

## SILICATE-SULFATE LIQUID IMMISCIBILITY: A STUDY OF INCLUSIONS IN MINERALS OF THE MUSHUGAI-KHUDUK CARBONATITE-BEARING COMPLEX, SOUTHERN MONGOLIA

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Late Mesozoic alkaine volcanoplutonic complexes with REE-bearing carbonatites and magnetite-apatite ores were discovered in southern Mongolia. A typical example of such objects is the Mushugai-Khuduk complex. It hosts a REE deposit of the same name, which is unique in size and REE concentrations. In this report, we present the results of an investigation of melt and crystal inclusions in minerals of ore-bearing garnet syenite porphyry, which was recovered during exploratory drilling in the region of the Mushugai ore occurrence. This peculiar rocks is composed of garnet crystals up to 5–6 cm across in a syenite mesostasis. The phenocryst assemblage of the syenite porphyry is dominated by potassium feldspar, diopside, and plagioclase. Sphene, phlogopite, zircon, apatite, magnetite, ilmenite, and pyrite are accessory and minor minerals. It is significant that a number of salt minerals including calcite, celestite, and fluorite were detected in the accessory mineral association.

Primary crysalline and melt inclusions were found and studied in garnet, diopside, sphene, and potassium feldspar from this rock. It is noteworthy that melt inclusions in garnet have been very rarely described in the literature (Chupin, 2001; Titov, 2001).

Crystalline inclusions coexisting with melt inclusions are represented by phlogopite, potassium feldspar, albite, sphene, apatite, magnetite, and calcite in diopside; diopside, sphene, and fluorite in potassium feldspar; and celestite and magnetite in sphene. The garnet hosts crystalline inclusions of diopside, potassium feldspar, gypsum, calcite, wollastonite, and a phosphate minerals (16–23 wt % P<sub>2</sub>O<sub>5</sub>) with elevated contents of SiO<sub>2</sub> (10 wt %), Ce<sub>2</sub>O<sub>3</sub> (5–7 wt %), La<sub>2</sub>O<sub>3</sub> (3 wt %), F (2–3 wt %), S (up to 3 wt %), ThO<sub>2</sub> (up to 2.5 wt %), Nd<sub>2</sub>O<sub>3</sub> (up to 1.7 wt %), and Sm<sub>2</sub>O<sub>3</sub> (up to 1 wt %). The composition of this phase is transitional between those of apatite and bristolite.

The minerals of the garnet syenite porphyry bear crystallized silicate (in diopside, sphene, and potassium feldspar) and salt (in garnet and diopside) melt inclusions. The silicate melt inclusions in sphene and potassium feldspar are made up of a fine-grained aggregate of isotropic and anisotropic crystals, which were not identified because of their small sizes. Amphibole and calcite were detected among the daughter minerals of silicate melt inclusions in diopside. Calcite and Na-Ca sulfate occur as daughter crystals in the salt melt inclusions in garnet. A similar Na-Ca sulfate was found by us among the daughter minerals of fluoride-sulfate and chloride-sulfate inclusions in fluorite from the fluorite-celestite rock of the Mushugai-Khuduk complex.

In order to estimate the physicochemical parameters of magma crystallization, thermometric experiments were performed with melt inclusions in minerals of the garnet syenite porphyry. The silicate and salt melt inclusions were homogenized at 1080–1010°C in diopside, 1030–1010°C in sphene, 1040 in potassium feldspar, and 930°C in garnet. The behavior of the salt melt inclusions during thermometric experiments was rather peculiar. Salt melt inclusions cannot be usually quenched to glasses even at very fast cooling and produce aggregates of small crystals. In contrast, homogeneous glasses were obtained in the thermometric experiments with salt melt inclusions in diopside and garnet from the Mushugai-Khuduk complex. Nonsilicate carbonate-rich glasses were obtained in the experiments of Jones and Wyllie (1983) in the CaCO<sub>3</sub>-Ca(OH)<sub>2</sub>-CaF<sub>2</sub>-BaSO<sub>4</sub>-La(OH)<sub>3</sub> system.

Homogeneous silicate and salt glasses obtained after thermometric experiments were analyzed with an electron microprobe (Table). The silicate glasses in diopside showed elevated contents of FeO (up to 6 wt %), CaO (3–7 wt %), MgO (up to 2.8 wt %), F (up to 1.6 wt %), Cl (up to 0.2 wt %), and ZrO<sub>2</sub> (up to 0.2 wt %). Their SiO<sub>2</sub> content varies from 56.6 to 63 wt %, and Al<sub>2</sub>O<sub>3</sub> from 15.5 to 17.0 wt %. Melts trapped in sphene are rich in FeO (up to 2.7 wt %), TiO<sub>2</sub> (up to 2.8 wt %), CaO (3–7 wt %), ZrO<sub>2</sub> (up to 0.8 wt %), and F (up to 0.9) and essentially free of MgO (0.03–0.08 wt %). Their SiO<sub>2</sub> contents range from 62–66 wt % and Al<sub>2</sub>O<sub>3</sub>, from 15.0–19.5 wt %. The compositions of homogenized glasses from potassium feldspar are high in FeO (3 wt %), CaO (3 wt %), BaO (0.3 wt %), and ZrO<sub>2</sub> (up to 0.13 wt %) and low in TiO<sub>2</sub> (0.06–0.20 wt %) and MgO (0.4–0.7 wt %) at an SiO<sub>2</sub> content of 64 wt % and Al<sub>2</sub>O<sub>3</sub> of 18 wt %. All the silicate melts studied are conspicuous in very high alkali contents: Na<sub>2</sub>O+K<sub>2</sub>O from 9 to 17 wt % and a predominance of K<sub>2</sub>O over Na<sub>2</sub>O (K<sub>2</sub>O/Na<sub>2</sub>O ~ 3 : 1). The concentrations of various components in the melts vary regularly with increasing SiO<sub>2</sub> content (differentiation degree): FeO, MgO, CaO, and F decrease and Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, BaO, and ZrO<sub>2</sub> increase. The compositions of silicate melts trapped in diopside, sphene, and potassium feldspar of the garnet syenite porphyry fall within the peralkaline syenite field of the SiO<sub>2</sub> – Na<sub>2</sub>O+K<sub>2</sub>O classification chart.

An important result of our investigation is the discovery of salt melt inclusions in garnet and diopside coexisting with silicate melt inclusions. The inclusions of silicate and salt melts were documented both in different crystals and coexisting in a

Table. Chemical composition of silicate and salt melts obtained from the study of inclusions in minerals of the garnet syenite-porphry, wt%

	1	2	3	4	5	6	7	8	9	10	11
SiO <sub>2</sub>	56.66	63.06	63.06	66.37	63.78	63.91	0.39	0.64	6.21	0.95	-
TiO <sub>2</sub>	0.78	2.59	2.59	1.43	0.17	0.06	0.02	0.05	0.25	0.00	-
Al <sub>2</sub> O <sub>3</sub>	15.49	15.12	15.12	18.10	18.17	17.90	0.14	0.14	1.87	-	-
FeO	3.71	2.62	2.62	1.39	3.20	2.83	0.44	0.44	1.24	0.94	-
MnO	0.08	0.10	0.10	0.06	0.06	0.00	0.03	0.05	0.03	-	-
MgO	2.23	0.06	0.06	0.27	0.41	0.67	0.00	0.21	0.32	-	-
CaO	6.74	4.34	4.34	2.01	2.81	3.12	31.35	32.95	34.11	30.61	35.0
BaO	0.04	0.12	0.12	0.00	0.30	0.34	0.09	0.60	0.57	0.60	1.2
SrO	0.31	0.11	0.11	0.00	0.37	0.17	1.50	1.72	1.48	1.76	9.9
Na <sub>2</sub> O	2.58	3.21	3.21	4.17	4.19	4.76	5.55	4.70	3.10	5.03	2.7
K <sub>2</sub> O	9.74	6.23	6.23	6.24	7.33	7.31	3.43	4.25	4.09	7.14	3.9
P <sub>2</sub> O <sub>5</sub>	0.00	0.05	0.05	0.01	0.01	0.04	0.37	0.56	0.52	1.23	-
Ce <sub>2</sub> O <sub>3</sub>	0.07	0.21	0.21	0.10	0.14	0.16	0.21	0.20	0.21	0.40	0.02
La <sub>2</sub> O <sub>3</sub>	0.01	0.11	0.11	0.07	0.00	0.06	0.02	0.00	0.06	0.13	0.3
ZrO <sub>2</sub>	0.11	0.53	0.53	0.85	0.08	0.13	-	-	-	-	-
F	1.12	0.59	0.59	0.95	0.02	0.28	1.68	1.88	1.61	1.96	5.5
Cl	0.18	0.14	0.14	0.04	0.02	0.00	1.02	1.01	1.13	-	0.1
SO <sub>3</sub>	0.17	0.37	0.37	0.08	0.08	0.05	42.30	40.42	30.65	42.62	33.1
CO <sub>2</sub>	-	-	-	-	-	-	-	-	-	-	2.1
H <sub>2</sub> O	-	-	-	-	-	-	-	-	-	-	6.0
Total	99.92	99.32	99.32	100.13	101.09	101.76	88.54	89.83	87.45	93.37	100.00

Note: FeO is total iron. Homogenized glasses of melt inclusions in (1) - (2) and (10) clinopyroxene, (3) - (4) sphene, (5) - (6) alkali feldspar, (7)-(9) garnet of the garnet syenite-porphry. (10) calculated chemical composition of salt melt in fluorite from the celestite-fluorite rock of the Mushugai-Khuduk complex.

single diopside grain. The compositions of salt melt inclusions show high concentrations of CaO (32-38 wt %), SO<sub>3</sub> (37-40 wt %), Na<sub>2</sub>O+K<sub>2</sub>O (up to 8 wt %), Cl (up to 1.2 wt %), and F (up to 3.8 wt %), i.e. they are dominated by Ca and alkali sulfates. Chemically similar sulfate melts were found previously in fluorite from the celestite-fluorite ore of the Mushugai-Khuduk complex (Andreeva et al., 1998).

The investigation of melt inclusions in minerals of the garnet syenite porphyry demonstrated that this rock crystallized from a silicate melt compositionally similar to peralkaline syenites and a sulfate melt. The occurrence of syngenetic silicate and salt melt inclusions with identical homogenization temperatures (1080°C) in diopside grains suggests that this rock was formed under conditions of silicate—sulfate liquid immiscibility. The occurrence of unusual (for an igneous rock) minerals as daughter phases in melt inclusions and as crystalline inclusions in phenocrysts testifies for their crystallization from a magmatic liquid.

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