 within a single sample. The primary diopside has been partly transformed by late magmatic events (compaction, recrystallisation, Ti-rich magnetite exsolution...) and locally by metasomatic event related to the emplacement of thin ( $\approx 1$  to 2 cm) carbonatite veins.

This metasomatism has completely transformed the primary (=magmatic) assemblage of the clinopyroxenite to secondary (=metasomatic) assemblages. Three distinct zones can be recognized from the carbonatite vein to the clinopyroxenite wall-rock. Each zone is characterized by its mineral association and petrographic texture (Table 1). Similar zones have been described by Morbidelli *et al.* (1986) in the Jacupiranga carbonatite complex of Brazil.

The composition of the cumulus clinopyroxenes is not clearly correlated with the trace element content of the whole rocks. In fact, the amount of interstitial liquid (that crystallised to phlogopite, cancrinite or calcite) is very variable from rock to rock and thus directly influences the whole rock trace element content. For example,  $\Sigma REE$  varies from 510 ppm (in magnetite clinopyroxenite VJA60) to 2392 ppm (in nepheline clinopyroxenite VJA73) (Fig. 2). The (La/Yb)<sub>N</sub> ratio is in the range 59-160. The spidergrams are also variable, the trace element enrichment factors are in the range 20-50 except for Nb, Ta and LREE that are strongly enriched in the sample VJA73, related to the high content of interstitial liquid.

# *The alkaline silicate rocks (ijolite-melteigite series)*

The alkaline silicate rocks are mainly ijolites (urtites and melteigites are subsidiary). They contain aegirine-augite and nepheline with accessory apatite, titanite, magnetite, sulphides and mica. Alkali feldspar is typically absent. Nevertheless, one sample is albite-rich; if interpreted as a magmatic rock, this aegirineaugite and albite rock is modally close to a shonkinite (according to the classification scheme of alkaline rocks by Le Bas, 1977). However, Khukarenko et al. (1965) interpreted this rock as a kind of fenite. Petrographically, there appears to be two groups of ijolites : 1) ijolites interpreted as cumulates of euhedral aegirine-augite and nepheline with interstitial calcite (<0.7% SrO) and skeletal magnetite; 2) ijolites with euhedral aegirine-augite and titanite in a fine-grained recrystallised matrix of cancrinite, nepheline, calcite and apatite. Clinopyroxenes from the ijolites are very complex; they are partly resorbed and show both normal and reverse zoning. Their Mg#





The metasomatic zones developed at the contact between a carbonatite vein and a clinopyroxenite wall-rock. Cc = calcite, Tph = tetraferriphlogopite, Am = Na-rich amphibole, Mt = magnetite and Di = diopside.

	Metasomatic zones						
	Clinopyroxenite	Zone1	Zone2	Zone3	Carbonatite vein		
Thickness	-	≈ 0.3 cm	≈l cm	≈ 0.5 cm	≈l cm		
Mineralogy	Di + Mt	Di + Am + Cc + Mt + Tph	Am + Tph + Cc + Mt	Tph + Am +O	Cc Cc + Tph		
Texture	Mesocumulate	Reaction rim of Na-rich amphibol mantling cpx crystal	Modal e varying s in zone in	proportions 1 from Tph-rich 3 to Am-rich zone 2.	Elongated polygonal		



Fig. 2 – Pyrolite-normalized trace element abundances for the clinopyroxenites, the alkaline silicate rocks and the carbonatites of the Vuorijarvi massif. <u>A</u>: Multi-element diagrams; <u>B</u>: Chondrite-normalized REE abundances. (Normalizing values from McDonough and Sun, 1995). Average calcio- and magnesio-carbonatites (CC & MC; Woolley & Kempe, 1989) have been reported for comparison.



varies from 77 to 44, with Na content varying from 0.05 to 0.19 p.f.u. Clinopyroxene in the aegirine-augite albite rock has a high Mg#  $(\sim 0.75)$  and a slightly higher Na content  $(\sim 0.2)$ Na p.f.u.). This rock is tentatively interpreted as an orthocumulate with zoned aegirine-augite and intercumulus poikilitic albite. The textures of the ijolites, and more particularly of their clinopyroxenes, could be explained either by chemical disequilibrium (resorption and growth) and/or by thermal variations related to the possible mixing of two magmas of different temperatures. The  $\Sigma REE$  content of the ijolites is quite high (up to 1740 ppm), however, the aegirine-augite albite rock is less enriched (520 ppm) and quite comparable to some of the clinopyroxenites. For most trace elements, the enrichment factors are lower than in the clinopyroxenites. Some elements (Rb, K and Sr) are depleted and form negative anomalies while others, especially Nb and Ta are strongly enriched (Fig. 2). It is interesting to note that Ta<sub>N</sub> is higher than Nb<sub>N</sub>, presumably due to the presence of cumulus titanite.

### Carbonatites and related phoscorites

Carbonatites and phoscorites (apatiteforsterite-magnetite rocks) are intimately related in the field. The petrographic nature of the carbonatites (cumulates or liquid) is difficult to determine because the primary (probably magmatic) textures have been largely blurred through several subsolidus transformations (recrystallisation, hydrothermalism...) giving rise to consertal and/or polygonal texture of the carbonates. Two types of carbonatites have been described (Khukarenko et al., 1965). The most common carbonatites are those of the earlier stages, they are calcitic (0.7-1.13% SrO) and occur as lens-shaped large bodies and as veins of variable thickness (few centimeters up to 10-20 m). The later carbonatites are dolomitic, they are widely distributed throughout the massif as thin (1cm up to 0.5 m) veins cutting the calcite carbonatites. Calcite has been strongly deformed through twingliding as shown by the development of polysynthetic twins. Olivine (Fo86 to 88; Mn content: 0.3 to 0.4 p.f.u.), monticellite (replacing olivine), phlogopite (Mg#: 91-88), magnetite and apatite are common in the earlier calcite carbonatites that also contain accessory diopside (in small grains or transformed to Narich amphibole), perovskite, baddelevite, zircon, monazite, ilmenite, dolomite and sulphides. The late calcite and dolomite carbonatites amphibole, contain tetraferriphlogopite and apatite with minor pyrochlore, ankerite, Sr-REE-carbonate, barite and sphalerite. The carbonatites are generally enriched in trace elements (100 to 700 x pyrolite) and in REEs ( $\Sigma REE = 870 - 3617$ ppm) with (La/Yb)<sub>N</sub> varying from 40 to 88. Nevertheless, these carbonatites are less enriched than the average carbonatites of Woolley and Kempe (1989). Phoscorites, which are genetically linked to the carbonatites, are strongly enriched in apatite and consequently in REEs. The spidergrams show well-defined depletions in Rb, K and Zr, Hf, Ti.

Most REE patterns are roughly subparallel. All the rocks (ultramafic rocks, ijolites and the various carbonatites) broadly display similar patterns and enrichment factors in their spidergrams. Some elements have distinct behavior: i.e. Nb-Ta enrichment is related to the presence of titanite and perovskite, P enrichment is due to apatite, ...

### PETROGENETIC RELATIONSHIPS BETWEEN THE THREE GROUPS OF ROCK

Apatite is ubiquitous in the Vuorijarvi massif; its chemistry (Table 2) can be interpreted in terms of the substitution  $2Ca^{2+} =$  $REE^{3+} + Na^{+}$  (Fig. 3). There is a good correlation of increasing LREE content (La+Ce+Na) with decreasing Ca in the sequence clinopyroxenites-ijolites-carbonatites. The clinopyroxene also shows a regular trend of decreasing Mg# from 86 in the clinopyroxenites to 44 in the ijolites. Clinopyroxene in the carbonatite is enriched in Mg (Mg#: 94), which can be explained by the preferential uptake of Fe by coexisting magnetite. The presence of accessory minerals which concentrate some trace elements as Nb-Ta. Zr-Hf and U-Th and which can fractionate one element of the pair prevents the use of bielement diagrams to test the comagmatic

	Pyroxenite	Ijolite	Silicate-rich carbonatite	Carbonatite		
	N=5	N=4	N=3	N=9		
SiO <sub>2</sub>	0.65-0.89	0.62-0.95	1.14-1.16	0.75-1.74		
$Al_2O_3$	0.00-0.03	0.00-0.03	0.00	0.00		
FeOt	0.10-0.13	0.04-0.08	0.05-0.06	0.00-0.06		
MnO	0.05-0.12	0.00-0.05	0.00-0.04	0.00		
MgO	0.00	0.00	0.00-0.04	0.00-0.05		
CaO	55.75-55.99	56.29-56.39	55.18-55.48	54.57-54.98		
Na <sub>2</sub> O	0.00-0.07	0.10-0.13	0.05-0.07	0.04-0.26		
$P_2O_5$	39.03-39.48	40.04-40.10	38.97-39.56	37.99-39.84		
$La_2O_3$	0.02-0.05	0.16-0.24	0.21-0.27	0.25-0.26		
$Ce_2O_3$	0.09-0.2	0.52-0.74	0.58	0.71-0.86		
F	1.24-1.27	1.59-1.72	2.63-3.20	2.73-2.81		
Cl	0.00-0.01	0.00-0.02	0.00-0.03	0.00-0.03		

 TABLE 2

 Range of apatite composition (in wt%) for the various rocks of the Vuorijarvi massif.



Fig. 3 – Variations of apatite composition in the Ca (p.f.u.) vs La+Ce+Na (p.f.u.) diagram.



Fig. 4 – Nd-Sr isotopic diagram for the Vuorijarvi massif (Balaganskaya *et al.*, 2001; this study). Comparison with other massifs of the Kola Alkaline and Carbonatite Province: Kovdor (Verhulst *et al.*, 2000), Khibina (Kramm and Kogarko, 1994), Sebljavr (Verhulst, unpubl. thesis, 2001).

character between the ultramafic rocks, the alkaline silicate rocks and the carbonatites.

The Nd-Sr isotopic data (Balaganskaya et al., 2001; this study) show that the three groups of rocks (ultramafic cumulates, ijolites and carbonatites) have similar initial isotopic compositions (calculated using an age of 380 Ma) and define a restricted field, although the ijolites tend to have slightly lower ENd. Nevertheless, one quartz-bearing (Kramm, pers. comm. 2000) carbonatite has isotopic compositions (87Sr/86Sr: 0.7046; ɛNd: - 1.9; Kramm, 1993) clearly outside this field suggesting that, locally, crustal contamination could have played a role. The range of I(Sr) values (0.7030-0.7033) and  $\epsilon$ Nd (+1.8 to +5.9) is quite narrow. Our isotopic data (Fig. 4) define a field close to those of several other ultramafic and carbonatite intrusions of the Kola Alkaline Carbonatite Province (Kovdor, Sebljavr, Khibina). These isotopic data fall in the depleted quadrant of the Sr-Nd diagram and point to a mantle source that shows timeintegrated Rb- and slight LREE-depletion, comparable to the OIB-type source (Figure 4). Thus, despite the complex magmatic and postmagmatic emplacement history of the Vuorijarvi massif, it appears that it could result from the differentiation by fractional crystallisation of a homogeneous batch of mantle-derived magma (presumably a single batch) under closed system conditions. This is quite unusual in the Kola province as other massifs (Kovdor: Verhulst et al., 2000; Turvi Peninsula: Dunworth and Bell, 2001) show quite a range of Sr-Nd isotopic composition implying multistage, open-system behaviour.

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