

## **Noble gas isotopes in minerals from phoscorites and carbonatites in Kovdor and Seblyavr ultramafic-alkaline complexes (Kola alkaline province, NW Russia)**

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**ABSTRACT.** — Abundances of He and Ar isotopes in minerals from rocks composing the Paleozoic carbonatite-bearing Kovdor and Seblyavr alkaline-ultramafic complexes (the Kola Alkaline Province NW Russia) have been preliminary studied. The data obtained are to estimate their use as geochemical indicators, informative on conditions of the mineral-forming alkaline and carbonatite systems and sequence of mineral formation in these media. Noble gas isotope compositions show the extractable fluid phase in the most minerals studied to have varying input of the mantle, crustal and atmospheric components as well. All of these are found in both magmatic and postmagmatic minerals. Mixing of the mantle and crustal fluid phases might begin during the pre-crystallization and continue during differentiation and fractional crystallization of the mantle-derived magma. The most part of the mantle fluid (considered as primary fluid) is lost during magmatic evolution of alkaline and carbonatite complexes. Abundance patterns of the noble gas isotopes suggest predominantly autometasomatic character of higher-temperature postmagmatic processes and increasing input of exogenous fluid phase (meteoric water) at later postmagmatic stages. Distribution of the He and Ar isotopes and variations of  $^3\text{He}/^4\text{He}$  and  $^3\text{He}/^{36}\text{Ar}$  ratios, can be employed as an informative tool for recognizing of fluid sources cognate to the ore-forming and barren magma(s), and serve as a basis for reconstruction of the physical-chemical conditions of valuable mineralization typical of alkaline-ultramafic complexes (apatite, magnetite, phlogopite, minerals of high-field strength element like to Nb, Zr, Sc, LREE).

**RIASSUNTO.** — In questo contributo viene presentato uno studio preliminare sulle concentrazioni degli isotopi di He e Ar nei minerali che formano le rocce Paleozoiche contenenti carbonatiti dei complessi alcalini di Kovdor e Seblyavr (Provincia alcalina di Kola, NW Russia). I dati ottenuti vengono utilizzati per valutare la possibilità di utilizzare i gas nobili come indicatori geochimici, che forniscano informazioni sulle condizioni di formazione dei minerali costituenti i sistemi alcalini e carbonatitici e la sequenza di formazione di questi minerali in detti sistemi. Le composizioni isotopiche dei gas nobili mostrano che, nella maggior parte dei minerali studiati, la fase fluida estraibile, ha componenti provenienti dal mantello, crosta e atmosfera. Tutte queste componenti sono state trovate sia nei minerali magmatici sia in quelli postmagmatici. Il *mixing* di fasi fluide mantelliche e crostali potrebbe iniziare già prima dell'inizio della cristallizzazione e continuare durante la differenziazione e cristallizzazione frazionata di questi magmi di origine mantellica. La maggior parte del fluido mantellico (considerato primario) è perso durante l'evoluzione magmatica dei complessi alcalini e carbonatitici. Le distribuzioni delle abbondanze degli isotopi dei gas nobili suggerisce un carattere predominante autometasomatico, postmagmatico di alta temperatura e un incremento nel contributo di fase fluida esogena (acqua meteorica) nella fase postmagmatica tardiva. La distribuzione degli isotopi del He e dell'Ar e le variazioni dei rapporti  $^3\text{He}/^4\text{He}$  e  $^3\text{He}/^{36}\text{Ar}$ , possono essere usati come uno strumento informativo per riconoscere le sorgenti dei fluidi affini ai magmi che producono mineralizzazioni o sono sterili, e sono utilizzabili

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come base per la ricostruzione delle condizioni fisico-chimiche che hanno prodotto mineralizzazioni coltivabili tipiche dei complessi alcalini-ultrafemici (apatite, magnetite, flogopite, minerali di elementi ad alta forza di campo quali Nb, Zr, Sc, LREE).

KEY WORDS: *Noble gases, isotopes, mineral, phoscorite, carbonatite.*

## INTRODUCTION

The Kola Alkaline Carbonatite Province (*henceforth* KACP) covers the NE segment of the Baltic Shield. It is a territory of active ultramafic-alkaline and peralkaline magmatism. Typical products of the magmatism are dunites, clinopyroxenites, melilitites, foidolites, alkaline syenites, phoscorites (olivine/clinopyroxene-apatite-magnetite rocks; Tomkeieff, 1983; Egorov, 1993) and carbonatites, which have intruded into late Archaean crust and occur mostly within differentiated complexes. Among these rocks, the mantle origin of carbonatites and cognate phoscorites is now well proven, so the isotope composition of their parental silicate-carbonate melts is representative of isotope signatures of sublithospheric sources. It can also be used as a monitor of the evolution path of mantle-generated magmatic systems.

More than 25 complexes of Paleozoic alkaline-ultramafic and peralkaline rocks occur in the KASP. Sixteen of which are known to contain carbonatites and phoscorites. The largest constituents of the Province are the Khibina and Lovozero giant peralkaline complexes. At present, geology, petrology and mineralogy of the most KACP complexes have been studied in details and described in numerous publications, mostly in the Russian editions. In the same time some points of genesis and crystallization paths of carbonatites and phoscorites still remain disputable (Dunworth and Bell 2001, Kramm *et al.* 1993, Kramm 1993, Kramm and Kogarko 1994, Veksler *et al.* 1998, Verhulst *et al.* 2000, Zaitsev and Bell 1995, *etc.*).

Enrichment of carbonatites and phoscorites

in volatile components favors the study of noble gas isotopes, which are conventional geochemical tracers of global geological processes, including magma generation provoked by ascending mantle plumes. In the many cases, a reliable data sets on distribution of He and Ar isotopes in igneous suits and representative minerals allow to identify source(s) and to evaluate input of fluids responsible for the magma generation, as well as to reconstruct dynamic evolution to ore-forming systems related to the mantle-derived magma; noble gas isotopy avails reconstruction of degassing pattern and allows estimation of country rocks assimilation as well as input of exogenous fluids.

The summary on noble gases investigations in the Paleozoic complexes within the KACP has been published recently by Tolstikhin *et al.* (1999, 2002), Nivin *et al.* (2001), Nivin & Ikorsky (2002), *see also references therein*). In particular, He isotope ratios close to values typical of the deep-seated plumes rising from the lower-mantle, were first found in the orthomagmatic suits of the Province as well as the highest concentrations of the primordial  $^3\text{He}$  found to date in terrestrial rocks.

This paper presents an attempt to estimate the applicability of noble gas isotope systematic in particular minerals as a tool for reconstruction of source, sequence and conditions of mineralization as well as reconstruction of evolution paths of cognate phoscorites and carbonatites series rocks in Kovdor and Seblyavr complexes, taken as the most representative among the carbonatite-alkaline-ultramafic complexes (CAUCs).

## BRIEF GEOLOGICAL OUTLOOK

The igneous Kovdor ring complex occurs in the SW part of the Kola peninsula (67°35'N, 30°20'E). Covering an area of 40.5 km<sup>2</sup>, this body is the largest of its type within the KACP. The geology of this intrusion has been described in detail by Kukharenko *et al.* (1965), Ternovoi (1977), Kapustin (1980),

Arzamastsev (1994), Kogarko *et al.* (1995), and Verhulst *et al.* (2000). The intrusion has a concentric structure with steeply-dipping contacts between adjacent units. An ultramafic core (dunite, clinopyroxenite and clinopyroxene-olivine rocks) is surrounded by relatively younger turjaite, melilitolite, phlogopite-bearing clinopyroxene-olivine rock, garnet-amphibole-monticellitite rock, nephelineclinopyroxenite, phoscorite-carbonatite series rocks, the outer zones are composed of foidolites (jacupirangite, ijolite-melteigite) and fenites formed after country gneiss.

The largest multistage body of carbonatites and phoscorites is a 0.8 – 1.3 km stock traced down by drilling deeper than 1.970 m. This body has intruded clinopyroxenite and ijolite-melteigite at the intersection of N- and NE-trending faults 380±4 Ma ago (Dunaev, 1982; Bayanova *et al.*, 1997; Amelin and Zaitsev, 1997). The stock is studied in great detail (Ternovoi, 1977; Krasnova & Kopylova, 1988; Verhulst *et al.*, 2000 and references therein). There is rough spatial zoning in distribution of phoscorites and carbonatites, presumably coincident with consequence of emplacement of the rock units. From periphery to stock epicenter fine-grained apatite-forsterite, and coarse-grained apatite-forsterite-magnetite rock suits gave way to all varieties of calcite-forsterite-magnetite, apatite-calcite-magnetite and dolomite-magnetite rocks; late magnesiocarbonatites are controlled by NW-trending and meridional fault systems and form vein systems cutting through both carbonatite stock and silicate country rocks (*e.g.*, so called satellite body of dolomite-apatite-amphibole-magnetite “phoscorite” and magnesiocarbonatite veins, formed in vicinity to eastern contact of the main stock). The available geological and isotope data shows Kovdor phoscorite-carbonatite stock to have been formed by means of superimposition of carbonate-silicate intrusive series which have been affected by intense postmagmatic activity within the intrusive structure.

The Sebyavr complex is located in the NW

part of the KACP (68°43'N, 32°08'E). It largely consists of variety of clinopyroxenites, as well as of foidolites (mostly ijolites), phoscorites and carbonatites. Data on its structure and composition are provided by numerous boreholes and geophysical studies. The complex is deeply steeping concentrically zoned stock, oval in shape, and covers area 4 – 5 km in plan. Its core is composed of clinopyroxenites, containing blocks of forsteritic rocks (up to 150 m across), bearing perovskite and magnetite with minor phlogopite, calcite and serpentine. Zones of forsterite-clinopyroxene rocks surround the olivinite blocks. Clinopyroxenites consist of diopside, phlogopite, titanomagnetite and perovskite with subordinate amphibole, apatite and calcite. They contain lens-like schlieren of perovskite-titanomagnetite rocks. Clinopyroxenites have mostly been superimposed with metasomatic amphibole, phlogopite and apatite mineralization and sometimes grade into phlogopite-clinopyroxenite, apatite-clinopyroxenite and apatite-garnet-amphibole metasomatites. The unaltered clinopyroxenites often gradually merge into nepheline clinopyroxenites, which form a discontinuous ring zone along the margins of the clinopyroxenite core. Lens-like bodies of ijolite are situated between the nepheline clinopyroxenites and the country Archaean gneisses.

Phoscorites and carbonatites are considered to have emplaced in the Sebyavr complex in four main consecutive stages (Balaganskaya *et al.*, submitted). The phoscorites and carbonatites were intruded during four successive stages and formed a concentric network of dykes and veins of greatly varying thickness (from first centimeters up to 100-120 meters and even more) cutting through clinopyroxenites and ijolites. The earliest calciocarbonatites and calcite-bearing phoscorites dominate at the current erosion level of the complex, and form stocks up to 160-300 m and a network of concentric dykes and veins, which vary from 1-2 cm to 40-200 m in thickness and cross-cut through the

clinopyroxenites and commonly having sharp contacts.

A discontinuous weathering crust covers the present day surface of the Sebyavr complex. It is generally a few meters thick with local crater-like depressions up to 220 m thick in the central area of the complex. Sebyavr was explored as an apatite deposit. The main apatite ore types are as follows: amphibole and phlogopite clinopyroxenites (garnet-amphibole and diopside-phlogopite rocks), forsterite-magnetite, "tetraferriphlogopite"-calcite-magnetite and amphibole-calcite-pyrrhotite varieties of phoscorites and calcite carbonatites (Subbotin & Mikhaelis, 1986). Averaged sequence of Sebyavr complex formation, reconstructed from geological data, is as follow (in order of formation): apatite-phlogopite-clinopyroxene rocks, apatite-forsterite-magnetite rocks (phoscorites), calcite-"tetraferriphlogopite"-magnetite and sulphide-bearing amphibole rocks (Subbotin & Mikhaelis, 1986).

#### SAMPLES AND METHODS

Noble gas isotope concentrations and isotope ratios have been obtained in minerals composing rock units representative of Kovdor and Sebyavr complexes. These are mostly phoscorites and carbonatites, and in the lesser extent – ultramafic rocks. In the whole, 48 mineral samples were investigated (Table 1), among which 23 samples were analysed as whole minerals (*WM*) and 38 samples were employed for extraction and analyses of gases trapped into fluid inclusions (*FI*). Methods of He and Ar measurements have been described in details elsewhere (e.g., Marty *et al.*, 1998; Tolstikhin *et al.*, 1999). It is worth to note that the rare gas extraction from mineral samples (like to conventional rock samples) was performed through two approaches: by means of sample melting in high-vacuum furnace and sample milling in previously pumped-out glass ampoules. If the first approach provides the total gas extraction from the whole sample, the

second one allows extraction of the gases mainly from fluid inclusions of the host minerals. A comparison between *WM* He and Ar isotope abundances and those values which would be expected for closed systems basing on abundances of elements parental for noble-gases (such as U, Th, Li, K) and rock age, allows us to estimate the trapped gas constituent.

In the most of the *FI*, the isotopic composition of trapped noble gases is known to retain over a long time close to the initial composition and with lesser input of radiogenic component as compared to the noble gases embedded into crystal lattice of rock-forming minerals.

The following recently published estimations of isotope ratios in the Earth's reservoirs were used for interpretation of the obtained data:  $^3\text{He}/^4\text{He}$  (the most informative indicator of deep fluid sources) for crust  $\sim 2 \cdot 10^{-8}$ , for upper mantle  $\sim 1.1 \cdot 10^{-5}$ , for lower mantle  $\sim 1.1 \cdot 10^{-5}$ ;  $^{40}\text{Ar}/^{36}\text{Ar}$  for atmosphere – 295.5, for upper mantle  $\sim 40.000$ , for lower mantle  $\sim 5.000$ - $6.000$  (Tolstikhin & Marty, 1998).

#### RESULTS AND DISCUSSION

Broad (several orders of magnitude) variations in concentrations and isotope composition of He and Ar have been revealed in whole minerals (*WM*) and in fluid inclusions (*FI*) both in associated minerals from the same sample of a phoscorite or a carbonatite and in the similar minerals from the different samples of these rocks. This finding agrees with the empirical data showing significant variability of rare gas isotope composition in phoscorite-carbonatite rock series as compared to other (silicate) constituents of CAUC (Tolstikhin *et al.*, 1999; Nivin *et al.*, 2001; Tolstikhin *et al.*, 2002).

High bulk concentrations of *WM*  $^4\text{He}$  are found in perovskite and in the latest apatite generations (most probably, enriched in radioactive elements), which compose "apatitolite" segregation within Kovdor

TABLE 1  
Brief description of samples employed for the present study.

Sample #	Index	Rock	Representative mineral
<b>Sebyavr Complex</b>			
1px	Sja-114/55-pr	Clinopyroxenite (perovskite-magnetite)	Clinopyroxene
1mg	Sja-114/55mf	The same	Magnetite
1pr	Sja-114/55-prs	- " -	Perovskite
2px	BEG-8p	Phoscorite (apatite-phlogopite-clinopyroxene-magnetite)	Clinopyroxene
2mg	BEG-8m	The same	Magnetite
2ap	BEG-8a	- " -	Apatite
2cc	BEG-8c	- " -	Calcite
3mg	BEG-9m	Phoscorite (apatite-forsterite-magnetite)	Magnetite
3ap	BEG-9ap	The same	Apatite
3ph	BEG-9ph	- " -	Phlogopite
3cc	BEG-9cc	- " -	Calcite
4dl	16-333/249.8	Magnesiocarbonatite	Dolomite
4an	16-333/249.8	The same	Ankerite
4sl	16-333/249.8	- " -	Sulphide fraction
5dl	BEG-14do	- " -	Dolomite
5sl	BEG-14	- " -	Sulphide fraction
6dl	NSB-351-6do	Calcio-magnesiocarbonatite	Dolomite
6sl	NSB-351-6su	The same	Sulphide fraction
<b>Kovdor Complex</b>			
7mg	NKV-585-1	Magnetite schlieren in dunite	Magnetite
8px	KD-2	Clinopyroxenite pegmatite	Clinopyroxene
8mg	KD-1	The same	Magnetite
9fr	NKV-1s-16f	Phoscorite (forsterite-apatite-magnetite)	Forsterite
9mg	NKV-1s-16m	The same	Magnetite
9ap	NKV-1s-16a	- " -	Apatite
10fr	NKV-19f	- " -	Forsterite (+Apatite)
10mg	NKV-19m	- " -	Magnetite
10ap	NKV-19a	- " -	Apatite
11fr	NKV-8f	Phoscorite (calcite-forsterite-magnetite, clinopyroxene-bearing)	Forsterite
11mg	NKV-8m	The same	Magnetite
11cc	NKV-8c	- " -	Calcite
12mg	NKV-15m	Phoscorite (calcite-magnetite, bearing forsterite and apatite)	Magnetite
12ap	NKV-15a	The same	Apatite
13mg	KD-3	Phoscorite (magnetite-calcite)	Magnetite
14mgL	Yak-1mL	The same	Magnetite (large crystals)
14mgS	Yak-2mS	- " -	Magnetite (small crystals)
14ccl	Yak-1cc	- " -	Calcite
14ccs	Yak-2cc	- " -	Calcite
15mg	4/83-KS/m	Phoscorite (magnetite-calcite with green phlogopite)	Magnetite

CONTINUED: *Table 1*

Sample #	Index	Rock	Representative mineral
15cc	4/83-KS/k	The same	Calcite
16mg	NKV-2s-12m	Magnetite rock bearing calcite, phlogopite and apatite	Magnetite
17mgL	KOV-1mL	Phoscorite (magnetite-dolomite)	Magnetite (large crystals)
17mgS	KOV-1mS	The same	Magnetite (small crystals)
17dl	KOV-1d	- " -	Dolomite
18px	158-KS	Calciocarbonatite (clinopyroxene-phlogopite)	Clinopyroxene
18ph	158-KS	The same	Phlogopite
18cc	158-KS	- " -	Calcite
19ap	NKV-1	Apatitolite	Apatite
20kd	K-112/96	Postmagmatic mineral assemblage	Kovdorskite

Note: Sulphides are dominated by pyrrhotite.

TABLE 2  
*Bulk noble gas isotope abundances*

Sample #	$^4\text{He}$ $\mu\text{cm}^3/\text{g}$	$^3\text{He}/^4\text{He}$ E-8	$^{40}\text{Ar}$ $\mu\text{cm}^3/\text{g}$	$^{40}\text{Ar}/^{36}\text{Ar}$
1px	340	174	5.1	1644
1mg	1435	299	10.9	2185
1pr	9930	1.3	3.9	687
2px	91.0	528	7.2	697
2mg	155	283	11.2	1208
2ap	155	26.7	8.6	590
4dl	21.4	1125	37.1	349
4an	27.0	198	9.5	952
4sl	4.5	430	0.9	383
8px	27.4	407	6.3	632
8mg	53.8	971	11.2	3507
9fr	22.6	538	2.5	974
9mg	16.8	412	7.0	2238
9ap	33.6	73.7	2.3	1076
11fr	3.5	636	1.3	330.4
11mg	9.4	390	9.5	719
12mg	866	60.0	4.3	1261
13mg	22.7	465	3.5	1658
16mg	10.3	670	3.2	1550
18px	191	552	16.9	7250
18ph	11.0	64.0	157	50000
18cc	14.7	77.0	128	7400
19ap	2500	3.3	3.7	770

Notes: # of samples correspond to those in table 1; the mass-spectrometer measurements have been mostly performed by Dr. I.L. Kamensky.

clinopyroxene-phlogopite pegmatoid rock (the latest derivatives of the ultramafic magmatic suit), and in magnetite representative of calcite-apatite-forsterite-magnetite phoscorite (Table 2). The highest  $^3\text{He}/^4\text{He}$  ratios are typical of rock-forming carbonate in Seblyavr magnesiocarbonatite, as well as of forsterite, clinopyroxene and some magnetite fractions of phoscorites from the both complexes (Fig. 1). Phlogopite and calcite are the main Ar concentrators among the studied minerals. The first one shows the highest  $^{40}\text{Ar}/^{36}\text{Ar}$  values. The lowest  $^{40}\text{Ar}/^{36}\text{Ar}$  values ( $<10^3$ ), in some cases close or comparable to atmospheric one, are found in dolomite, sulphide fraction (mostly pyrrhotite) and ankerite from a Seblyavr magnesiocarbonatite, as well as in apatite samples, in forsterite and magnetite fractions from some Kovdor phoscorites.

A comparison of the measured concentrations of He and Ar isotopes and those expected (calculated from abundances of parental elements) in 9 samples from Kovdor complex (Table 3) shows that the most of the radiogenic  $^4\text{He}$  has been lost, whereas measured  $^3\text{He}$  concentrations are 2-5 orders of magnitude higher than the calculated values. It means light He isotope being trapped by the minerals. Note that highest  $^3\text{He}_{\text{meas}}/^3\text{He}_{\text{cal}}$  ratios are found in clinopyroxene and magnetite

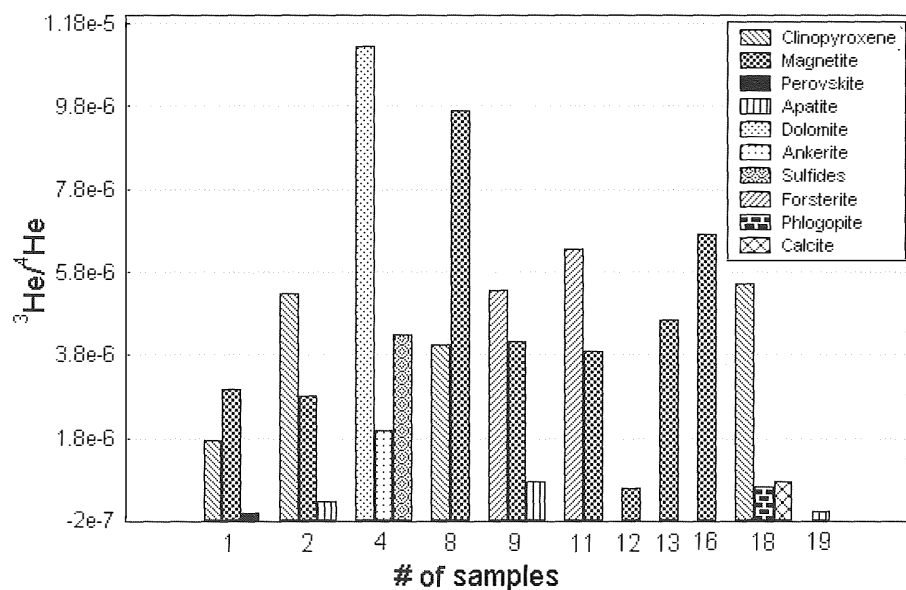


Fig. 1 – Variations in  $^3\text{He}/^4\text{He}$  ratio in whole minerals. # of samples as in Tables 1 and 2.

samples (#16mg and #13mg) representative of magnetite-calcite phosphorite whereas the same ratio in case of magnetite from another sample of the similar phosphorite (#11mg) is the lowest of estimated values. The most part of Ar in studied minerals also can be considered as trapped volatile phase as long as the  $^{40}\text{Ar}_{\text{meas}}/^{40}\text{Ar}_{\text{cal}}$  ratio in the minerals ranges from 1.3 to 32.8.

There are some trends of bulk noble gases isotope values both in associated minerals (in this case the trends correlate well to sequence of crystallization of the minerals or to metasomatic events) and in the similar minerals appearing through variety of rocks in the studied complexes (in the latter case the trends agree with sequence of rock unit emplacement according to geological observations). In particular, there is decreasing of the  $^3\text{He}/^4\text{He}$  ratio in sequence clinopyroxene-(forsterite)-magnetite- fluorapatite in phosphorites. Nevertheless in Sebyavr clinopyroxene (sample #1px), the  $^3\text{He}/^4\text{He}$  value is lower that

those found in associated magnetite (sample #1mg). In carbonatites  $^3\text{He}/^4\text{He}$  ratios decrease from dolomite towards sulphides and ankerite and from clinopyroxene towards calcite and phlogopite (Fig. 1).  $^{40}\text{Ar}/^{36}\text{Ar}$  value gradually increases from clinopyroxene (forsterite) towards magnetite sample representative of phosphorites. The  $^3\text{He}/^{36}\text{Ar}$  ratio decreases in the cognate (paragenetic) consequences “dolomite-ankerite-pyrrhotite” and “clinopyroxene-phlogopite-calcite” in the carbonatites from both complexes. In Kovdor magnetite samples the trend of decreasing of  $^3\text{He}/^4\text{He}$  ratio from earlier rock units towards latest ones is failed by magnetite-calcite phosphorites, which are characterized by considerable variations of the ratio. This finding could mean at least two generations of magnetite to be present in varying proportions in some phosphorites.

Gases trapped into fluid inclusions (FI) concentrate 1-40 % of  $^4\text{He}$ , 10-90% of  $^3\text{He}$  and 5-55% of  $^{40}\text{Ar}$  and  $^{36}\text{Ar}$  of total gases extracted from whole minerals (see Tables 2 and 4). Our

TABLE 3  
Concentrations of parent elements and a comparison between calculated and bulk measured He and Ar abundances

Sample #	U ppm	Th ppm	K wt. %	Li ppm	Calculated			Measured		
					<sup>4</sup> He μcm <sup>3</sup> /g	<sup>3</sup> He pcm <sup>3</sup> /g	<sup>40</sup> Ar μcm <sup>3</sup> /g	<sup>4</sup> He μcm <sup>3</sup> /g	<sup>3</sup> He pcm <sup>3</sup> /g	<sup>40</sup> Ar μcm <sup>3</sup> /g
8px	2.3	0.5	0.08	0.05	112	0.0025	1.3	27.4	111.5	6.3
8mg	0.8	0.5	0.06	7.8	42.6	0.034	0.92	53.8	522.2	11.2
9fr	0.5	5.7	0.05	6.0	85.4	0.35	0.79	22.6	121.6	2.5
9ap	0.8	15	0.004	0.1	196	0.005	0.07	33.6	24.8	2.3
11mg	3.8	177	0.03	1.8	2065	0.38	0.53	9.4	36.7	9.5
12mg	1.2	1.0	0.03	1.0	66.2	0.007	0.53	866	48.6	4.3
13mg	0.8	0.5	0.02	1.0	43.5	0.0046	0.29	22.7	105.6	3.5
16mg	0.15	1.5	0.05	1.0	23.0	0.0024	0.80	10.3	69.0	3.2
19ap	17.9	1623	0.18	0.4	18153	0.68	2.9	2500	82.5	3.7

Note: # of samples correspond to those in table 1.

data obtained on mineral separates representative of Kovdor and Sebyavr CAUCs show the isotope composition of noble gases in WM to have experienced less impact of the radiogenic isotopes produced *in-situ* as compared to those of crystal structure of rock-forming minerals. This finding is argued by higher correlation between <sup>4</sup>He and <sup>3</sup>He

concentrations and weak positive correlation <sup>40</sup>Ar and <sup>36</sup>Ar in fluid inclusions whereas such kind relations lack in case of bulk gas compositions. Trends revealed for abundances of He isotopes vs. their ratios show that the <sup>3</sup>He/<sup>4</sup>He values in WM depends mostly on <sup>4</sup>He concentration, whereas in FI it depends mostly on <sup>3</sup>He concentration.

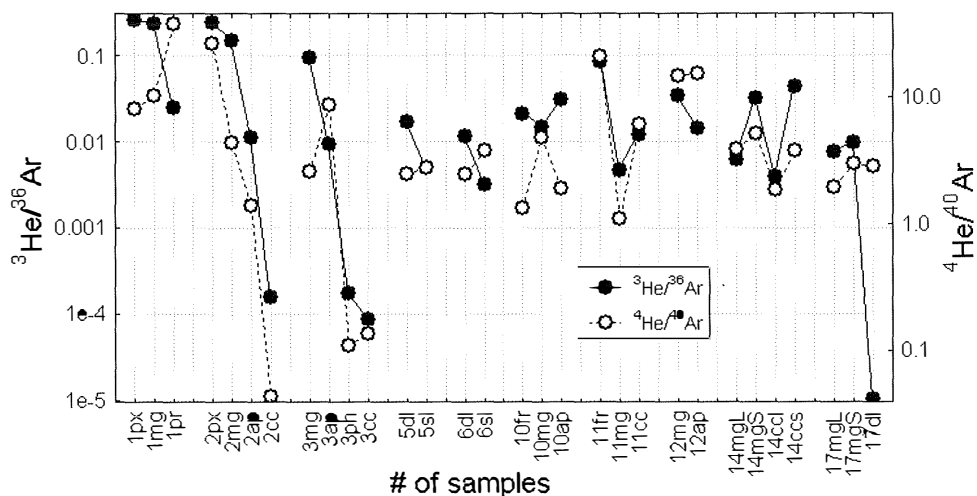


Fig. 2 – Relations of He and Ar isotopes in fluid inclusions. # of samples as in Tables 1 and 4.



TABLE 4  
He and Ar isotope abundances  
in fluid inclusions

Sample #	<sup>4</sup> He μcm <sup>3</sup> /g	<sup>3</sup> He/ <sup>4</sup> He E-8	<sup>40</sup> Ar μcm <sup>3</sup> /g	<sup>40</sup> Ar/ <sup>36</sup> Ar
1px	16.3	2381	2.5	1603
1mg	27.8	2165	3.5	1325
1pr	65.8	91	2.5	1016
2px	20.6	2557	1.5	650.5
2mg	17	2471	4.8	1678
2ap	3.8	552	3.3	1736
2cc	0.2	215	4.3	1924
3mg	12	2535	5.6	1706
3ap	4.2	213	0.8	790
3ph	0.3	182	3.4	1168
3cc	0.4	41	3.3	1837
5dl	2.8	1551	1.9	735
5sl	0.4	1045	0.4	465
6dl	1.9	1248	1.4	663
6sl	0.6	875	0.7	390
7mg	7.1	835	3.6	1883
8px	4.3	1348	1.2	2818
8mg	21.2	1406	n.d.	n.d.
10fr	20.1	351	16	4712
10mg	3.6	491	1.1	909
10ap	20.4	270	11.2	6077
11fr	1.1	1701	0.1	527
11mg	3.9	638	5.2	953
11cc	13.4	294	3.2	950
12mg	57.8	136	4.7	1974
12ap	29.7	68	2.4	1674
13mg	5.9	755	0.8	1509
14mgL	2.5	1280	2.2	419.4
14mgS	6.8	1545	2.3	690
14ccl	9.1	69	5.4	3266
14ccs	16.4	705	5.2	1930
15mg	26	513	n.d.	n.d.
15cc	134	251	n.d.	n.d.
17mgL	2.3	580	1.7	961
17mgS	15.7	339	7	1240
17dl	0.2	56	2.6	302
19ap	336	74	2.1	1490
20kd	0.04	260	0.2	296

Notes: # of samples correspond to those in Table 1; the mass-spectrometer measurements have been mostly performed by Dr. I.L. Kamensky.

The <sup>3</sup>He/<sup>4</sup>He ratio in *FI* of some samples is found to be mostly higher than the <sup>3</sup>He/<sup>4</sup>He value typical of MORB and always higher than those found in *WM*. So, the He isotope compositions in CAUC minerals confirm earlier revealed contributions of the upper mantle (predominant) and lower mantle fluid sources in complexes under consideration (Tolstikhin *et al.*, 1999). As a rule, Sebyavr rocks and minerals show higher <sup>3</sup>He/<sup>4</sup>He values than their Kovdor counterparts (Table 4). Similarly to *WM*, <sup>3</sup>He/<sup>4</sup>He ratios in *FI* extracted from the cognate minerals, as a rule, gradually decrease in phoscorite mineral consequence (forsterite-magnetite-phlogopite-calcite) and in magnesiocarbonatite (from dolomite to sulphides), but this trend in case of *FI* is more evident and reflects sequence of fractional crystallization or selective metasomatic recrystallization of the minerals. <sup>3</sup>He/<sup>4</sup>He value in some magnetite samples tends to be higher than those in co-existing clinopyroxene (sample #8) or forsterite (sample #10). This effect along with wide variations of <sup>3</sup>He/<sup>4</sup>He value in Kovdor magnetite samples representative of early magnetite-calcite phoscorites, might be superimposition of various factors like to several generations of magnetite and/or several generations of fluid inclusions in minerals, or in some extent – contamination of samples by associated and/or accessory minerals. Variations of Ar isotopes distribution and <sup>3</sup>He/<sup>36</sup>Ar and <sup>4</sup>He/<sup>40</sup>Ar (Fig. 2) ratios in couples magnetite-calcite and magnetite-fluorapatite from the same and from different samples of phoscorites can argue for the first of above-mentioned factors. Of the similar meaning are differences of isotope gas characteristics discovered for different magnetite generations (in case of morphologically distinctive generations of the mineral) from the same Kovdor magnetite-calcite phoscorite (sample #14). Well-formed large magnetite crystals have lower <sup>3</sup>He/<sup>4</sup>He, <sup>40</sup>Ar/<sup>36</sup>Ar, <sup>4</sup>He/<sup>40</sup>Ar and <sup>3</sup>He/<sup>36</sup>Ar values as compared to anhedral smaller grains of the same mineral. The latter is contrary to some suggestions (*e.g.* Seryodkin, 2001) concerning

to relict nature of the large well-developed magnetite crystals and their origin by desegregation of the earliest phoscorite units. The coincident differences in the same isotope ratios with exception of  $^{40}\text{Ar}/^{36}\text{Ar}$  are found in calcite samples, associated to large euhedral magnetite crystals and aggregates of anhedral magnetite grains.

In case of different magnetite generations from the Kovdor magnesiocarbonatite #17, the difference of isotope compositions is not so distinctive: in relatively large-crystalline magnetite aggregate lower  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^4\text{He}/^{40}\text{Ar}$  values are found, but  $^3\text{He}/^4\text{He}$  value is higher than those in smaller-grained magnetite. We can suppose in the case of the latter sample the different generations of magnetite to be not properly separated.

The  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio in *FI* is mostly lower those in *WM*. The lowest values, comparable to atmospheric constant, are found in postmagmatic (hydrothermal) Kovdor mineral assemblages developed within vuggy magnesiocarbonatite veins and in dolomite composing the latest dolomite phoscorite. These observations confidently testify to increasing of meteoric water input at the late stage of CAUC evolution at the upper crustal levels.

#### CONCLUSIONS

Our data allow the next conclusions. Fluid extractable from the most studied minerals, including those of economic value, has been formed by mixing of different proportions of mantle, crustal and atmospheric components at the consecutive stages of formation of CAUCs. The mantle fluid (taken as an juvenile end-member) was characterized by high  $^3\text{He}/^4\text{He}$  and probably rather low  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios. The crustal fluid could be the deep-circulated or stale underground waters, which had low  $^3\text{He}/^4\text{He}$ , variable  $^{40}\text{Ar}/^{36}\text{Ar}$  and elevated  $^4\text{He}/^{40}\text{Ar}$  values. Atmospheric input in phoscorite-carbonatite system was provided due to circulation of meteoric waters possessing the air-type  $^{40}\text{Ar}/^{36}\text{Ar}$  coupled to low  $^4\text{He}/^{40}\text{Ar}$  and  $^3\text{He}/^{36}\text{Ar}$  values. Also

magmatic and postmagmatic fluids can be distinguished.

Mixture of initial mantle and crustal fluids could happen both during pre-crystallization evolution of magmatic systems or be coincident with differentiation and fractional crystallization of the mantle-derived magma intruded at crustal level. The primary fluid mostly had been lost during these magmatic stages. At late postmagmatic stage, parallel to cooling of CAUC intrusives, the input of meteoric water to mineral-forming systems within these complexes was instantly increasing. The early postmagmatic processes within CAUCs were mostly of autometasomatic character and were caused by cognate fluid phase.

Distribution of the He and Ar isotopes and variations of their ratios, first at all  $^3\text{He}/^4\text{He}$  and  $^3\text{He}/^{36}\text{Ar}$  values, are illustrative of fluid sources coincident with ore-forming mineralization, conditions and consequence of associated minerals crystallization, formation of rock units and rock associations. Further study of rare inert gases systematic in rocks and minerals of the CAUCs, coupled with other mineralogical-geochemical characteristics would allow us to make clearance in disputable theories of mantle genesis and crustal evolution of ultramafic-alkaline complexes, and related phoscorites and carbonatites bearing economically important deposits. The authors highly acknowledge Dr. I. L. Kamensky for his making the majority of gas isotope measurements and Dr. I. N. Tolstikhin for his useful consultations in gas-isotope data interpretation.

#### ACKNOWLEDGEMENTS

This study was supported by Russian Foundation for Basic Research (grant 00-05- 64174) and NSERC Foundation, Canada.

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