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

# Magma compositions and genesis of the rocks of the Mushugai-Khuduk carbonatite-bearing alkaline complex (southern Mongolia): evidence from melt inclusions

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ABSTRACT. — Inclusions in mineral-forming media were studied using various techniques including X-ray spectral and ion microanalysis. Based on this study, the compositions, formation conditions, and magma evolution were evaluated in the silicate rocks and ores of the Mushugai-Khuduk carbonatite-bearing alkaline complex in southern Mongolia. It was found that the rock-forming minerals of melanephelinite, leucite phonolite, shonkinite, theralite, quartz syenite, rhyolite, magnetite-apatite and celestite-fluorite rocks crystallized from silicate, salt-silicate, and salt melts. The silicate melts form a continuous series from basic to rhyolitic compositions with SiO<sub>2</sub> contents from 47 to 77 wt %. The salt-silicate melts are silicate-phosphate in composition containing up to 10-20 wt % of P<sub>2</sub>O<sub>5</sub>. The salt melts show phosphatecarbonate, phosphate-sulphate, fluoride-sulphate, and chloride-sulphate compositions. The analysis of changes in melt composition during the crystallization of the complex allowed us to distinguish the processes that were responsible for the formation of specific rocks and ores and their evolution. It was established that the process of crystal fractionation played a leading role in the genesis of the volcanic and plutonic rocks. In addition, liquid immiscibility contribute to the formation of the rocks. The processes of liquid immiscibility were probably crucial for the genesis of the ore-bearing rocks.

RIASSUNTO. — Inclusioni in minerali costituenti le rocce sono state studiate utilizzando varie tecniche che includono spettrometria a raggi-X e microanalisi ionica. Sulla base di questi studi, la composizione, le condizioni di formazione e l'evoluzione del magma sono stati valutati per le rocce silicatiche e depositi minerari del complesso alcalino-carbonatitico di Mushugai-Khuduk, Mongolia meridionale. E'stato scoperto che nei minerali costituenti le rocce melanefelinite, leucite fonolite, shonkinite, theralite, quarzo sienite, riolite, magnatite-apatite e celestinafluorite sono cristallizati da un fuso silicatico, salesilicatico e salitico. I fusi silcatici formano una serie continua con composizione da basica a riolitica con contenuti di SiO<sub>2</sub> variabili tra 47 e 77 wt%. I fusi sale-silicatici hanno composizioni di silicati fosfatici con P2O5 fino a 10-20 wt%. I fusi salivi hanno composizioni di fosfato-carbonato, fosfato-solfato, fluoruro-solfato, cloruro-solfato. L'analisi del cambiamento di composizione del fuso durante la cristallizzazione del complesso, ci ha consentito di distinguere i processi che furono responsabili della formazione ed evoluzione di specifici tipi di rocce e mineralizzazioni. È stato stabilito che i processi di cristallizazione frazionata hanno giocato un ruolo fondamentale nella genesi di rocce vulcaniche e plutoniche. Inoltre, immiscibilità allo stato liquido ha contribuito alla formazione di queste rocce. I processi di immiscibilità allo stato liquido sono stati probabilmente cruciali per la formazione delle mineralizzazioni.

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KEY WORDS: Alkaline rocks, carbonatites, melt and fluid inclusions, silicate and salt magmas, crystal fractionation, liquid immiscibility.

#### INTRODUCTION

The problem of the origin of carbonatitebearing complexes has attracted considerable attention from researchers. The ore potential, diversity, and often uniqueness of rock compositions aroused a prolonged debate on the genesis of such complexes. The modern literature contains a considerable body of data petrology, mineralogy, and on the geochemistry of carbonatite-bearing associations from the world's regions. A number of experimental studies of carbonate and silicate-carbonate systems have been carried out. Nevertheless, the problem of carbonatite genesis is still controversial. In recent years, a number of researchers have studied fluid inclusions in minerals and gained valuable insights into the physicochemical conditions of formation of igneous complexes. However, until recently, melt inclusion studies have not been actively applied to the determination of magma composition of carbonatite-bearing complexes. There is limited evidence on the chemical compositions of magmas from such occurrences relating mainly to the carbonatite complexes of sodium-rich compositions. Potassium-rich carbonatitebearing alkalic complexes have hardly been touched in this respect. This paper presents results of a comprehensive study of the chemical and mineral compositions of magmas related to the alkalic and ore-bearing rocks of the Mushugai-Khuduk potassic carbonatitebearing complex (southern Mongolia), and their formation and evolution paths are evaluated on the basis of the analysis of inclusions of mineral-forming media.

#### SHORT GEOLOGICAL BACKGROUND

The geological structure of the Mushugai-Khuduk was considered in detail by Samoilov and Kovalenko (1983). The geological structure of the region is dominated by the rocks of Mesozoic and Palaeozoic age. The Mushugai-Khuduk complex is composed of a variety of extrusive, subvolcanic, and intrusive alkalic and subalkalic rocks varying in composition from melanephelinite and nepheline melaleucitite to trachydacite and latite in the volcanic facies and from shonkinite to quartz syenite in the plutonic facies. The orebearing rocks of the complex are spatially and genetically related to the alkalic magmatism. They are represented by mineralized breccias with carbonate cement, carbonatites, and apatite-rich rocks. The carbonatites are dominated by calcite varieties: fluorite-calcite, quartz-fluorite-calcite, barite-calcite, and others with varying amounts of non carbonate minerals. They are connected through gradual transitions with a series of vein rocks, where carbonate either occurs in subordinate amounts or is completely lacking. These rocks are represented by calcite-fluorite, fluorite-barite, celestite-fluorite, fluorite, calcite-fluoritequartz, fluorite-ankerite-quartz, calcite-baritefluorite-quartz, and quartz-fluorite-celestite varieties. Apatite-bearing rocks include magnetite-apatite, fluorite-celestite-magnetiteapatite, feldspar-apatite, and phlogopite-apatite varieties. They form veins and stockworks. Overall, in the area of the Mushugai ore occurrence, the volumes of carbonatite proper and other rocks of the carbonatite association (magnetite-apatite, fluorite, celestite-fluorite, etc.) are approximately equal. All the rocks of the Mushugai-Khuduk complex are enriched in rare earth elements, strontium, barium, and fluorine.

### INVESTIGATIONS OF MELT INCLUSIONS IN MINERALS

Primary inclusions of mineral-forming media represented by crystallized silicate, silicate-salt (silicate-phosphate) and salt melts were studied in different rock-forming minerals (apatite, diopside, phlogopite, potassic feldspar, sphene, zircon, quartz, fluorite) in the melanephelinites, phonolites, shonkinites, theralites, quartz syenites, rhyolites, magnetite-apatite and celestite-fluorite rocks (Andreeva *et al.*, 1998, 1999). Inclusions of mineral-forming media were studied using various techniques including X-ray spectral and ion microanalysis.

A wide spectrum of daughter minerals were revealed in melt inclusions in minerals of silicate rocks. Among them we identified apatite, celestite, baritocelestite, calcite, ankerite, and anhydrite, which are unusial for silicate rocks and compose the ore-bearing rocks of the complex (carbonatites and apatitemagnetite rocks). Crystallization of these minerals is caused by high P,  $CO_2$ , F and S contents in the alkaline silicate magma.

Inclusions of salt melts (phosphatecarbonate, phosphate-sulphate, fluoridesulphate, and chloride-sulphate) were detected in apatite and fluorite from theralite, orebearing apatite-magnetite and celestite-fluorite rocks. Apatite, calcite, magnetite, and sulphide were found as daughter minerals in salt melt inclusions in apatite from theralite. Microprobe investigations showed that the sulphide phase is chalcopyrite. Homogenization of salt inclusions appeared impossible because of their decrepitation at 400-500°C. Apatite, anhydrite, baritocelestite, calcite, fluorite, and magnetite were identified among the daughter crystalline phases in salt melt inclusions from the orebearing apatite-magnetite rocks. The daughter minerals of the salt inclusions in fluorite from celestite-fluorite rocks are represented by unusual sulphate phases, calcite, and halite (Andreeva et al., 1998).

Thermometric experiments with melt inclusions demonstrated that the alkalic rocks crystallized in a wide range of temperature, from 1220° to 850°C. The earliest rocks of the complex, melanephelinites, yielded the highest temperatures. The crystallization of their liquidus minerals, apatite and diopside, occurred at 1220-1200°C. The minerals (clinopyroxene, apatite, zircon, sphene, and alkali feldspar) of shonkinites, theralites, and phonolites were formed at temperatures from 1190° to 1110°C. The minerals of the quartz syenite (sphene, potassium feldspar, quartz), which is one of the latest rocks of the complex, crystallized at lower temperatures (except for apatite), from 1110° to 950°C. Very high homogenization temperatures obtained for melt inclusions in apatite of the quartz syenite (1200°C) are worth noting. They could result from the intratelluric nature of this mineral. The lowest homogenization temperatures (850°C) were obtained for melt inclusions in quartz of the rhyolite. The temperature of homogenization of salt melt inclusions from apatite-magnetite rocks is very high and extends above 1200°C. The celestite-fluorite rocks were formed at lower temperatures of 670-600°C.

The thermometric and cryometric investigations of melt and fluid inclusions in the minerals of the alkalic rocks allowed us to estimate the pressure of rock formation. During thermometric experiments, decomposition of daughter calcite crystals was repeatedly observed at 1100°C in melt inclusions from the melanephelenites. It was accompanied by the separation of carbon dioxide fluid. The fluid contained liquid and gas phases at ambient temperature and homogenized into a liquid phase at a temperature of +24.6°C. This temperature corresponds to a density of 0.72 g/cm<sup>3</sup>. The obtained parameters of mineral formation and P-V-T diagrams (Naumov, 1982) allowed us to estimate the pressure of melanephelinite (earliest rocks of the complex) crystallization as about 3 kbar. The presence of aqueous fluid inclusions coeval with melt inclusions in quartz from the syenite allowed pressure estimation for this rock, which was also no higher than 3 kbar.

The composition of silicate inclusions in minerals varies within a wide range of SiO<sub>2</sub> content, from 48 to 78 wt % (Table 1). The lowest concentration was found in the clinopyroxene of the melanephelinite. The composition of the earliest melts trapped in clinopyroxene from the melanephelinites is high in Fe, Ca, Ba, Sr, P, Ce, F, and S. Water content was determined on an ion microprobe as 0,11 wt %. The concentration of CO<sub>2</sub> is 0.55 wt %. Silicate-phosphate inclusions were found in apatites from all the rocks studied except for the rhyolite. Silicate inclusions with low P contents

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	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
SiO <sub>2</sub>	48.44	47.33	53.91	46.98	56.09	61.39	54.44	58.64	58.60	61.76	60.10	64.55	67.37	67.78	67.17	72.32	75.85
TiO <sub>2</sub>	0.88	0.90	1.26	2.56	0.81	0.61	6.63	5.28	0.47	0.15	0.74	2.66	4.26	1.40	0.46	0.06	0.05
Al <sub>2</sub> O <sub>3</sub>	10.05	10.60	15.12	9.31	15.34	19.33	16.57	17.61	18.20	19.21	19.10	10.30	9.84	11.12	16.54	12.01	9.68
FeO	7.34	6.22	5.16	10.58	4.77	1.84	5.07	3.83	3.74	0.64	3.13	3.30	2.48	2.45	1.13	1.25	1.26
MnO	0.17	0.10	0.10	0.40	0.21	0.08	0.07	0.11	0.00	0.01	0.11	0.20	0.07	0.03	0.00	0.06	0.73
MgO	10.07	9.85	4.57	8.90	5.16	0.97	0.34	0.32	2.06	0.16	0.12	0.36	0.10	0.10	0.08	0.06	0.04
CaO	12.08	11.93	6.11	12.63	6.54	2.63	5.58	4.76	1.11	3.11	2.91	3.91	5.01	1.78	0.24	0.13	0.10
BaO	0.34	0.73	0.46	0.23	0.07	0.61	0.15	0.09	0.03	0.61	0.99	0.22	0.13	0.06	0.06	0.02	0.04
SrO	0.73	1.47	0.48	0.00	0.00	0.49	0.06	0.00	0.05	0.51	1.28	0.19	0.00	0.05	0.00	0.06	0.03
Na <sub>2</sub> O	4.14	-3.54	3.86	1.89	5.96	4.86	3.33	2.74	4.50	6.08	4.66	2.11	1.91	3.31	5.18	4.99	4.37
K <sub>2</sub> O	4.03	6.05	3.91	3.59	3.97	5.34	4.96	5.61	9.48	6.79	5.99	6.85	4.83	7.06	8.52	5.24	3.44
$P_2O_5$	0.88	0.96	0.52	0.00	0.21	0.22	0.05	0.04	0.02	0.02	0.00	0.02	0.00	0.02	0.00	0.00	0.00
Ce <sub>2</sub> O <sub>3</sub>	0.09	0.23	0.01	0.15	0.10	0.23	0.43	0.35	0.04	0.09	0.05	0.61	0.00	0.15	0.13	0.26	0.42
La <sub>2</sub> O <sub>3</sub>	0.00	0.04	0.13	0.00	0.00	0.00	0.09	0.09	0.08	0.30	0.01	0.22	0.04	0.02	0.00	0.05	0.16
ZrO <sub>2</sub>	-	-	-	0.04	0.11	-	0.63	0.45	2.64	0.00	0.00	0.07	0.15	0.07	0.12	0.06	0.14
Cl	0.31	0.03	0.10	0.04	0.27	0.10	0.27	0.25	0.25	0.09	0.00	0.10	0.08	0.24	0.15	0.12	0.00
F	0.90	0.35	1.17	2.62	0.87	0.42	0.75	0.12	0.54	0.02	0.07	0.58	0.30	0.30	0.00	0.00	0.06
S	0.32	0.34	0.25	0.05	0.10	0.08	0.10	0.14	0.10	0.03	0.04	0.12	0.07	0.05	0.05	0.05	0.16
Rb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.16	0.40
Total	100.77	100.67	97.12	99.97	100.58	99.20	99.41	100.43	101.91	99.71	99.33	96.46	96.64	95.99	99.66	96.90	96.93
CO <sub>2</sub>	0.54	0.54	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H <sub>2</sub> O	0.11	0.12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Note: FeO is total iron. Homogenized glasses of melt inclusions in (1), (2) clinopyroxene of melanephelinite; (3) clinopyroxene of shonkinite; (4), (5) clinopyroxene of theralite; (6) potassium feldspar of shonkinite; (7), (8) sphene of theralite; (9) zircon of theralite; (10), (11) alkali feldspar of syenite; (12) -(14) sphene of syenite; (15) quartz of syenite; and (16), (17) quartz of rhyolite.

TABLE1

were found together with silicate-phosphate inclusions in apatite from the basic rocks (shonkinite). The glasses of silicate and silicatephosphate inclusions differ significantly in concentrations of P, Si, Ti, Al, Fe, Mg, Ca, and S (Table 2). It is very important that evidence of liquid immiscibility was found in several homogenized inclusions during electron microprobe investigations. These inclusions contain two glasses with different Ca and P contents (table 2, analyses 7-8).

The phosphate-carbonate melt that took part in formation of the theralites has high concentrations of REE elements and fluorine. The phosphate-sulphate melt, which was responsible for the formation of the magnetiteapatite ores, was characterized by high contents of Sr, F, and  $CO_2$ . The fluoride-sulphate and chloride-sulphate melts that was involved in the formation of the celestite-fluorite rocks are enriched, in addition to sulphur and calcium, in Sr,  $CO_2$  and Cl (Table 3). These elements are concentrated in the carbonatites and magnetite-apatite rocks of the Mushugai-Khuduk complex.

# GENESIS AND EVOLUTION OF MAGMAS OF THE MUSHUGAI-KHUDUK CARBONATITE-BEARING COMPLEX

According to modern petrogenetic concepts, alkalic magmas are derived from mantle sources and the formation of alkalic rocks is controlled by two major processes: (1) magma generation through partial melting of mantle material and (2) subsequent differentiation, which changes the composition of primary magmas in the course of their ascent toward the surface. The most probable mantle source of potassic alkalic rocks are phlogopite-bearing

TABLE 2

Chemical composition (wt %) of glasses from homogenized melt inclusions in apatite phenocrysts from the rocks of the Mushugai-Khuduk complex

	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	39.45	61.18	60.60	42.12	35.05	58.16	42.27	26.43	31.39	29.93
$TiO_2$	0.83	0.16	0.10	2.28	4.29	0.83	2.70	1.79	3.07	2.15
$Al_2 \tilde{O}_3$	11.86	18.83	19.60	14.79	10.78	15.52	14.53	9.63	11.02	6.87
FeO	7.27	1.10	0.73	6.31	8.37	4.93	5.80	3.44	7.48	10.35
MnO	0.03	0.17	0.12	0.19	0.25	0.05	0.10	0.08	0.30	0.45
MgO	10.01	0.33	0.31	9.66	10.13	2.35	6.52	5.19	12.16	8.14
CaO	12.22	2.88	2.84	10.39	13.39	6.52	10.31	24.16	14.22	20.14
BaO	0.64	0.55	0.68	0.71	0.63	0.24	1.09	0.07	0.53	0.01
SrO	0.95	0.17	0.18	0.29	0.24	0.86	0.51	1.28	0.07	0.29
Na <sub>2</sub> O	2.14	4.45	4.61	1.48	3.03	2.45	2.54	1.72	0.71	0.66
K <sub>2</sub> Ō	6.25	8.16	8.47	4.62	4.81	5.47	7.23	4.84	4.55	5.67
$P_2O_5$	7.87	0.12	0.54	7.12	8.70	2.30	6.59	14.22	9.41	13.31
$\tilde{Ce}_2O_3$	0.20	0.26	0.29	0.34	0.42	0.04	0.30	0.41	0.64	0.28
$La_2O_3$	0.04	0.06	0.08	0.14	0.14	0.00	0.07	0.18	0.25	0.10
Cl	0.05	0.01	0.01	0.05	0.31	0.02	0.02	0.16	0.00	0.01
F	0.25	0.02	0.02	0.40	0.33	0.08	0.15	3.93	0.56	0.37
S	0.20	0.08	0.12	0.14	0.24	0.13	0.29	0.81	0.10	0.47
Total	100.26	98.53	99.30	101.03	101.11	99.95	101.02	98.34	96.46	99.64

Note: FeO is total iron. Homogenized glasses of (2), (3), (6) silicate and (1), (4), (5), (7)-(10) salt-silicate melt inclusions in apatite of (1) melanephelinite; (2) - (4) phonolite; (5) - (8) shonkinite; (9) theralite; (10) quartz syenite.

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Calculated composition (wt %) of salt melts
in minerals from the ore-bearing rocks
of the Mushugai-Khuduk complex

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	1	2	3	4
$SiO_2$	0.8	0.5	-	-
FeÕ	2.6	0.5	-	-
CaO	54.5	44.0	35.0	26.0
BaO	-	0.45	1.2	1.9
SrO	-	6.0	9.9	5.7
Na <sub>2</sub> O	0.1	-	2.7	11.1
K <sub>2</sub> Õ	-	-	3.9	3.7
$P_2O_5$	17.6	17.0	-	-
Ce <sub>2</sub> O <sub>2</sub>	1.7	0.7	0.2	0.1
$La_2O_2$	0.7	0.3	0.3	0.3
Cl	-	0.05	0.1	10.9
F	1.8	3.7	5.5	2.1
$SO_2$	0.5	24.9	. 33.1	29.0
$CO_2$	19.7	1.9	2.1	4.5
H <sub>2</sub> Ô	-	-	6.0	4.7
Total	100.0	100.0	100.0	100.0

Note: phosphate-carbonate (1), phosphate-sulphate (2), fluoride-sulphate (3), chloride-sulphate (4) melts.

peridotites and clinopyroxenites, which could be produced in the course of intense mantle metasomatism (Ryabchikov, 1987). The mantle nature of magmas (including ore-bearing ones) of the Mushugai-Khuduk complex is consistent with the results of Rb-Sr isotope investigations (Samoilov and Kovalenko, 1983). The initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio of the rocks is 0.7054-0.7068, which agrees with the data on mantle-derived alkalic rocks and carbonatites from other world's regions. In this context, it is very important to estimate the composition of the primary magma and distinguish processes of its differentiation resulting in the formation of the diversity of rocks and ores of the Mushugai-Khuduk complex. As was mentioned above, the investigation of trace-element composition of the alkalic rocks supported the existence of a genetic link between them and their formation in the course of the differentiation of a single primary magma.

The analysis of our results allowed us to distinguish crystal fractionation and liquid immiscibility as being responsible for the formation of the rocks. Below, we consider in detail the role of each of these processes.

### Crystal Fractionation

The investigation of melt inclusions in the rock-forming minerals of the whole series of alkalic rocks allowed us to trace the evolution path of igneous melt during the process of formation of the Mushugai-Khuduk complex. Melts in the inclusions vary considerably in silica content and form a continuous series from ultrabasic and basic to silicic compositions. In order to assess the role of crystal fractionation, the behaviour of major components (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, FeO, MgO, CaO, P<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, and Ce<sub>2</sub>O<sub>3</sub>) was considered as a function of the Mg/(Mg + Fe) ratio in the melt (Fig. 1).

On the  $SiO_2 - Mg\# (Mg/(Mg + Fe))$  diagram, the compositions of silicate melts form a single trend of increasing SiO<sub>2</sub> content with decreasing Mg#. The highest Mg# is typical of from clinopyroxene in melts the melanephelinites, and the lowest, of melts from quartz of the syenites and rhyolites. At Mg# values from 0.6 to 0.1, the melts show a gradual increase in SiO<sub>2</sub> content, which is probably controlled by the crystal fractionation of clinopyroxene and minor amounts of other minerals: phlogopite, apatite, and magnetite. At Mg# = 0.1, there is a sharp increase in  $SiO_2$ content, which results from the fractionation of alkali feldspar from syenite melt with a minor role of Fe-Mg minerals.

The accumulation of  $Al_2O_3$  in the melts is related to the predominant role of clinopyroxene. In the intermediate compositions, the role of clinopyroxene diminishes and phlogopite fractionation becomes significant. The abrupt decrease in  $Al_2O_3$  content at low Mg# values is explained by the extensive fractionation of potassium feldspar from magma of a syenite composition. The decrease of CaO content in melts is controlled by clinopyroxene and apatite

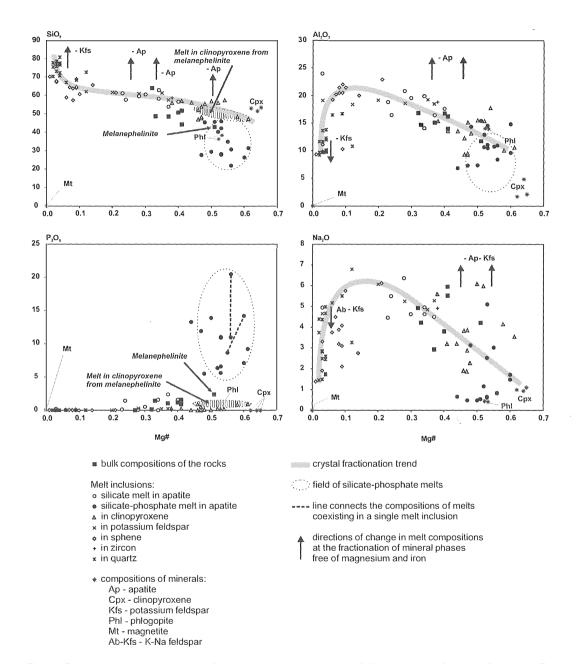
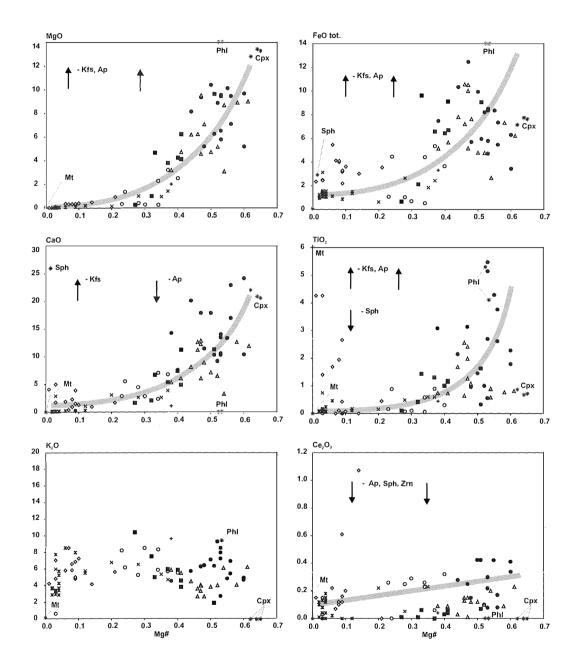


Fig. 1 – Compositional variations (wt %) of melt inclusions in the minerals of alkalic rocks as a function of Mg/(Mg + Fe) (Mg#) ratio in the melt.

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fractionation. At Mg# from 0.3 to 0, the evolution path flattens and melt fractionation occurs with an increasing role of potassium feldspar and sphene. The contents of FeO and  $TiO_2$  in the melt decrease with decreasing Mg#. The significant depletion of melt in FeO and TiO<sub>2</sub> at the transition from basic to intermediate melts is probably due to extensive phlogopite fractionation along with clinopyroxene, magnetite, and titanomagnetite. In the more silicic melts, fractionation processes are controlled by other assemblages with sphene instead of phlogopite.

The behaviour of  $Na_2O$  in the melts is similar to that of  $Al_2O_3$ .  $Na_2O$  increases in melts with decreasing Mg#. At the transition from intermediate to silicic compositions, there is a significant impoverishment of melts in this component owing to the extensive crystallization of alkali feldspar. The concentrations of  $K_2O$  in the melts are high and rather constant.

The variation diagrams reveal the main regularities in silicate melt evolution. The general trend is a decrease in the contents of MgO, CaO, TiO<sub>2</sub>, FeO, and  $Ce_2O_3$  and an increase in the contents of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and alkalis with decreasing Mg#. It should be noted that the trends formed by melt inclusions are consistent with the stoichiometry of the crystallizing minerals and bulk compositions of the rocks. The gradual and continuous changes in melt composition allow us to suggest the existence of a single initial magma responsible for the formation of the whole series of alkalic rocks of the complex. The major process was probably the crystallization differentiation of magma compositionally similar to the melanephelinite. The role of crystal fractionation is supported by the homogenization temperatures of melt inclusions, which demonstrate that the rocks formed at gradually decreasing temperatures, from 1220 to 850°C. On the other hand, the significant scatter of concentrations of the elements in the melts at constant Mg# value deserves special attention. Part of this scatter could be related to local effects and liquid immiscibility processes.

### Liquid Immiscibility

The investigation of inclusions in apatite demonstrate that almost all of the Mushugai-Khuduk rocks studied contain inclusions of silicate-phosphate melts with P<sub>2</sub>O<sub>5</sub> contents from 8 to 20 wt %. These melts are also characterized by high contents of Fe, Mg, Ca, Ba, Ce, La, and F. In addition to the saltsilicate inclusions with high P, Fe, Mg, and Ca contents, apatite phenocrysts in the phonolites and shonkinites bear inclusions of silicate melts with low contents of these components. An important result of our study is the finding of phosphate-silicate inclusions formed at the earliest stage of complex formation, in apatite from the melanephelinites, which supports the crystallization of this mineral from silicatephosphate melt.

The compositions of the silicate-phosphate inclusions in apatite do not follow the trend formed by silicate melts. They cluster within a narrow interval of Mg#, from 0.5 to 0.6, which corresponds to the range of the basic melts (Fig. 1). Silicate-phosphate melts were found in apatite from all the rocks studied including the quartz syenites. These melts show similar characteristics: high Mg# and а homogenization temperature of about 1200°C. It is probable that the apatite with silicatephosphate melt inclusions from the quartz syenites is an intratelluric mineral, which could occur suspended in magma and was then transported mechanically into the zone of residual liquid. Such a mechanism of mineral distribution in the course of apatite-bearing magma differentiation (gravitation kinetic hypothesis) was proposed by Kogarko (1977, 1999) as a model for the genesis of apatite deposits. Apatite and clinopyroxene are liquidus minerals of the melanephelinite and both silicate and silicate-phosphate melts contributed to their formation. This suggests that the magmatic system was heterogeneous at the moment of melanephelinite formation and the minerals crystallized from at least two melts of silicate and silicate-phosphate compositions.

The data obtained demonstrate that already at

the early stages of alkalic magmatism at temperatures higher than 1220°C, the initially homogeneous melt enriched in P, CO<sub>2</sub>, F, and S was separated into two independent liquids of silicate and silicate-phosphate compositions.

Salt inclusions of phosphate-carbonate compositions coeval with silicate-phosphate inclusions were found in the apatite of the theralites. The coexistence of phosphatecarbonate and silicate melts enriched in salt components in the same growth zones of apatite suggests that the latter crystallized under conditions of phosphate-carbonatesilicate liquid immiscibility. The high homogenization temperatures of the phosphatesilicate inclusions allow us to conclude that the separation of the salt melt of phosphatecarbonate composition from silicate-phosphate magma occurred at early magmatic stages of the formation of the complex and was accompanied by considerable enrichment of the salt melt in Ca, P, F, S, and rare earth elements. The possibility of phosphate salt melt generation at high temperature through liquid immiscibility is supported by direct observations in inclusions. As was noted above, two immiscible glassy phases with a distinct boundary between them were obtained in a single inclusion in apatite from shonkinite at a temperature of 1200°C.

## The general scheme of magma evolution for the formation of Mushugai-Khuduk rocks

Melanephelinitic magma was parental for the whole series of alkalic rocks. The magma was heterogeneous and consisted of silicate and silicate-phosphate melts. The available experimental and theoretical data provide evidence for the existence of anomalous segments in the upper mantle composed of phosphate-bearing peridotite, whose melting of which could produce phosphorus-rich melts (Kogarko and Ryabchikov, 1983). The content of phosphorus in the mantle is comparable with that of the CO<sub>2</sub> content: 100-700 ppm CO<sub>2</sub>

(Ryabchikov, 1988) and 170-210 ppm of  $P_2O_5$ (Ryabchikov *et al.*, 1989; Sun, 1982). Such melts could yield immiscible silicate and silicate-phosphate liquids even at early stages of evolution. The crystallization of the melanephelinite magma that was parental of the whole alkalic series began under dry conditions at a temperature of 1220°C. The differentiation of the silicate-phosphate melt resulted in the appearance at 1200°C of salt melt of a carbonate-phosphate composition via the mechanism of liquid immiscibility. Probably, the genesis of rare earth elementbearing carbonatites was related to such melts.

The ore-bearing magnetite-apatite rocks of the complex were generated from salt magmas. which were characterized by great diversity and unusual compositions, including phosphate-sulphate, fluoride-sulphate, and chloride-sulphate melts. We emphasize that these data demonstrate that the evolution of alkalic magmas may be accompanied by the formation of immiscible carbonate melts, which is recognized by many petrologists, and, more unusual sulphate-dominated melts with high Cl and F contents. The subsequent evolution of salt fluoride-sulphate and chloridesulphate melts resulted in water accumulation in residual liquids and formation of hydrous salt melts and eventually, concentrated aqueous solutions.

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