The behaviours of Mg and Ca in some types of ultramaphic alkaline melts in the presence of H$_2$O at high temperature and pressure (the experimental data)

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Abstract

The sample has been investigated, which was composed of olivine-melilite rock from the south-western part of the Kugda intrusion, situated in the eastern margin of the Maimecha-Kotuiskay alkaline- ultramaphic province (northern part of Siberia platform). The experiments were carried out using a high-pressure apparatus of the "piston-cylinder" type. The pressure was 5-15 kb and the temperature – 800-1250^0 C. The water content in the system was 3 and 9 wt. All experiments were carried out in hermetically sealed Pt or Au ampoules. The samples were chemically analyzed using a scanning electron microscope (SEM). Besides, the chemical composition of the experimental phases was determined by means of more than 40 electron microprobe in 20 experimental samples. For phase identification the X-ray method was used too. The structural peculiarities of rocks and mineral compositions were studied by optical methods in polished and thin sections prior and after the experiment. It was shown that at pressures above 7.5-8 kb the olivine-melilite melt is separated into two melts: pyroxenite and melilite. Most part of Mg in this system was concentrated in a high temperature phase of diopside type. The remaining melt was depleted of Mg and enriched by Ca. The mineralization vapour practically did not contain Mg. The main components of the mineralization vapour were Ca, Na, Si and Fe.

Key words: high pressure and temperature apparatus, magnesium, calcium, ultramaphic alkaline rocks, diopside, mervinite, liquation.

Introduction

Many authors (Smolin 1991 & oth.) reported a special role of Mg in the formation of the upper Earth's shell (earth crust, upper mantle). The main geochemical peculiarities of magnesium are the following: Mg has high clark and, correspondingly, the status of rock-forming cation of high chemical activity and with marked halo-oxi-hydrophility. The highest refractory of Mg silicates is also known and compared to other silicates of the rock-forming cations. According to these properties, Mg is concentrated in a subcrustal zone in the mantle silicate restite. The system "melt + Mg restite + fluid" can be formed by partial melting of mantle rocks. The majority of authors who studied mineral equilibriums, characterized for P, T conditions of the upper mantle, suggest that H$_2$O content there does not exceed 0,1-0,3% (Mysen & Boettcher 1979, Ringwood 1981). The main phase of the mantle fluid is CO$_2$. The formation of the high-magnesium fluid is not possible in these conditions. This conclusion is supported by the high content of calcium and the low one of magnesium in oceanic sediments near abyssal faults. In order to understand the behavior of Mg in the system "melt + crystal + H$_2$O vapour" it was decided to study the evolution of Mg melt characteristic for the deep-seated levels of the Earth shell (15 – 45 km). It is important to understand, if it is possible or not the formation of deep-seated solutions enriched with magnesium in this conditions. The olivine-melilite rock was taken for the experiment. As may be seen from the foregoing, the present experiments have been carried out to determine

the Mg distribution between melt, solid phase and water vapour at the pressure range of 5-15 kb and the temperature range of 600-1200⁰C with 3 and 9% of H_2O.

The description of sample

Olivine-melilite rock (kugdite) occurs at the eastern margin of the Maimecha-Kotuiskay alkaline- ultramaphic province (northern part of Siberia platform). Eighteen alkaline-ultramaphic intrusions are present here. One of them, the Kugda intrusion, occupies an area of almost 16 km². This one consists of the central olivinite core and the north-eastern and south-western margin zones. The southwestern zone is presented by olivine-melilite rock or "kugdite".

The sample used in the study was composed of kugdite having the following mineral composition (vol.%) : melilite -58, olivine -32, ore mineral - 5, the remaining were single grains of pyroxene and sphene (fig. 1).
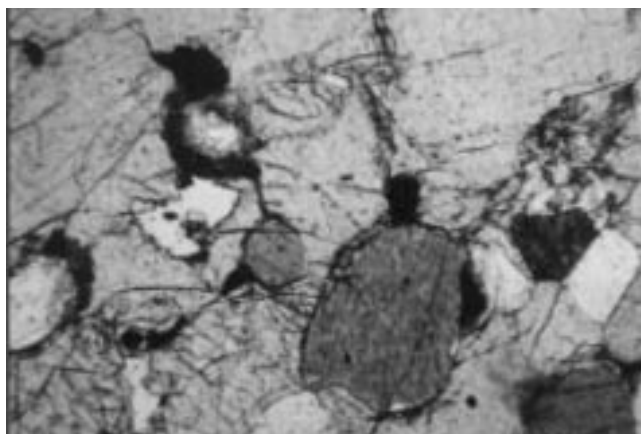
Fig. 1. Photomicrograph of the original sample of olivine-melilite rock (kugdit). The rounded olivine grains in melilite aggregate, magnitude 70, plane polars. Ol-olivine, Mel – melilite, Phl-phlogopite.
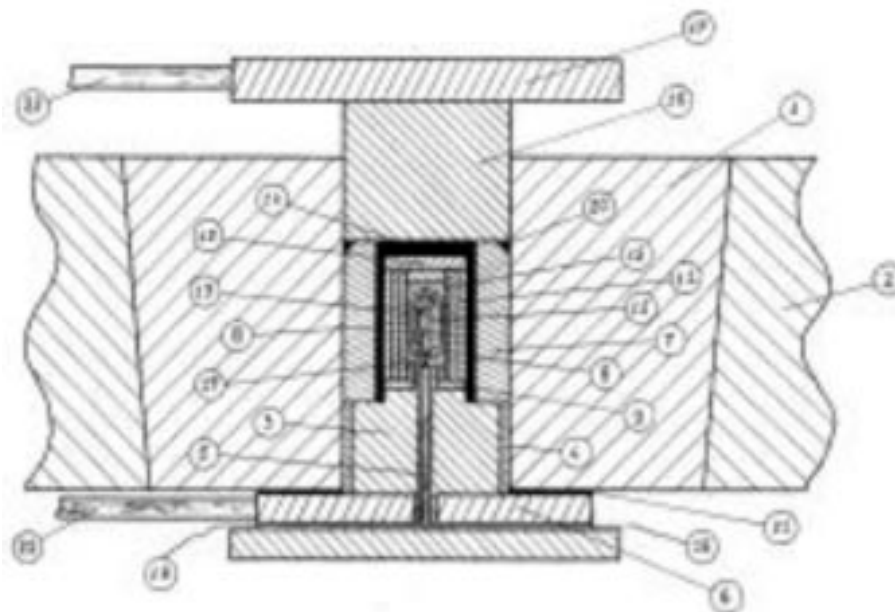
Fig. 2. The apparatus for experiments at high temperature (up to 1350⁰ C) and pressure (up to 30 kb) . 1 - tungsten carbide pressure vessel, 2 - steel upporting ring, 3 - immobile steel piston, 4 - pyrophyllite insulation tube, 5 - ceramic insulation, 6 - immobile base plate, 7 - pyrophyllite insulation tube, 8 - graphite furnace, 9, 10 - pyrophyllite disks; 11, 12 - pyrophyllite tubes, 13 - "heat shunt", 14 - graphite disk, 15 - sample, 16 - mobile piston, 17 - mobile base plate, 18 - thermocouple leads, 19 - thermojunction, 20 - sealing ring, 21 - mica insulation, 22 - graphite furnace electrodes.

Olivine (Fo$_{88}$Fa$_{12}$) was presented by rounded grains up to 0,1-0,3 mm in diameter. Melilite (Ok$_{70}$Na melilite $_{25}$Gel$_5$) formed isometric grains of 0,05-1,0 mm in size. The ore minerals present were magnetite and ilmenite inter-grown. The kugdite chemical composition (wt.%) was the following: SiO_2 - 40,96; TiO_2 – 0,63; Al_2O_3- 1,82; FeO – 3,78; CaO – 30,30; MgO- 16,77; MnO- 0,00 BaO- 0,43; Na_2O – 1,70; K_2O – 0,08; P_2O_5 – 0,06; H_2O^+ 0,06; H_2O^- 0,00; CO_2 –0,05, in total – 100,23.

The apparatus and experimental methods

The experiments were carried out using a high-pressure apparatus of the "piston-cylinder" type. The main scheme is shown on the Fig. 2.

The high pressure camera was made of hard alloy and had the shape of a tapered cylinder approximately 40 mm long, 80 mm in diameter and with a bore of 20 mm. The high pressure was created by a hydraulic press. The pyrophyllite was used as a pressure medium. The high pressure apparatus was calibrated according to the phase transformation of KCl-RbCl solid solutions (Livshitz & Larionov, 1970). The accuracy of pressure measurement was ± 5%.

The working volume of the camera was heated using a graphite heater placed inside the pressure vessel. The furnace was insulated by pyrophyllite from the run and vessel.

The temperatures were usually measured with chromel-alumel thermocouples. The thermocouple was placed at the center of the furnace through two holes drilled along of the axis of the cylindrical heater. The thermocouple junction was placed in contact with a run capsule. The maximum gradient observed did not exceed 2°C. The temperature uncertainly was ± 5°C.

The experiments were carried out at the temperature
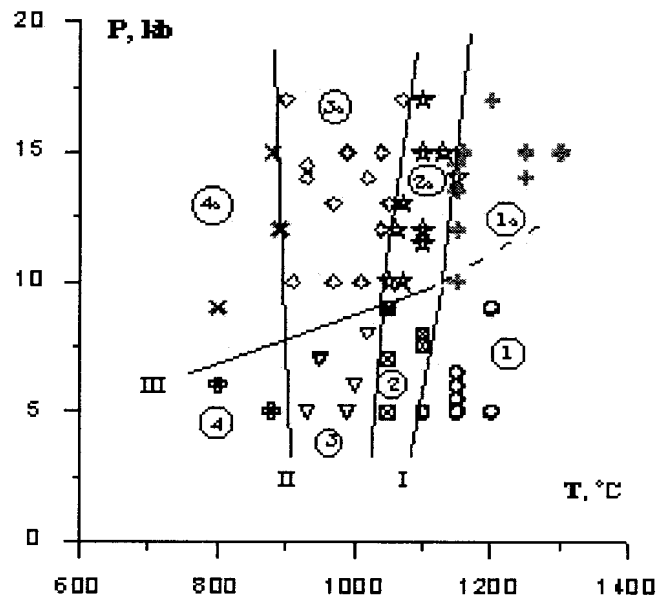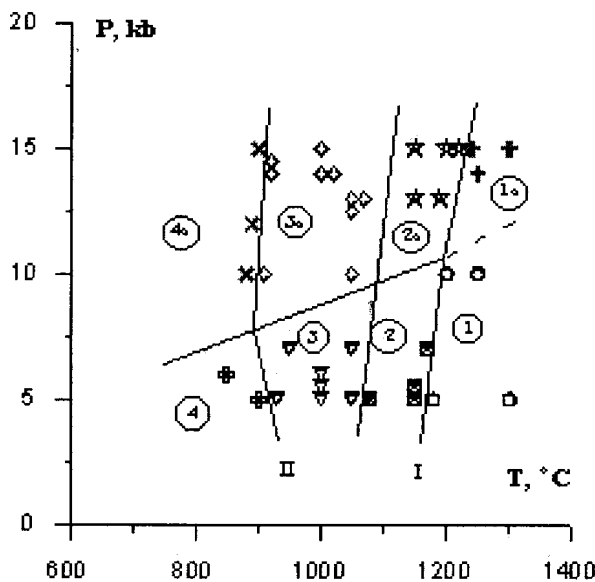
Fig. 3. The P-T diagrams for olivine-melilite rock (kugdite) at high pressure and temperature.
1,1a …..4,4a - stability fields, 1 - liquidus , 11 - solidus , 111 - equilibrium line of melelite-merwinite transformation .Gl - glass, Di - diopside, Ol - olivine, Ak - akermanite, Sp - spinel, Mrv - mervinite, Gr - garnet, Mnt - monticellite, Fl - fluid. a- 3% H₂O system , b-9% H₂O system.

range from 600 to 1200 ^{0}C. There were two variants of experiment: an approach to equilibrium "from above" and "from below". In the first case, the temperature was increased up to 1200^{0}C, followed by a two hours exposure and after that, the sharp decrease of the temperature down to a predetermined value was done with a 5 hours exposure. In the second case, the temperature was increased to a predetermined value with the followed exposure in 7-8 hours. About 40 mg of finely crushed kugdite and an appropriate amount of distilled water were encapsulated in a welded thin-wall platinum tube. The water contents were selected 3 and 9 % (wt).

The capsule content was controlled by heating at 120°C during 2 hours. The capsules were weighted before and after heating, and only those capsules, which weight did not change after that procedure, were used in the experiments. To insure that water did not leak out during the runs, the capsules were also weighted before and after each run. The capsules were made of two kinds of material: platinum and aurum.

There was some loss of iron from the sample into the Pt container during a run, but this has been monitored by microprobe analyses of samples after the runs.

We showed that the loss of iron for the experimental procedures was usually less than 30-35% of the total iron presented and there was only a small change in the oxidation state.

The run products were picked out carefully and examined under an optical microscope.

Experimental results

The results of the kugdite experimental study with 3 and 9% H_2O are shown in Fig 3, a-b. The system with 3% H_2O. The heavy lines (1) and (11) mark the kugdite liquidus and solidus, correspondingly. The most striking features of the melting curves in figure 3 are the changes in the slope occurring where they cross the line of the transition "melilite $\leftrightarrow$ mervinite" (111). This line has the extension to the field of liquid state. Above this line, all runs are characterized by the presence of two glasses of different composition as the phases of quenching. Below this line only one glass is present.

All runs below the equilibrium line of "melilite $\leftrightarrow$ mervinite" were characterized by Ca melilite and olivine presence. The subsolidus, run at < 7.5 kb, led to the yield of original mineral assemblage of the kugdite (Ol+Ak+Fl)+spinel (Sp).

At pressures higher than 7,5-8,5 kbar, melilite disappeared, mervinite and diopside were the main crystalline phases. As it was explained above, there were two variants of running the experiment, if the pressure was constant. The first variant: an approximation to equilibrium from high to low temperatures and the second variant from low to high temperatures. In the first case, we observed the separation the of sample into two parts: the lower and the upper. In runs with 3% H_2O, the lower part of the sample consisted of the glass and mervinite crystals, the upper from diopside crystals. The boundary between the upper and lower parts was sharp. The subsolidus run at 7,5 kb and higher showed the disappearance of spinel and appearance of garnet. The chemical composition of the phases synthesized in 3% H_2O system is shown in Table 1. The pyroxene with higher Mg content was crystallized at higher pressure.

**Table 1:** The chemical composition of high pressure phases (system with 3% H_2O).

Oxide	1	2	3
SiO_2	53,26	55,12	36,78
TiO_2	0,12	0,04	-
Al_2O_3	1,29	0,65	0,08
FeO	2,27	0,65	0,63
CaO	25,93	25,87	49,41
MgO	15,82	18,25	12,05
Na_2O	0,13	-	-
K_2O	-	-	-
Total	99,81	100,58	98,94

1,2 – Pyroxene (1- run 955,15 kb, 1000°C; 2- run 455,17 kb, 1070°C); 3-mervenite , run 887,14 kb, 1020°C.

Table 2: The chemical composition of synthesized phases with 9% H_2O.

Oxide	1	2	3	4	5	6
SiO_2	40,97	43.50	38,31	36.78	55,19	36.53
TiO_2	0,02	0	0,04	-	0,11	0.18
Al_2O_3	0,22	2.87	0,08	0.08	0,62	0.24
FeO	8,56	2.59	4,66	0.63	0,45	0.78
CaO	3,12	36.81	32,83	49.14	25,1	48.98
MgO	46.50	10.21	24,21	12.05	18.63	13.37
Na_2O	-	2.12	-	-	0.16	0.64
K_2O	-	0	-	-	-	-
Total	99.41	98.10	100,12	98.97	100.26	100.72

1 - Olivine, run 886, 6 kb, 1000°C ; 2 - melilite, r. 956,5 kb, 1000°C; 3 - r. 886, 6 kb, 1000°C; 4 - mervinite, r. 887, 14 kb, 1020°C; 5 - diopside, r. 893, 13 kb, 1050°C; 6 - remaining glass, r.465, 17 kb, 1100°C
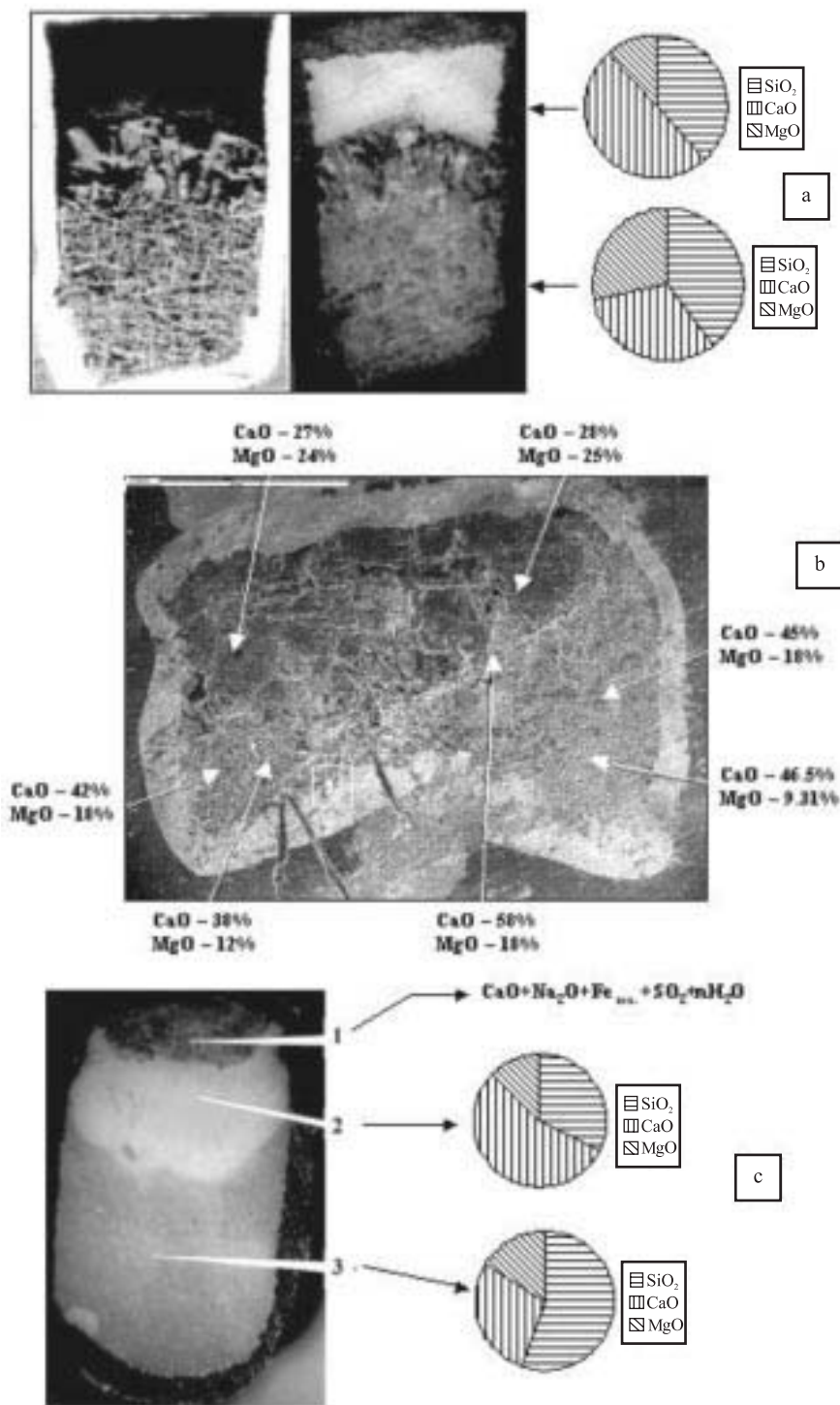
Fig. 4. The photomicrographs of experimental samples in olivine-melilite H_2O system. The ring diagrams (to the right) – oxide relations, %). a,b – separation on two liquids, the upper part of the sample – mervinite the below part – diopside with small quantity of olivine, run 885, T –1050⁰C (approach from above) , P – 13 kb, time 2+5 hours, 9% H_2O ,magn. 4x , in reflected light. c- separation on two liquid : in upper part of sample – diopside, in the bottom of the sample – mervinite melt , run 882, T-1000⁰C (an approach from above), P –10 kb, time 2+5 hours, 3% H_2O , magn. 4x, d – sample consists of 3 zones: upper – quenched fluid, middle – mervinite, below – diopside, P-13 kb, T- 1070⁰ C, time 2+5 hours, 9% H_2O , magn. 4x,

The system with 9% H_2O. The increase in water content in the system led to the decrease of temperature range for crystallization. The synthesized crystals as a rule had more regular shape. The fluid phase as drop-shaped bodies were presented in the upper part of the capsules practically in all runs. The phases obtained at high pressures and temperatures are listed in Table 2. In runs with 9% H_2O, the upper part of the sample consists of a mervinite melt, and below, one of diopside melt.

Conclusion

A scanning electron microscope was used to determine the average chemical composition of the different zones in experimental samples, including the fluid phase. Scanning was produced along 3-4 profiles by crossing the sample in transverse directions (Table 3).

As the experiments at high pressure and temperature were shown, there were two kind of mineral differentiation. At the pressure above 7 kb, an ultramaphic alkaline melt was separated into 2 liquids: one liquid of pyroxenite and one of mervinite. At the lower pressure, usual crystal differentiation was present. In both cases, Mg had a tendency to enter into higher temperature phases: diopside, olivine. The remaining part of the system became enriched with Ca. The fluid phase contained Mg in small proportion, rather as traces. The preliminary analysis of experimental data leads to the conclusion that deep-seated subcrustal ultramaphic magmas can not produce large volumes of Mg solutions, which could be the source of magnesite occurrences.

Table 3: The distribution of MgO and CaO between the phases in process crystal fractionation (on results of scanning)

Mineral association															
Above melilite ↔ mervinite line								Lower melilite ↔ mervinite line							
$1200-1080^0 C$				$1080-920^0 C$				$1170-1070^0 C$				$1070-920^0 C$			
Solid		Liquid		Solid		Liquid		Solid		Liquid		Solid		Liquid	
MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO
32	25	12	49	18	25	12	50	30	22	12	48	18	38	12	47

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