Different styles of evolution of CO_2-rich alkaline magmas: the role of melt composition in carbonate-silicate liquid immiscibility

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ABSTRACT. — Melt and fluid inclusions were studied in olivine from the olivine melilitite of the Mahlberg complex, Germany. It was shown that the magmas were saturated in CO_2 at a pressure higher than 5 kbar and 1220°C and showed low SiO_2 and high CaO and alkali contents. The magma composition is similar to that of the melilitolites of the Gardiner massif in Greenland (Nielsen *et al.*, 1997), which associate with carbonatite bodies and where evidence for carbonatite-silicate liquid immiscibility was detected in melt inclusions. The absence of carbonatite liquids in Mahlberg is probably related to a relatively high Al_2O_3 content, which shifted the composition of magma away from the carbonate-silicate liquid immiscibility field.

RIASSUNTO. — Inclusioni di fuso e fluide in olivina, sono state studiate in rocce del complesso di olivina melilitite di Mahlberg, Germania. Dallo studio risulta che i magmi erano saturi in CO_2 a pressioni superiori a 5 kb e 1220°C e che contenevano poca SiO_2 ma alti tenori di CaO e alcali. La composizione del magma è simile a quella delle melilitoliti del massiccio di Gardiner in Greenland (Nielsen *et al.*, 1997), a cui sono associati corpi di carbonatiti e vi sono evidenze di immiscibilità allo stato liquido nelle inclusioni di fuso. L'assenza di liquidi carbonatitici a Mahlberg è probabilmente legata al contenuto relativamente alto in Al_2O_3, che ha provocato uno spostamento della composizione del magma lontano dal campo di immiscibilità tra liquidi carbonatitici e silicatici.

KEY WORDS: *melilitite, Rhinegraben, melt inclusion, carbonatite, liquid immiscibility.*

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INTRODUCTION

Most of igneous carbonatites are thought to result from silicate-carbonate liquid immiscibility during the evolution of alkaline fluid-saturated silicate magma. The role of fluid regime and melt composition is still not fully understood. Because of this, it is instructive to compare carbonatite-bearing and carbonatite-free igneous complexes with similar compositions of silicate rocks. Many igneous carbonatites associate with alkaline rocks dominated by Na or K. There are also examples of carbonatites in association with Ca-rich igneous rocks (melilitites). According to Rass (1998), they were formed from a specific high-Ca initial magma similar to group IB kimberlite (Smith *et al.*, 1985). Nielsen *et al.* (1997) studied melt inclusions in the melilitolites of the carbonatite-bearing Gardiner massif, Greenland and determined the compositions of melts and conditions of carbonatite melt separation. Melilite-bearing rocks are well known in the Upper Rhinegraben igneous province (Dunworth and Wilson, 1998). This paper presents the results of a study of olivine melilitites from Mahlberg, 100 km north of Keiserstuhl. There is no carbonatite in the Mahlberg massif, which will be compared with carbonatite-bearing melilite-bearing rocks of the Gardiner.

Our approach is based on the investigation of melt and fluid inclusions in minerals, which bear direct evidence on the composition and conditions of initial and evolved melts. The inclusions were studied using various microscopic heating and cooling stages. Crystal phases and glasses were analyzed by an electron microprobe.

PETROGRAPHY AND MINERALOGY

The olivine melilitite sample (XKR 37 OM) studied is composed of olivine and clinopyroxene phenocrysts enclosed by a fine-grained groundmass. Olivine phenocrysts (0.2-1.0 mm, forsterite mole fraction of 0.89-0.92) show wide ranges of CaO (0.18 - 1.1 wt %), NiO (0.05 – 0.32 wt %) and MnO contents (0.15-0.71 wt %), which are linearly dependent of mg = Mg/(Mg+Fe). In addition to phenocrysts, there are numerous olivine xenocrysts in the rock. They differ from the phenocrysts in larger size (up to 5 mm), lower mg (up to 0.81), and lower CaO (0.1-0.2 wt %) and MnO contents (up to 0.3 wt %).

Clinopyroxene occurs as large and small phenocrysts and in the groundmass. The phenocrysts show distinct zoning. Lighter zones in grain margins near late fractures and melt inclusions are enriched in Al_2O_3 (up to 11.7 wt %), FeO (up to 8.7 wt %) and TiO_2 (up to 5.6 wt %) (Table 1). Clinopyroxene from the groundmass show mg of 0.65. In addition, clinopyroxene occurs as (1) crystalline inclusions in phenocrysts of olivine, (2) crystals in late miarolitic cavities, and (3) daughter minerals in melt inclusions in olivine. Except for Na_2O, the compositions of all clinopyroxenes show regular changes in element concentrations versus mg value.

The holocrystalline groundmass consists of olivine, clinopyroxene, melilite, nepheline, phlogopite, Ti-magnetite and perovskite. There are also miarolitic aggregates up to 5 mm across (Fig. 1). They are composed of euhedral clinopyroxene, nepheline, melilite, Ba-rich phlogopite (Dunworth and Wilson, 1998), perovskite and Ti-magnetite crystals (Table 2) cemented by secondary hydrous minerals (wairakite, lawsonite, and others).

INCLUSIONS IN MINERALS

Olivine phenocrysts bear numerous melt inclusions containing a variety of daughter crystals including monticellite (FeO = 10.4 wt%), olivine (Fo_{88-83}, up to 1.2 wt % CaO), clinopyroxene, melilite, Ba-rich phlogopite, nepheline, F-bearing apatite and magnetite (with up to 10.5 wt % Al_2O_3) (Table 3). The inclusions are partially decrepitated and loosed part of their fluid constituents. Because of this, the inclusions were not homogenized during thermometric experiments. The melting temperatures of daughter phases ranged from 1130-1220°C. Some late and secondary melt inclusions were homogenized at 1160-1100°C.

Clinopyroxene crystals in the miarolitic aggregates contain rare silicate melt and low-density fluid inclusions (Figs. 1c, 1d). The homogenization temperature of the melt inclusions is 1130-1140°C. The density of fluid inclusions is lower than 0.01 g/cm³.

Melt in the inclusions are low in SiO_2 and high in CaO (up to 18 wt. %) and alkalis (Table 4). Sodium dominates over potassium in early melts and K/Na ratio increases toward more evolved compositions reaching 1.4. MgO contents are no higher than 9 wt %. The melts are rich in P_2O_5 (up to 1.6 wt %), BaO (up to 0.65 wt %), SrO (up to 0.3 wt %), and F (more than 0.5 wt %). The concentration of Cl was always below the electron microprobe detection limit (0.1 wt %).

In addition to melt inclusions, olivine contains abundant fluid inclusions of the gas ± liquid type (Fig. 2). They are dominated by CO_2 (melting temperature of pure CO_2 = –56.6°C) with a density from 0.30–0.73 g/cm³. Similar fluids were detected in gas bubbles of melt inclusions. All fluid inclusions are partially decrepitated.

TABLE 1

Representative clinopyroxene compositions, wt.%

	1	2	3	4	5	6	7	8
SiO_2	40.83	47.51	40.52	37.23	44.42	50.66	47.27	43.83
TiO_2	4.94	2.29	4.69	6.20	3.17	1.96	1.49	4.68
Al_2O_3	10.63	5.44	10.68	12.74	7.34	2.60	7.74	8.77
Cr_2O_3	0.00	0.15	0.00	0.04	0.00	0.00	0.58	0.67
FeO	8.05	5.73	7.91	9.11	6.94	5.45	4.28	5.20
MnO	0.10	0.09	0.08	0.15	0.10	0.16	0.01	0.05
MgO	10.99	14.50	10.74	9.68	12.85	15.03	15.22	12.47
CaO	24.11	24.38	24.00	23.11	24.34	24.45	21.54	24.10
Na_2O	0.40	0.27	0.42	0.50	0.34	0.46	1.12	0.71
K_2O	0.01	0.00	0.00	0.03	0.00	0.00	0.01	0.18
P_2O_5	0.02	0.03	0.01	0.03	0.05	0.01	-	-
NiO	0.03	0.03	0.03	0.03	0.00	0.01	-	-
Total	100.10	100.41	99.09	98.84	99.55	100.78	99.26	100.66
mg	0.71	0.82	0.71	0.65	0.77	0.83	0.87	0.81

Note: (1)-(3) Phenocrysts: (1) light green zone, (2) dark green zone, small phenocryst. (4), (5) Groundmass clinopyroxene. (6) Clinopyroxene from miarolitic aggregate. (7) Solid inclusion in olivine. (8) Daughter mineral in melt in olivine.

TABLE 2

Representative compositions of phases from miarolitic aggregates, wt.%

	Cpx	Ne	Phlg	Ap	Per	Ti-Mt	Mel
SiO_2	49.56	40.91	29.15	1.36	0.50	2.47	43.08
TiO_2	1.78	0.04	8.01	0.04	51.26	4.28	0.08
Al_2O_3	2.47	34.44	16.29	0.39	0.16	1.42	6.52
FeO	5.41	1.05	7.23	0.40	1.51	82.20	3.27
MgO	14.87	0.18	17.35	0.02	0.16	0.74	8.57
MnO	0.15	0.01	0.12	-	-	0.80	0.07
CaO	23.80	0.56	0.22	52.50	33.26	2.82	33.88
Na_2O	0.59	14.89	0.22	-	1.84	0.10	3.40
K_2O	0.19	9.03	4.51	0.02	0.04	0.07	0.18
C_2O_3	-	-	-	-	0.05	0.17	-
BaO	-	-	14.98	0.15	-	-	0.07
F	-	-	4.55	8.38	-	-	-
Total	98.82	101.11	102.62	100.95*	88.78**	95.07	99.12

Note: *Including 37.69 wt% of P_2O_5. **Low total of perovskite is due to high REE content (Dunworth, Wilson, 1998).

TABLE 3

Representative compositions of daughter minerals in melt inclusions, wt.%

	Mont	Ol	Cpx	Ne	Per	Ap	Ti-Mt
SiO_2	37.05	41.62	41.44	42.20	0.45	1.77	0.90
TiO_2	0.00	0.00	3.94	0.10	46.78	0.00	13.34
Al_2O_3	0.00	0.00	11.95	31.13	0.16	0.00	3.26
FeO	10.41	11.81	8.47	1.99	1.82	0.79	71.72
MgO	20.42	46.94	10.73	1.11	0.18	0.67	6.08
MnO	0.16	0.22	0.05	0.04	0.02	0.00	0.77
CaO	33.23	1.19	24.44	0.96	31.11	52.98	0.06
Na_2O	0.00	0.00	0.39	13.99	2.75	0.00	0.06
K_2O	0.00	0.00	0.03	8.94	0.05	0.00	0.12
Cr_2O_3	0.11	0.09	0.00	0.00	0.00	0.07	0.58
Total	101.38	101.87	101.44	100.45	83.32	56.28	96.91

TABLE 4

Representative compositions of melts from inclusions, wt.%

	1	2	3	4	5	6	7
SiO_2	38.95	37.89	40.98	37.57	38.99	46.31	69.16
TiO_2	2.59	3.03	2.05	4.25	2.60	2.07	0.89
Al_2O_3	10.22	14.44	15.37	12.55	14.31	18.01	14.12
FeO	10.71	9.18	5.90	10.37	10.44	7.13	2.04
MgO	15.27	8.10	7.76	7.08	7.26	5.80	0.32
MnO	0.19	0.09	0.10	0.13	0.04	0.11	0.03
CaO	14.08	17.74	16.32	19.04	14.61	6.18	0.42
Na_2O	2.57	6.49	7.36	5.23	5.72	7.18	2.51
K_2O	1.06	4.23	5.29	3.52	3.57	7.86	5.48
Total	95.64	101.19	101.13	99.74	97.54	100.65	94.97

Note: (1) Rock, (2)-(4) primary inclusions in olivine cores, (5) primary inclusion in olivine rim, (6) secondary melt inclusion in olivine, (7) residual melt in inclusion in Cpx of the miarolitic aggregate.
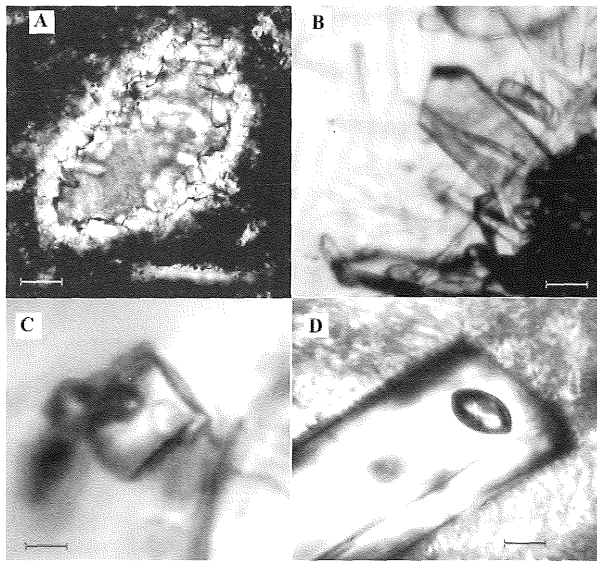
Fig. 1 – Photomicrographs of miarolitic aggregate in the groundmass of olivine melilitite, transmitted light. (a) General view showing extensive clinopyroxene growth on the walls. The central part is filled with secondary hydrous phases. Scale bar is 1 mm. (b) Fragment of the miarolitic aggregate. Clinopyroxene crystals near the wall. Scale bar is 100 µm. (c) Primary melt inclusion in clinopyroxene with a distinct fluid bubble and a daughter crystal. Scale bar is 10 µm. (d) Primary low-density CO_2 fluid inclusion in clinopyroxene. Scale bar is 10 µm.
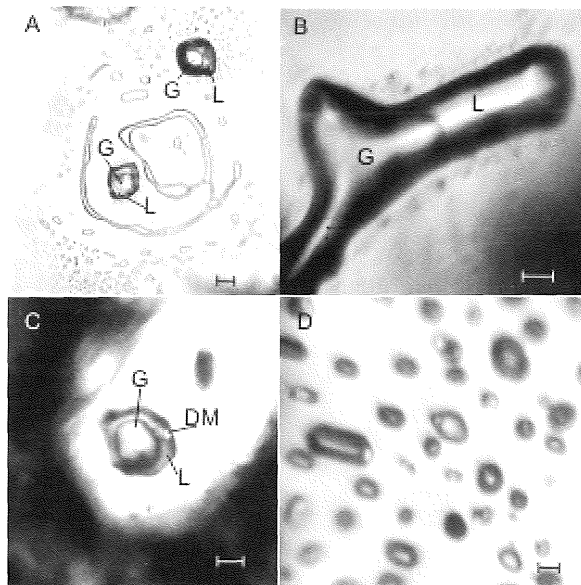
Fig. 2 – Partially decrepitated CO_2 inclusions in olivine. (a), (b) Primary liquid (L) + gas (G) CO_2 inclusions surrounded by aureoles of secondary satellite inclusions. CO_2 density is (a) 0.73 g/cm^3, P = 5 kbar at 1220°C, (b) 0.49 g/cm^3, P = 1.1 kbar at 1130°C, (c) Pseudosecondary fluid inclusion (liquid + gas, d = 0.33 g/cm^3, P = 0.7 kbar at 1130°C) with crystals (DM) in liquid CO_2. (d) Secondary low-density CO_2 fluid inclusion in olivine. Scale bars are 10 µm. *L* and *G* are CO_2 liquid and gas, respectively.

Discussion

The results of melt and fluid inclusions show a considerable role of CO_2 in the genesis and evolution of the magma. The maximum density of CO_2 fluid inclusions (0.73 g/cm^3) suggests a fluid pressure of 5 kbar at 1220°C. Note that the real pressure was probably even higher, because of the partial loss of fluid components. The distribution of fluid inclusions in phenocrysts suggests at least two stages of phenocryst crystallization differing in the fluid regime. At early stages, cores of olivine and clinopyroxene were formed under relatively stable fluid-saturated conditions. This was followed by a rapid decrease of pressure accompanied by extensive degassing and growth of outer phenocryst zones with abundant fluid inclusions of varying density.

The compositions of the least evolved melts trapped in melt inclusions (Table 4) are characterized by low SiO_2 and high CaO and alkali contents. CaO-rich melts were reported from melt inclusions in olivine from the olivine-melilite rock of the Guli alkaline carbonatite-bearing complex, Polar Siberia (Rass and Plechov, 2000). Similar melts were found by Nielsen *et al.* (1997) in melilite from Gardiner melilitolite, which shows evidence for silicate-carbonate liquid immiscibility. In contrast, melt inclusions in the Mahlberg melilitite contain no carbonate phases, which is in agreement with the absence of carbonatite occurrence. However, both melt compositions and fluid conditions in Mahlberg were similar to those of Gardiner. There are, however, some important differences in melt compositions at similar MgO contents. The melts from Gardiner are in general lower in Al_2O_3 and SiO_2 (Fig. 3) than those of Mahlberg. Although this difference is not very considerable and comparable with the scatter of microprobe analyses, it could be critical in determining degassing behavior and carbonate stability.

Experimental investigations of silicate-carbonate liquid immiscibility determined a two-liquid field in the $SiO_2+Al_2O_3+TiO_2$ $-CaO+MgO+FeO$ – Na_2O+K_2O ternary

diagram (Fig. 4). On this diagram, the least evolved melts from melilites of the Gardiner rocks fall within the field of silicate liquid, but their differentiation (melilite fractionation) shifts melt composition toward the two-liquid boundary. This is consistent with the appearance of carbonatite melts at late stages of melt evolution. In contrast, melts from the Mahlberg melilitites were initially richer in Al (and Si) and plot further from the liquid immiscibility field. Moreover, higher Al content at high Na expanded the nepheline stability field and resulted in early crystallization of nepheline (together with olivine) from the melt. The resulting liquid evolution path passes parallel to the liquid immiscibility boundary (fig. 4) and even the most evolved melts remain outside the carbonate-silicate field. Thus, the minute
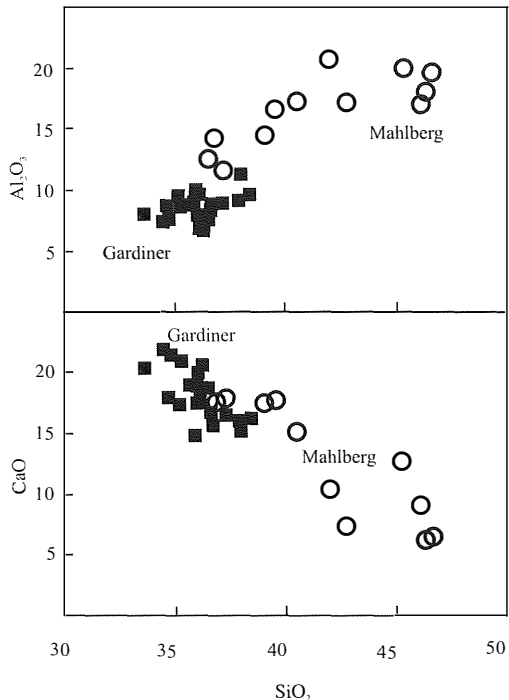

Fig. 3 – Variations of CaO and Al_2O_3 versus SiO_2 in melts from melt inclusions in minerals of Malhberg and Gardiner.
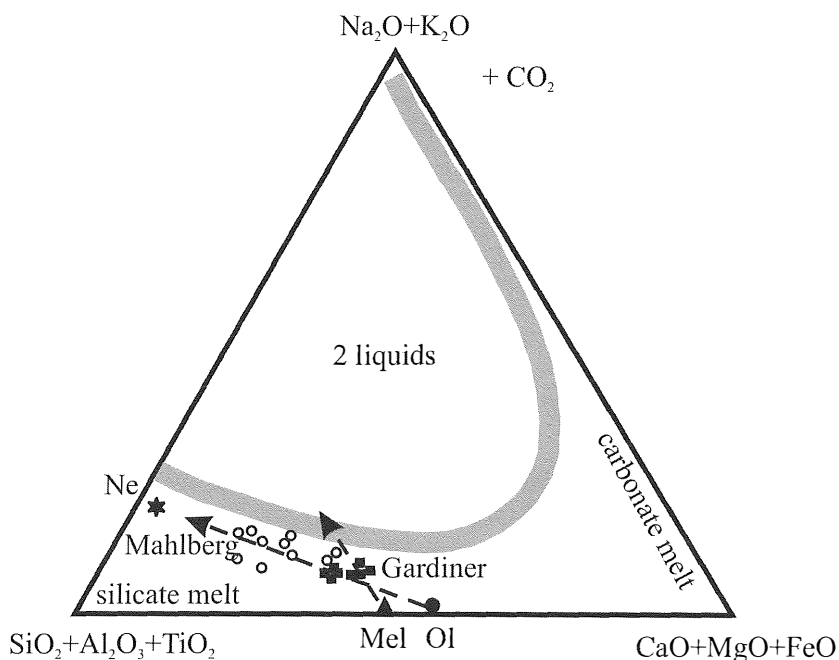
Fig. 4 – Different evolution paths of the Gardiner and Mahlberg melts (compositions from melt inclusions) projected into the $SiO_2+Al_2O_3+TiO_2$ – $CaO+MgO+FeO$ – Na_2O+K_2O plane. The carbonate-silicate liquid immscibility field is given for CO_2-saturated pressures of 2-5 kbar (Freestone, Hamilton, 1980; Kjarsgaard, Peterson, 1991).

differences in melt composition have a dramatic effect on the behavior of volatile components. In the case of Gardiner, the formation of carbonate melts consumed a considerable portion of CO_2 and the crystallization of evolved melts occurred under subvolcanic conditions. In contrast, the accumulation of CO_2 in the melt of Mahlberg resulted eventually in rapid degassing and a catastrophic eruption.

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