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Immiscibility of Silicate and Salt (Li, Na, F) Melts in Comendite at the Zaart Khudag Ore Occurrence, Central Mongolia: Evidence from Melt Inclusions

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The continental rift-related magmatism is characterized by abundant rocks of elevated alkalinity and bimodal igneous associations with predominance of alternating basic and silicic rocks. The alkaline felsic rocks, including alkali granite and comendite, pantellerite, and trachyte as its volcanic equivalents, often contain diverse rare-metal and rare-earth mineralizations (REE, Zr, Nb, Ta, Li, Be, and others) that attain economic importance in some cases. Although rift-related bimodal magmatism is widespread in central Asia, the information on the composition and physicochemical parameters of such magmas is obviously insufficient.

The objective of this work is to determine formation conditions and evolution of felsic (comenditic and pantelleritic) rocks of the bimodal series and to ascertain the mechanism of fractionation that initiates ore formation. We investigated the Zaart Khudag rare-metal occurrence (central Mongolia) with a particular emphasis on the role of the Li- and Na-rich natural salt fluoride melts in the formation of bimodal associations. We discovered the melt inclusions in quartz phenocrysts of comendite. The results of our investigation of them are presented below.

The Zaart Khudag paleovolcano, more than 120 km^2 in area, was found in the course of regional geological mapping. The U–Pb zircon age of syenite located in this paleovolcano is 211 Ma. The paleovolcano is composed of intercalating alkali trachydacite, comendite, pantellerite lavas, tuffs, and ignimbrites. The volcanic sequence more than 600 m in thickness is crosscut by subvolcanic comendite intrusions and peralkaline syenite. Fluidal, eutaxic, aphyric, and porphyritic lavas are prevalent, while ignimbrites are less abundant. The rocks are often altered and replaced with chalcedony, especially near subvolcanic bodies. The unaltered varieties correspond to alkali silicic rocks of K–Na series with $(Na_2O + K_2O)/Al_2O_3 > 1$. These rocks are enriched in F, REE, Zr, and Rb (Table 2, analysis 1). The REE content in the rocks replaced with chalcedony increases to *n* wt %.

Comendite with crystalline and melt inclusions is a porphyritic rock that contains up to 20% alkali feldspar, quartz, and alkali amphibole phenocrysts. The felsitic groundmass consists of alkali feldspar, quartz, alkali amphibole, and fluorite. Zircon is the most abundant accessory mineral.

Primary melt and coexisting crystalline inclusions were recorded in the quartz of comendites.

The chemical composition of crystalline inclusions, mineral phases in melt inclusions, and residual and homogenized glasses from melt inclusions were determined with electron X-ray microprobe (major elements) and secondary-ion mass spectroscopy (H_2O and trace elements). The electron microprobe analysis was performed at an accelerating voltage of 15 kV and current of 30 nA. The ion microprobe analysis (SIMS) was carried out with an IMS-3F Cameca microanalyzer at the Institute of Microelectronics, Russian Academy of Sciences, Yaroslavl (S.G. Simakin, analyst).

Amphibole, fluorite, ilmenite, and chevkinite (REE diorthosilicate) were identified in crystalline inclusions. In chemical composition, amphibole corresponds to riebeckite with an extremely high F content (up to 4 wt %). The K_2O content in riebeckite reaches 1 wt % (Table 1, analysis 1). The ilmenite inclusions contain up to 6.5 wt % MnO. In addition to major oxides, up to 38 wt % Ce_2O_3 and La_2O_3, 0.9 wt % Nb_2O_5, 0.5 wt % Y_2O_3, 0.24 wt % ZrO_2, and 0.6 wt % F were detected in chevkinite (Table 1, analysis 2). Thereby, the deficiency in total is 6.5 wt %, probably owing to the presence of Pr, Nd, Sm, and Gd. The high concen-

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Table 1. Chemical composition of crystalline inclusions and residual glasses in melt inclusions in quartz from comendite, wt %

Component	1	2	3	4	5	6	7	8	9	10
SiO_2	51.25	20.63	1.42	66.75	66.90	67.47	68.74	68.92	69.77	70.70
TiO_2	1.28	19.58	51.32	0.09	0.23	0.24	0.24	0.27	0.23	0.26
Al_2O_3	1.54	0.07	0.09	14.31	11.85	11.93	12.19	12.46	11.70	11.83
FeO	31.69	12.04	41.89	1.97	4.97	4.76	4.25	4.40	4.34	4.34
MnO	0.52	0.01	6.45	0.11	0.08	0.11	0.08	0.04	0.08	0.07
MgO	0.00	0.03	0.01	0.02	0.04	0.04	0.05	0.04	0.04	0.04
BaO	–	–	–	–	–	–	–	–	–	–
SrO	–	–	–	–	–	–	–	–	–	–
CaO	1.51	1.65	0.00	0.10	0.13	0.16	0.18	0.19	0.17	0.16
Na_2O	8.20	0.02	0.00	7.91	8.64	9.91	8.44	6.31	8.64	7.29
K_2O	0.92	0.00	0.00	5.11	5.61	5.61	5.28	5.39	5.27	5.10
Ce_2O_3	0.02	21.04	–	–	–	–	–	–	–	–
La_2O_3	0.00	17.24	–	–	–	–	–	–	–	–
Nb_2O_5	–	0.93	–	–	–	–	–	–	–	–
F	4.35	0.61	–	0.24	0.32	0.43	0.44	0.72	0.26	0.27
Cl	0.02	0.00	–	0.34	0.39	0.32	0.36	0.32	0.34	0.36
S	–	–	–	–	0.01	0.00	0.00	0.01	0.00	0.01
Total	101.30	94.55	101.18	96.95	99.17	100.99	100.24	99.08	100.82	100.43

Note: (1–3) Crystalline inclusions: (1) amphibole (riebeckite?), (2) chevkinite (total is given with account of 0.46 wt % Y_2O_3 and 0.24 wt % ZrO_2), (3) ilmenite; (4–10) residual glasses of melt inclusions.

trations of these elements (total 5.7–6.8 wt %) were established in chevkinite from alkali granite in Sichuan Province, China [1]. Let us also note that chevkinite is a characteristic accessory mineral of alkali granites and syenites and related pegmatite veins [2, 3] but a rather rare mineral in volcanic rocks [4].

The quartz-hosted primary melt inclusions in comendite lack zonality. They occur as negative crystals, commonly varying in size from 30 to 40 μm. The inclusions contain glass, a gas phase, and a fine-crystalline (usually elongated and wormlike) salt aggregate (Fig. 1). The examination with electron and ion microprobes has shown that this aggregate consists of two phases: griceite (rare lithium fluoride) and villiaumite (sodium fluoride). To date, griceite was mentioned in the literature only once, as an inclusion in sodalite in hornfels at Mt. Saint-Ellier in Canada [5]. Villiaumite as a daughter phase of melt inclusions in rocks from Zaart Khudag massif was known previously [6]. The F content in griceite determined with the ion microprobe is 66.9–68.8 wt %; the high Li content was corroborated with the ion microprobe in qualitative terms. Villiaumite contains 49.3–50.4 wt % Na and 42.3–46.7 wt % F.

The residual (unheated) glasses in melt inclusions are characterized by elevated (relative to rock) Na_2O contents reaching 6–10 wt %, F (0.2–0.7 wt %), and Cl (up to 0.4 wt %) at 66.7–70.7 wt % SiO_2 and 11.7–14.0 wt % Al_2O_3 (Table 1, analyses 4–10). The water content in glass does not exceed 0.5–0.7 wt %. In the SiO_2–(Na_2O + K_2O) diagram, the compositions of the studied residual glasses from melt inclusions fall into the pantellerite field.

Observation of inclusion behavior during heating on a Linkam TS 1500 microscope heating stage with visual control allowed us to point out the following changes of their phase composition (Fig. 2).

The first signs of melting are observable at 600°C. A gas bubble appears in a salt segregation. During the heating, this bubble was displaced repeatedly indicating a low viscosity of the salt melt. The gas phase in salt segregation dissolved completely at 700°C and always before the complete melting of crystalline phases. The salt segregation undergoes intense melting and becomes spherical in shape at 750°C. Further increase in temperature leads to the almost complete melting of salt minerals within the segregation. Immiscibility of silicate and fluoride melts is established in fluid inclusions at 810°C. At 860°C, the salt melt completely dissolves in the silicate melt. The temperature of partial homogenization with formation of a homogeneous melt and a gas bubble is 900°C. The ultimate homogenization of inclusions is achieved at 1030°C.

In chemical composition, the homogenized melt inclusions are close to comendite and characterized by high contents of SiO_2 (72.0–78.6 wt %), FeO (up to 5 wt %), Na_2O (5–7 wt %), and K_2O (3.6–4.7 wt %) and a relatively low content of Al_2O_3 (7.8–10.0 wt %). The

Table 2. Major oxides (wt %), volatile components (wt %), and trace elements (ppm) in rocks and quartz-hosted melt inclusions in comendite from the Zaart Khudag massif

Component	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	71.75	72.14	76.67	75.53	76.92	77.24	75.57	76.63	77.79	78.66	77.88	77.35
TiO_2	0.32	0.26	0.16	0.20	0.18	0.21	0.14	0.20	0.19	0.14	0.14	0.20
Al_2O_3	10.86	10.38	8.52	8.08	8.49	8.90	8.37	8.24	8.43	8.74	7.86	8.12
FeO	7.16*	4.86	3.02	3.03	2.77	2.79	2.91	3.14	2.62	2.69	2.53	2.60
MnO	0.03	0.05	0.00	0.07	0.00	0.12	0.05	0.03	0.04	0.07	0.00	0.05
MgO	0.08	0.04	0.01	0.01	0.06	0.00	0.02	0.03	0.01	0.02	0.02	0.03
CaO	0.15	0.10	0.15	0.12	0.10	0.11	0.14	0.10	0.12	0.07	0.09	0.09
Na_2O	2.69	6.35	6.75	6.80	6.50	6.01	6.64	6.32	6.57	5.13	6.69	6.84
K_2O	4.22	4.75	4.21	4.10	4.23	4.33	4.18	4.12	3.79	3.81	3.62	3.64
F	0.03	2.84	0.88	1.37	1.55	1.63	1.44	0.98	1.62	2.33	1.15	1.27
Cl	0.03	0.07	0.22	0.19	0.22	0.23	0.18	0.26	0.18	0.22	0.21	0.22
H_2O	1.85	0.38	1.43	0.67	0.45	–	0.87	0.61	0.63	0.74	0.58	0.76
F=O	–	1.19	0.37	0.57	0.65	0.68	0.60	0.41	0.68	0.98	0.48	0.53
Total	99.17	101.03	101.65	99.60	100.82	100.89	99.91	100.25	101.31	101.64	100.29	100.64
Li	37.9	486	1936	1832	1074	631	1794	1665	753	335	1095	424
Be	13.8	29.0	18.6	23.4	22.2	16.3	27.9	26.2	19.6	21.4	22.0	15.6
B	–	42.5	28.6	39.6	39.6	27.7	45.1	40.0	34.9	40.0	40.2	27.8
V	4.0	8.1	3.1	7.4	5.7	2.4	3.0	3.7	9.0	7.5	8.0	9.5
Rb	598	499	308	431	396	261	353	383	465	545	516	424
Sr	17.3	4.6	2.7	3.5	2.8	5.8	3.1	3.0	3.8	3.9	4.0	3.4
Y	373	243	129	163	144	108	142	147	155	191	196	144
Zr	3533	3737	1602	1786	1867	1300	1579	1535	1912	2584	2398	1488
Nb	169	173	127	126	118	92.7	113	112	133	165	173	118
Ba	111	6.5	5.9	6.5	5.2	8.2	6.1	5.9	7.6	7.7	7.3	7.0
La	228	116	73.7	94.0	91.0	61.6	79.0	80.4	96.6	114	113	90.5
Ce	415	256	187	219	207	144	188	188	222	270	277	211
Nd	161	109	66.1	88.1	80.3	55.1	68.4	70.9	87.2	110	110	83.4
Sm	39.4	28.0	17.0	21.9	20.0	13.2	17.3	18.3	21.8	26.5	27.5	20.9
Eu	0.4	0.4	0.2	0.3	0.2	0.2	0.2	0.2	0.3	0.4	0.4	0.3
Gd	38.4	28.1	19.4	27.2	17.7	14.4	17.1	25.1	0.0	0.0	29.1	26.0
Dy	43.0	37.6	21.8	25.1	21.1	16.5	19.4	20.6	24.7	33.0	33.4	24.7
Er	28.5	28.2	17.5	19.7	16.5	13.3	15.9	15.7	20.1	25.4	28.6	18.6
Yb	27.7	33.5	18.0	23.3	19.1	14.7	16.7	18.9	21.8	29.7	29.2	22.8
Hf	59.5	85.0	42.0	39.4	41.9	32.3	33.3	32.7	45.1	64.8	60.4	35.0
Ta	9.8	11.1	8.2	7.5	7.1	5.8	5.8	6.8	8.8	9.1	11.5	7.8
Pb	187	84.9	30.7	61.3	57.0	42.1	44.8	51.1	67.8	94.2	90.2	70.8
Th	74.0	63.4	43.0	46.9	41.2	33.4	40.6	41.4	46.6	57.9	63.3	43.5
U	15.8	21.7	15.3	13.9	12.6	10.6	11.4	13.0	15.2	19.0	20.5	14.0
ΣTR	1039	722	463	558	515	365	455	471	540	674	709	533

Note: (1) Comendite; (2–12) glasses of homogenized melt inclusions. (*) Total iron.

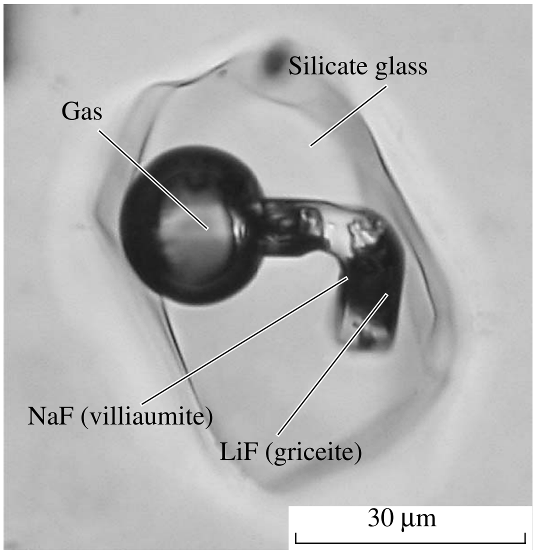

Fig. 1. A melt inclusion in quartz of comendite. Plane light, without analyzer.

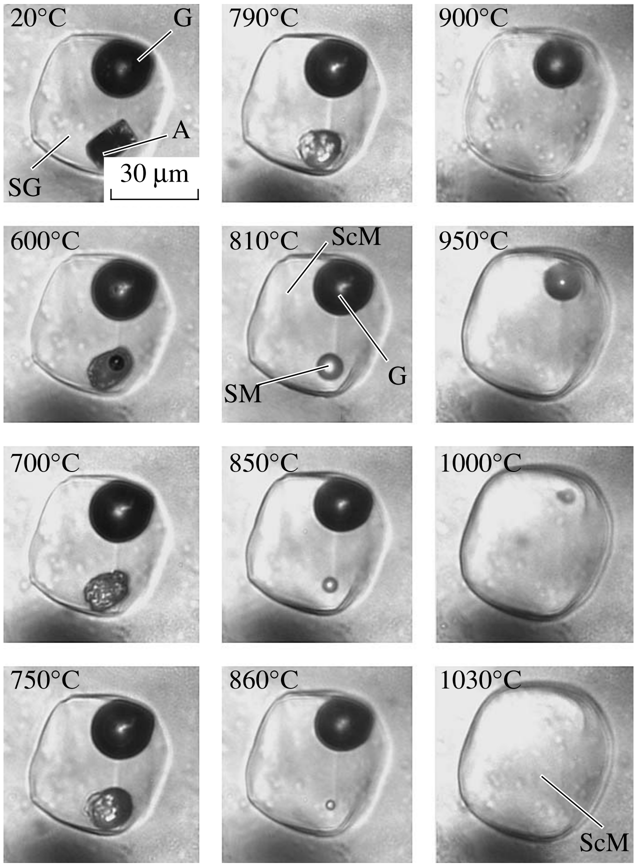

Fig. 2. Behavior of a melt inclusion in quartz of comendite during a thermometric experiment at 1 atm. (A) Fine-crystalline salt aggregate composed of villiaumite (NaF) and griceite (LiF); (G) gas phase; (SG) silicate glass; (SM) salt melt; (ScM) silicate melt.

agpaitic coefficient, i.e., $(Na_2O + K_2O)/Al_2O_3$ ratio, ranges from 1.20 to 2.05. According to the results of ion microprobe, the water content in the melt varies from 0.4 to 0.9 wt % and is broadly comparable with that in unheated inclusions. The F content in homogenized glasses of inclusions (1.0–2.8 wt %) is much higher than the F content in unheated residual glasses. The Cl content is 0.2–0.3 wt % (Table 2). Similar major oxide compositions have been reported previously by G.M. Tsareva et al. [6] who studied the fluid inclusions in quartz from Zaart Khudag comendite.

The trace element compositions of glasses from melt inclusions and rocks are presented in Table 2.

The comparison of chondrite-normalized trace element compositions of the homogenized melt inclusions and rocks has shown that they are close to each other (Fig. 3). The melts and rocks are sharply enriched in most HFSE (Th, U, Zr, Nb, Ta, Hf, Y) and reveal deep minimums of Ba, Sr, and Ti, because these elements were removed along with feldspar and ore minerals at the initial stage of melt fractionation.

The studied melt inclusions are distinguished by extremely high Li and Sr contents expressed in high peaks in the diagrams. The maximum Li concentration in glass of melt inclusions reaches 1800–1900 ppm, and the Zr content varies from 1300 to 3700 ppm. Such high Li contents exceed even those in melts parental for rare-metal granites. For example, the Li content in melt inclusions from alkali granite at the Khalzanburgedtei rare-metal deposit in western Mongolia does not exceed 230 ppm [7]. For the bimodal associations, the detected concentration of Li is comparable only with its contents in the quartz-hosted melt inclusions in comendite of the Tsagaan Khurtei massif in the western Transbaikal region [8] and in quartz from pantellerite in the Tost Range, southern Mongolia [9], where the Li concentrations reach 2040 and 1600 ppm, respectively. A substantial difference in Li behavior in rocks and melts should be noted. As follows from the diagram, in contrast to the melts, the rocks reveal a distinct Li minimum.

The chondrite-normalized REE patterns of glasses from melt inclusions and rocks are similar. In general, both varieties are enriched in REE with a slight prevalence of LREE over HREE. The total REE content in melts attains 720 ppm, while $(La/Yb)_N = 2–3$. A distinct Eu anomaly in melt inclusions testifies to the evolved character of comenditic melts, which likely correspond to the late magmatic derivatives of the Zaart Khudag Complex.

In the studied homogenized and residual (unheated) quartz-hosted melt inclusions in comendites, Zr, Th, Rb, Sr, Ba, Y, Eu, B, and Be reveal positive correlation with Nb. The incompatible behavior of these elements shows that minerals-concentrators of these elements were not fractionated at the given stage of the rock formation, so that the above elements were gained in the residual melt. In melt inclusions from all studied rocks,

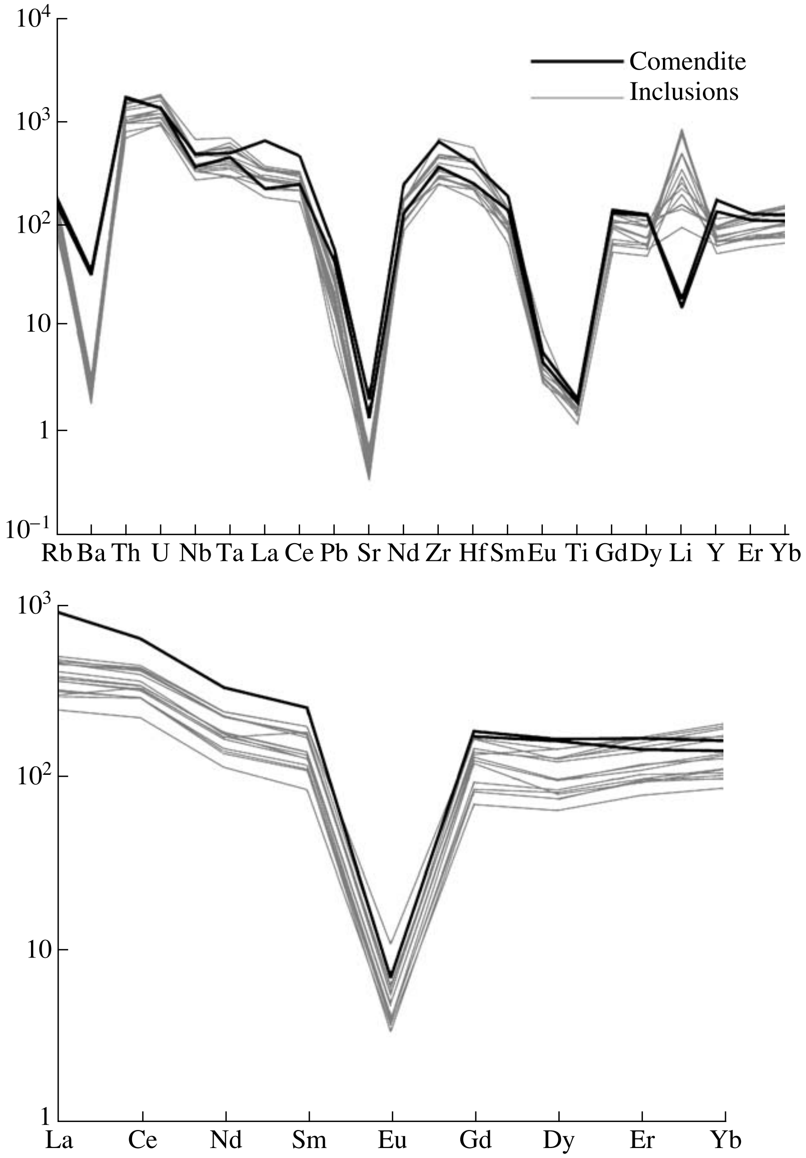

Fig. 3. Chondrite-normalized [13] spidergrams of rare-metal and rare-earth elements in homogenized glasses in quartz-hosted melt inclusions in comendite and rocks of the Zaart Khudag massif.

REEs are also positively correlated with Nb. A tendency to accumulation in residual melt is retained for HREE and MREE, and to a lesser extent, for LREE. Such behavior of trace elements relative to Nb allows us to conclude that evolution of the comenditic melt was mainly controlled by crystal fractionation.

At the same time, it should be noted that compositions of glasses from quartz-hosted melt inclusions demonstrate a wide range of Li contents at a relatively constant Nb content. A similar relationship is observed for F and Na. The behavior of these elements cannot be described in terms of crystal fractionation and suggests involvement of other processes in the melt evolution. Silicate–salt liquid immiscibility may serve as such a process. The effect of immiscibility of silicate and salt melts recorded during heating of inclusions clearly indicates that separation of Na- and Li-rich fluoride melts from alkaline silicate magma is a reality. The salt melt could subsequently be removed from the silicate melt providing a deep Li minimum in spidergrams of the studied comendite (Fig. 3). A great geochemical importance is attached to separation of a highly concentrated salt melt in the course of fractionation of F-rich silicate magma [10–12]. We believe that this process is a natural stage in the evolution of a magmatic system. Special attention is paid to the capacity of fluoride salt melts to extract many rare-metal and rare-earth elements.

Thus, study of quartz-hosted melt inclusions in comendite allowed us to detect the highly evolved alkaline rare-metal melts enriched in Na, F, Li, Zr, and REE and to ascertain the magmatic processes responsible for their formation. Therefore, the alkaline felsic rocks of bimodal associations may be regarded as a special type of volcanic-hosted rare-metal mineralization.

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