INHOMOGENEITIES OF CARBONATITIC MELTS

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Carbonatites are common components of alkali-basic and alkali-ultrabasic complexes. Effusive carbonatites generally have an alkali-calcian composition, whereas plutonic carbonatites mainly contain calcite and, rarely, Fe-Mg-Ca carbonates. Most researchers believe that carbonatites are igneous rocks, but a number of questions concerning their genesis still have to be answered: for example, the initial composition of carbonatitic melts; mechanism and P-T parameters of their generation and crystallization; reasons for enrichment of effusive carbonatites in alkalies and their absence in plutonic varieties; cause of enrichment of some carbonatites in S, F, P, Cl, etc. We found some answers to these questions while studying inclusions in minerals of the Krestovskaya intrusion (Polar Siberia), which is composed of ultrabasic rocks and contains bodies of melilitic and monticellitic rocks and thin dikes of calciocarbonatites.

According to data obtained on melt inclusions in minerals, all the rocks of this intrusion originated from one parental alkali-ultrabasic magma during crystal differentiation and fractionation. Magma crystallization started from the moment of separation of olivine and continued according to the following scheme: Ol (olivine) → Di (diopside) → Prv (perovskite) → Mel (melilite) → Mtc (monticellite) → Cal (calcite). In all inclusions in perovskite of melilitic rocks at 1250-1230°C we detected **silicate-carbonate liquid immiscibility**. The chemical composition of *silicate fraction* of inclusions (Table 1) corresponded to that of alkali-basic melts, while *carbonate fraction* had an alkali-calcian composition (CaO 2 19-24; alkalies 2 18-20 wt.%) enriched in SO_3 (5-10), P_2O_5 (1.5), and Cl (to 2 wt.%). This was comparable with the composition of carbonatitic lavas of Oldoinyo Lengai (Tanzania) and undoubtedly reflected the composition of initial carbonatitic melts. Inclusions with silicate-salt immiscibility were also found in meliltite, which crystallized at the same temperatures (1200°C) as perovskite. Melilite was also found to contain primary coexisting silicate and carbonate inclusions whose chemical composition is similar to that in fractions in immiscible inclusions (Table 1). Their presence supports silicate-carbonate immiscibility and suggests the started spatial separation of silicate and carbonate fractions. In addition, the minerals of the studied rocks also contain *4 types of primary carbonate inclusions* (Table 1): **alkali-sulfatic** (alkalies 2 35-45; SO_3 2 12-17 wt.%), **alkali-phosphatic** (alkalies 2 to 25-30; P_2O_5 2 20-25 wt.%), **alkali-chloridic** (alkalies 2 from 17 to 54; Cl 2 from 10 to 45 wt.%) and **essentially calcitic** (CaO 2 45-55; alkalies 2 0-7 wt.%). Occasionally, different types of inclusions coexists, which suggests their simultaneous entrapment by mineral as well as heterogeneity of carbonatitic melt owing to its separation into simpler fractions. The possibility of the alkali-calcian separation of carbonate liquids in the presence of chlorides and phosphorus is also supported by experimental data (Suk, 2001). This process has theoretical support as well. Carbonatitic melts are known (Kogarko, 1978) to be ionic liquids in which, according to the polarity rule, the equilibria of exchange reactions are shifted toward the combination of strong acid anions with the strongest basic cations. Inhomogeneity and immiscibility in these melts take place when the energy of interaction of some ionic pairs considerably exceeds others. Cations in studied initial carbonatitic melts were represented mainly by alkalies and Ca, while anions, by Cl, SO_3, PO_4, CO_3 (are listed in the decreasing order of their basic and acidic properties, respectively). The presence of acidic bases stronger than CO_3 in the melt, allowed alkalies (as stronger bases) to establish bonds mainly with them, causing inhomogeneity and broadening the fields of immiscibility when replacing a weaker acid anion by a stronger one. As Ca-carbonates are the lowest-energy pair, they terminate separation of carbonatitic melt.

Conclusions

The initial carbonatitic melts participating in the formation of alkali-ultrabasic complexes appeared at 1250-1230°C as a result of silicate-carbonate liquid immiscibility of primordial alkali-ultrabasic magma. Their chemical composition was enriched in alkalies, S, Cl, and P. It could have been preserved only at rapid eruption of lava on the surface and in the absence of intermediate magma chambers. At slow cooling and long-term evolution, the initial carbonatitic melt separated into simple fractions. The occurrence of this process in macroconditions might have caused the origin *of different types of carbonatites: alkali-sulfatic* (for example, carbonatites of Western Transbaikalia, Mushugai-Khuduk in Mongolia, Mountain-Pass in California), *alkali-phosphatic* (e.g., carbonatites of Tomtor in Siberia), *alkali-chloridic* and *essentially calcitic* (the most common type of intrusive carbonatites). Calciocarbonatites are a depleted residual melt of initial carbonatitic magma and originate at the final stages of its evolution (Panina, Usoltseva, 2000).

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Table 1. The chemical composition (wt. %) of inclusions in minerals of alkali-ultrabasic rocks of the Krestovskaya intrusion.

Host	SiO_2	TiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	BaO	SrO	P_2O_5	Cl	SO_3	Total
Inclusions with silicate-carbonate immiscibility														
Silicate fraction														
Prv	**31,66**	6,21	**6,51**	**9,73**	**6,99**	**14,51**	5,81	5,54	0,46	0,42	2,37	0,29	2,10	92,60
Prv	**32,24**	9,72	**8,82**	**9,61**	**6,61**	**16,43**	4,37	2,84	0,21	0,51	2,87	0,19	1,00	95,42
Prv	**32,83**	8,66	**9,08**	**10,39**	**7,09**	**16,12**	3,38	3,10	0,26	0,62	2,81	0,28	2,18	96,80
Prv	**32,08**	6,67	**5,52**	**9,83**	**6,61**	**14,80**	4,54	4,90	0,58	0,99	2,70	0,26	0,58	90,06
Carbonate fraction														
Prv	6,76	2,39	0,33	2,03	1,47	**18,72**	**10,01**	**7,93**	1,10	0,98	4,92	0,24	10,02	66,90
Prv	2,97	4,83	0,33	0,72	0,70	**24,01**	**4,00**	**17,50**	0,00	0,22	0,07	-	4,56	59,91
Mel	7,59	0,03	0,48	0,78	7,79	**22,15**	**5,01**	**13,69**	0,75	0,38	0,02	6,62	1,02	66,36
Mel	6,27	0,04	0,27	0,92	1,42	**23,52**	**8,69**	**11,59**	1,30	0,25	0,71	2,20	6,40	63,59
Alkali-calcian carbonate inclusions														
Mel	18,61	0,11	1,91	2,76	6,20	**24,06**	**4,39**	**7,52**	0,50	0,24	0,07	4,34	2,15	72,86
Mel	10,91	0,06	0,36	1,31	2,52	**20,76**	**9,24**	**11,20**	0,66	0,25	0,24	0,01	4,67	62,19
Mel	5,48	0,00	0,38	0,37	2,61	**25,04**	**9,46**	**6,05**	0,89	0,51	0,10	2,66	1,21	54,76
Mel	3,18	0,00	0,15	0,57	0,72	**25,35**	**7,20**	**9,52**	1,68	0,27	0,01	2,08	6,90	57,63
Mtc	4,08	0,00	0,00	0,89	1,24	**24,91**	**13,71**	**5,25**	0,22	0,94	0,99	1,22	4,86	58,31
Mtc	11,01	0,00	0,00	3,91	2,39	**23,83**	**10,66**	**3,58**	0,52	2,40	1,97	0,13	3,51	63,91
Mtc	1,29	0,00	0,00	0,36	1,27	**33,30**	**14,33**	**4,30**	0,00	0,96	0,75	2,40	3,51	62,47
Mtc	6,50	0,28	1,48	1,60	3,16	**33,72**	**5,92**	**4,47**	0,20	0,93	1,49	0,07	1,49	61,31
Mel	4,91	0,14	0,95	0,44	3,38	**32,92**	**5,84**	**10,48**	1,46	1,20	2,82	1,49	2,09	68,12
Mel	0,20	0,09	0,00	0,12	0,05	**32,86**	**9,23**	**7,65**	0,27	0,62	2,19	0,14	0,02	53,44
Alkali-sulfatic carbonate inclusions														
Mtc	1,52	0,00	0,00	0,32	0,72	15,34	**27,84**	**10,27**	0,51	1,54	4,56	1,45	**11,57**	75,64
Mtc	0,30	0,00	0,00	0,49	0,30	6,67	**20,20**	**12,58**	0,46	0,37	1,56	0,22	**13,79**	56,94
Mtc	1,75	0,00	0,00	0,28	0,98	7,32	**25,35**	**20,14**	0,33	0,09	4,31	0,25	**17,07**	77,87
Mtc	0,78	0,00	0,00	0,69	0,73	7,70	**28,11**	**7,32**	0,57	1,07	7,28	2,26	**12,56**	69,07
Mtc	0,70	0,09	0,00	0,85	0,50	6,69	**34,49**	**9,15**	0,62	0,93	2,67	0,60	**16,27**	73,56
Mtc	0,87	0,06	0,00	1,08	1,24	13,61	**18,59**	**8,66**	0,39	1,03	2,10	0,29	**6,88**	54,80
Alkali-phosphatic carbonate inclusions														
Mtc	1,69	0,02	0,00	0,85	2,67	**23,92**	**18,06**	**4,32**	0,06	**2,48**	**9,11**	0,64	5,88	69,70
Mtc	3,59	0,07	0,00	0,64	2,05	**37,42**	**6,65**	**2,96**	0,00	**2,21**	**13,39**	0,82	2,47	72,27
Mtc	4,05	0,00	0,00	1,06	3,70	**22,48**	**32,83**	**1,16**	0,16	**1,48**	**16,24**	0,07	4,82	88,05
Mtc	2,73	0,00	0,00	0,51	1,81	**23,95**	**15,90**	**3,43**	0,39	**1,56**	**20,18**	0,00	6,43	76,89
Mtc	0,14	0,00	0,00	0,21	1,27	**20,39**	**25,21**	**2,74**	0,69	**1,93**	**28,33**	0,00	4,50	85,41
Mtc	2,35	0,00	0,00	0,53	1,67	**25,83**	**22,84**	**2,26**	0,28	**1,63**	**31,56**	0,00	2,08	91,03
Mtc	1,86	0,05	0,00	0,41	1,24	**27,55**	**23,45**	**2,77**	0,00	**1,82**	**34,39**	0,00	1,01	94,55
Mtc	1,19	0,00	0,00	0,34	1,10	**27,02**	**24,59**	**3,37**	0,44	**1,29**	**35,09**	0,04	2,27	96,74
Alkali-chloridic carbonate inclusions														
Mtc	1,65	0,00	0,05	0,85	0,99	17,23	**6,15**	**11,13**	-	0,62	0,12	**9,20**	3,71	51,70
Mel	5,68	0,00	2,91	0,88	1,14	15,82	**8,13**	**1,34**	0,00	0,00	2,60	**14,86**	2,27	55,63
Mel	4,04	0,00	0,21	5,61	1,10	5,15	**6,59**	**30,63**	0,11	0,07	0,02	**21,33**	10,26	85,12
Mtc	0,00	0,00	0,02	0,81	0,21	1,74	**44,57**	**1,21**	-	0,04	0,00	**45,76**	0,43	94,79
Di	0,49	0,24	0,08	0,34	0,00	1,33	**38,30**	**16,98**	0,00	0,03	0,00	**41,78**	-	99,57
Di	3,30	0,12	0,24	0,69	0,00	1,85	**31,25**	**4,72**	0,00	0,00	0,10	**41,44**	0,13	83,84
Essentially calciocarbonate inclusions														
Di	0,61	0,15	0,00	0,13	0,11	**45,06**	7,56	5,87	0,00	1,98	0,17	0,00	0,00	61,64
Di	0,51	0,07	0,35	0,43	0,39	**54,73**	0,00	0,00	0,04	0,34	0,16	0,00	0,00	57,02
Di	1,20	0,00	0,00	0,27	0,37	**55,31**	0,00	0,00	0,00	0,21	0,15	0,00	9,00	66,51