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Superliquidus Differentiation of Fluid-bearing Magmatic Melts under Reducing Conditions as a Possible Mechanism of Formation of Layered Massifs: Experimental Investigations

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Received November 1, 2000

Abstract—Previous experimental work (Bezmen, 1992; Bezmen and Elevich, 1998) demonstrated that, at certain critical thermodynamic parameters (temperature, pressure, and fluid phase composition), melts become unstable and show cryptic or contrast layering. Layering in ultrabasic melts, separation from silicate melts of ore liquids enriched in chromite, ilmenite, and apatite were obtained under superliquidus conditions at H–O–C–S fluid pressure. The proportions of gases in the fluid phase were specified to provide the closest approach to the compositions of natural fluids. At constant thermodynamic parameters and the absence of temperature gradient, fluid-bearing melts exhibit liquid-state layering, which develops gravitationally on a macromolecular scale. An increase in the duration of experiments results in a stronger contrast and appearance of layers with new compositions. The transmission electron microscopic investigation of quench glasses revealed ellipsoid-shaped inclusions with a crystalline structure and diffuse outlines, 6 nm (60 Å) and more in size. It is supposed that these are cores of clusters, which occur in strongly depolymerized fluid melts. The formation of clusters is a consequence of the fluctuation quasi-crystalline structure of magmatic melts. According to modern data obtained in situ (Cohen and Knight, 1990), clusters are a transitional state of matter between liquid and crystal. The cluster is composed of an ordered core and a shell consisting of ligands (Tredoux et al., 1995). The latter provide cluster stability in time. Atoms in the ligand shell are more mobile and the structure as a whole is a pseudocrystalline core with a liquid-like surface. High-pressure experiments demonstrated that the presence of a fluid phase similar in composition to natural magmatic fluid provides necessary conditions for the gravitational movement of clusters and their aggregates. The liquid-state cluster differentiation of melts allows us to explain a number of issues in the evolution of differentiated complexes including the nature of cryptic layering, rhythmic structure of layered sections, selective concentration of ore components by melts, development of fine-grained and homogranular textures, concentration of dense minerals in the upper portions of massif sections, formation of monomineral rocks and massive ores, and others.

INTRODUCTION

The diversity of rocks in layered massifs resulted from the development of magmatic processes under the influence of a fluid phase. In this context, the experimental study of the role of fluid in the differentiation of igneous melts and separation of ore matter is a very important problem. Its solution will provide a more comprehensive insight into regularities in the structure of differentiated magmatic complexes and localization of ore mineralization in them.

A variety of features of the differentiation of igneous complexes including the selective concentration of ore components by rocks of a certain composition, formation of rocks with fine-grained and homogranular textures, which often show a monomineral composition, are difficult and sometimes impossible to explain in the context of crystallization differentiation. It is especially difficult to understand ore-forming processes at crystal settling, i.e., the confinement of various kinds of ore mineralization to certain types of differentiation and localization of ore matter in certain parts of the section of massifs.

As early as in 1955, F.Yu. Levinson-Lessing attached special significance to liquid immiscibility in melts. Processes of magma interaction with volatile components provided the basis of his syntectic–liquid immiscibility hypothesis of differentiation processes occurring in a liquid magma. However, the lack of experimental data on the fluid–magma system under conditions approaching natural ones resulted in a disappointment and, then, forgetting the ideas on liquid-state differentiation. The hypothesis of crystal fractionation was put forward as an universal mechanism of magma differentiation.

ANALYSIS OF THE FLUID REGIME OF IGNEOUS COMPLEX FORMATION

Before launching our experimental studies on fluid–magma interaction, it was necessary to analyze the nature and proportions of gases in magma-related fluids
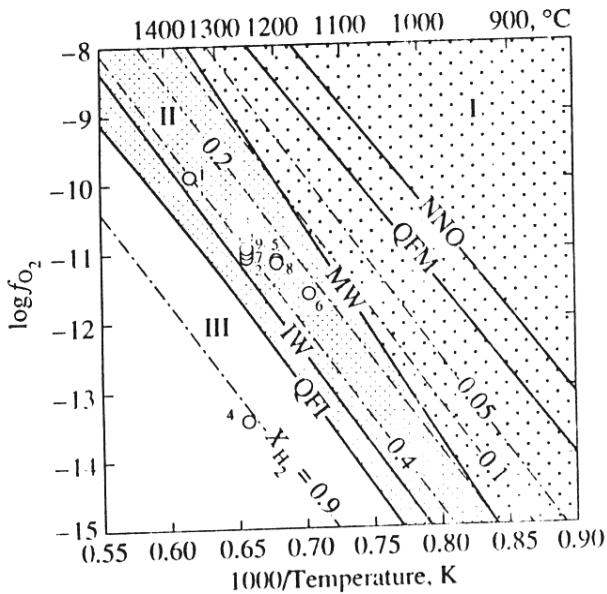
Fig. 1. Values of oxygen fugacity in the experiments in comparison with the redox conditions of formation of igneous complexes in the Earth's crust (Kadik *et al.*, 1990; Carmichael, 1991) and lunar rocks (Bezmen, 1992).

(I) Continental volcanic rocks; (II) layered intrusive complexes and ocean floor basalts; and (III) lunar rocks.

Numerals denote experiment numbers in the table; the dash–dotted line shows mole fractions of hydrogen relative to water as a function of oxygen fugacity at a total pressure of 1 kbar.

from complexes of various associations. The evolution of basic–ultrabasic magmatism occurs at a reduced fluid regime, especially at early stages of the Earth development. Owing to its high chemical affinity to iron, hydrogen was concentrated in the planetary core during the formation of the Earth's shells together with other hydrogen-bearing gases (Marakushev and Bezmen, 1983; Bezmen, 1992; Marakushev, 1994). During the subsequent evolution, hydrogen entered the upper shells, where it was oxidized and stimulated the processes of metamorphism and magmatism (Marakushev, 1994). According to Letnikov (1982), in Archean and Early Proterozoic time, metamorphism and magmatism were characterized by an areal reduced fluid regime. During that period, the majority of differentiated basic–ultrabasic complexes were formed. In the Late Proterozoic, the areal reduced regime was changed by linear one. Presently, the inflow of reduced fluids occurs probably in hot-spots and tectonically active structures: in mid-ocean ridges and along island arcs. Thus, in addition to water and carbon dioxide, the fluid phase of igneous melts contained hydrogen and hydrogen-bearing gases: methane, ammonium, and hydrogen sulfide interrelated by redox reactions. As the most mobile gas, hydrogen escapes from a magma chamber during crystallization, and subsequent oxidation processes disguise its presence in melts. In the magma–fluid system, hydrogen is connected in the presence of water by the

reaction with oxygen. Therefore, it is possible to estimate hydrogen mole fraction with respect to water through the oxygen fugacity of formation of volcanic and plutonic complexes in the Earth's crust (Fig. 1). There is considerable data in the literature on the redox conditions of crystallization of rocks, mineral assemblages, and individual minerals of igneous complexes of various associations. On average, the oxygen fugacities of continental basalt eruptions are close to the QFM buffer equilibrium (Carmichael, 1991). However, early crystallization phases show lower f_{O_2} values than lava flows (Sato, 1972), which allows us to suggest a more reduced character of basalt melts in the zones of their generation. The values of oxygen fugacity at the formation of oceanic basalts are between the WM and IW buffer equilibria (Kadik *et al.*, 1990). This means that hydrogen (and, of course, other reduced gases) must occur in substantial amounts in the fluid phase (Fig. 1). Owing to hydrogen dissipation in surficial environments, the magmas are oxidized and approach the QFM buffer. Probably, an increase in the oxidation potential proceeds in such a way during the crystallization of intrusions. In general, the oxygen fugacity value of layered complexes is often controlled by the presence of carbon and lies in the wüstite stability field, independent on the bulk composition and geologic environment of massif formation. The corresponding values of hydrogen fugacity suggest a significant fraction of hydrogen in the fluid (Fig. 1).

PREVIOUS WORK ON THE INTERACTION OF REDUCED FLUIDS WITH MAGMATIC MELTS

Because of methodic problems, there is a limited body of data in the literature on the interaction of fluids with aluminosilicates under reduced conditions. It includes mainly the results of investigations of melting of rock-forming minerals under pressure of essentially pure hydrogen, methane–hydrogen, and water–hydrogen fluids. A few publications presented evidence on the solubility of fluid components in magmatic melts including those with complex fluids of the H–C–O system containing H_2O, CO_2, CO, CH_4, and H_2.

It was established that pure hydrogen pressure decreased the melting temperatures of aluminosilicates. For instance, the liquidus temperature of albite falls by approximately 80°C at 5 kbar in comparison with the dry system (Persikov *et al.*, 1990), which is strongly different from the effect of water (ca. 400°C) under similar conditions (Burnham and Davis, 1974) The solubility of hydrogen in melts is low compared to that of water: 0.06 wt % of H_2 versus 6.55 wt % of H_2O at 2 kbar and 1200°C (Bezmen *et al.*, 1991). These results suggest that interaction with pure hydrogen does not cause significant depolymerization of silicate melt.

Eggler and Baker (1982) reported a depression of diopside liquidus temperature by approximately 100°C in a strongly reducing environment (near Si–SiO$_2$ equi-

librium) at a pressure of methane–hydrogen fluid of 21 kbar in equilibrium with graphite. A similar effect of 85°C was observed by Taylor and Green (1987) for the nepheline–forsterite–quartz composition at 28 kbar in the presence of methane-dominated fluid, $CH_4 : H_2 \approx 9 : 1$, which is comparable with the influence of pure carbon dioxide on the liquidus temperature (~90°C at 28 kbar).

Of special significance are data on the interaction of water–hydrogen fluid with silicate melt. The addition of hydrogen to the Ab–H_2O, Ab–Qtz–H_2O, and Ab–Or–Qtz–H_2O systems results in an initial decrease in the melting temperature of albite, albite–quartz eutectic, and haplogranite system relative to their melting temperatures at water fugacity equal to the value in the gas mixtures succeeded by an increase in this temperature at higher hydrogen contents in the system. At $X_{H_2O} = 0.95$–0.90 and a total pressure of 2 kbar, the melting curves show pronounced minima with a liquidus temperature depression by 30°C and more. However, further addition of hydrogen results in an increase in the liquidus temperature relative to that at pure water pressure (Bezmen et al., 1998, 1999). These data are consistent with the results reported by Luth and Boettcher (1986), who demonstrated that in a strongly reducing environment at equilibrium of water–hydrogen fluid with the IW buffer at pressures of 5–30 kbar, the liquidus temperatures of diopside, albite, and quartz decreased and the magnitude of this decrease was greater than that for $H_2O + CO_2$ pressure at the same water fugacity in fluid. The existence of minima on the melting curves of silicates is supported by an increase in water solubility in melts at low hydrogen activities (Bezmen et al., 1991). Holloway and Jakobsson (1986) determined experimentally the solubility of CO_2, CO, CH_4, H_2, and H_2O in albite melt at pressures of 10, 15, and 20 kbar and a temperature of 1200°C. Fluid phase of the H–O–C system was in equilibrium with graphite, wüstite, and metallic iron. These authors demonstrated that gases dissolved in melt showed substantially higher H_2O/H_2 and CO/CO_2 ratios than those in the fluid phase.

The dissolution mechanism of hydrogen, water–hydrogen fluid, and methane in silicate melts has been studied in general terms. At 2 kbar, pure hydrogen and its mixtures with water dissolve in melts as molecular water and OH⁻ species (Bezmen et al., 1991). However, at high pressures of $H_2O + H_2$ fluid (15–25 kbar), H–H vibrations were recorded in albite melt in equilibrium with the IW buffer (Luth et al., 1987). Methane also dissolves as OH⁻ species and molecular water, while carbon either forms Si–C bonds or distributes randomly in the melt structure reducing silicon to a divalent form (Taylor and Green, 1987).

It should be noted that except for our previous works (Bezmen et al., 1991, 1998, 1999), hydrogen mole fraction in the experiments was controlled by MW and IW

buffer reactions and it was assumed that hydrogen did not react with oxides and metals. However, according to our preliminary results from the investigation of buffer reactions, hydrogen reacts with wüstite and metallic iron and forms mixed compounds depending on its content in H_2O–H_2 mixtures at a total pressure of 2 kbar and temperatures of 700–1200°C. As a result, the reactions pass into divariant fields and shift toward more reduced conditions. For instance, the magnetite stability field expands to $\log f_{O_2}$ of MW – 1.21 at 950°C, and the wüstite stability field, up to IW – 0.63 at 1200°C (Bezmen and Suk, 1990). The ratio H_2O/H_2 in the fluid phase changes correspondingly. Because of this, the results of Schmidt et al. (1997, 1999) on the melting of silicates and water solubility in haplogranite seem to be incompatible with our data. The accounting for the shift of buffer reactions results in the complete consistency of these results with our data.

Thus, most of the published information is related to the investigation of the liquidus temperatures of individual minerals and their eutectic mixtures. The experiments were usually carried out with a small charge (up to 10 mg) and, because of high hydrogen mobility, the duration was low (3–30 min), which is not sufficient for gravitational melt separation.

Fluid-free silicate melts are network polymers, which are not capable of liquid immiscibility. Our previous work demonstrated that the dissolution of hydrogen-bearing gases resulted in such a degree of melt depolymerization that the microheterogeneous quasicrystalline structure of silicate liquids passed into cryptic layering manifested in a gradual change in melt composition with height in the gravitational field of the Earth. Contrast layering developed with increasing duration of experiments (Bezmen and Suk, 1983; Bezmen, 1992a, 1992b, 1994; Bezmen and Elevich, 1998; Fed'kin et al., 1999; Bezmen et al., 1999).

In addition to our publications, similar effects were reported by Persikov and Epelbaum (1985) and Persikov et al. (1986). They observed superliquidus layering of iron-rich gabbronorite at a pure hydrogen pressure of 0.75 kbar and 1250°C. The interaction of pure hydrogen with high-iron silicate melts during two hours resulted in the formation of cryptic layering with the gravitational accumulation of iron-rich melts in the lower portions of the capsule.

This paper presents new experimental data on the modeling of superliquidus differentiation of magmatic melts as a result of their interaction with fluid systems of various igneous complexes, whose fluid regime and other physicochemical parameters of formation are known. In this context, the obtained experimental data are compared with the differentiation characteristics of particular massifs. Special emphasis is placed on the consideration of the supposed mechanism of superliquidus differentiation and its probable role in the formation of differentiated massifs.
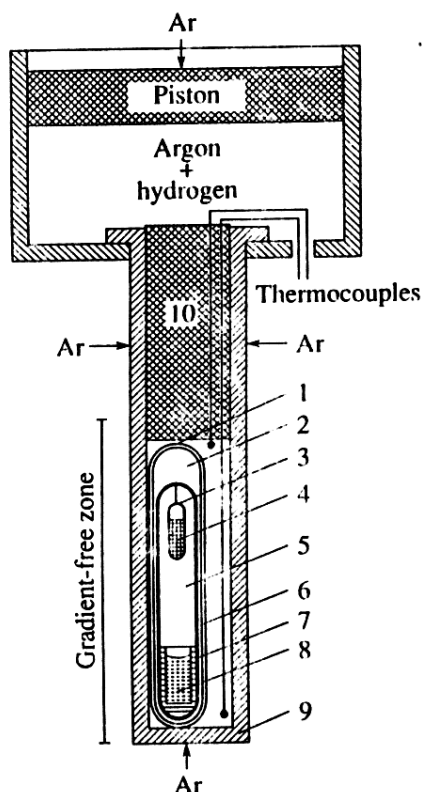
Fig. 2. A hydrogen cell attached to a high-pressure vessel.
1. Outer Pt capsule, 8 mm in diameter and 70 mm long; 2,
hydrogen–water fluid in the outer capsule; 3. open platinum
tube or alundum crucible for buffer mixtures or indicators of
gas fugacity hanged on a platinum wire; 4, buffer or indica-
tor of f_{O_2}, f_{S_2}, f_{HCl}, and other gases; 5, fluid of the system
H–O–C or H–C–O–S; 6, platinum capsule, 7 mm in diame-
ter and 50 mm long; 7, crucible of vitreous carbon, molyb-
denum, or Fe–Ni alloy; 8, silicate glass; 9. tungsten reactor;
and 10, alundum spacer.

EXPERIMENTAL METHOD

The experiments were carried out in a high-pressure
gas apparatus at controlled fugacities of gases in the
systems H–O–C or H–O–C–S, which comprise the
major constituents of magmatic fluids. A specific fea-
ture of our experimental method is the direct dozing of
hydrogen in the fluid composition by means of its dif-
fusion through the walls of platinum capsules and the
control of fugacities of other gases of the H–O–C–S
system by buffer reactions and indicators. The hydro-
gen cell with the capsule is schematically shown in
Fig. 2.

The initial silicate materials were represented by
glass columns of various compositions prepared from
oxides. Oxide mixtures were preliminary dried at
1000°C for 12 h and melted in a vacuum furnace at
1600–1700°C, which resulted in the formation of
homogeneous glasses. It was experimentally estab-
lished that during melting (25 min), 15–20% of alkalis

were lost. The charges contained excess alkalis to
account for the observed losses. In some experiments,
natural rocks were used for the preparation of initial
glasses. In order to prevent iron diffusion from the melt
into the platinum container, the experimental mixtures
were loaded into crucibles of vitreous carbon, molyb-
denum, or Fe–Ni alloy. Vitreous carbon crystallized
during the experiment and served simultaneously as an
indicator of carbon activity. The crucibles were placed
into a platinum capsule, 7 mm in diameter, 50 mm high,
and with a wall thickness of 0.2 mm. If necessary, the
control of composition of complex gas mixtures was
attained by means of an oxygen fugacity buffer (oxide
mixture), an HCl buffer (apatite), or an indicator of sul-
fur fugacity (pyrrhotite), which were placed in the cap-
sule in a separate container. Then, water was poured
into the capsule; its weight depended on pressure and
temperature and varied from 80 to 200 mg. In addition,
in order to accelerate the attainment of reducing condi-
tions, paraffin, C_nH_{n+2} was loaded into the platinum
capsule in some experiments. It was experimentally
established that at high temperature (higher than
1200°C) and long run duration, especially in the pres-
ence of iron-bearing melts, oxygen diffusion occurred
through the walls of the Pt capsule. In order to diminish
water loss in the reaction Pt capsule, it was welded and
placed into a larger Pt container (8 mm in diameter and
70 mm in height), which was filled with water (250–
300 mg) and also welded (Fig. 2). The presence of
water in the reaction capsule after the experiments was
a necessary prerequisite for the reliability of the exper-
iment. The welded capsule was loaded into a tungsten
or rhenium reactor (Fig. 2), which was filled at a pres-
sure of 100 atm with an argon–hydrogen mixture hav-
ing a desired hydrogen mole fraction. According to
Chou (1986), hydrogen fugacities in the reactor and Pt
capsules converged during a few minutes at tempera-
tures of 1200°C. The inner volume of the reactor was
separated from the pressure-transmitting medium
(argon) in a high-pressure gas vessel by a piston equal-
izer.

Negligible gradients of intensive parameters are
major requirements for the experimental method used
in a study of differentiation. The gradient-free temper-
ature zone was monitored by two independent heating
coils and was controlled by two thermocouples inserted
into the reactor. Temperature gradient was within ±1°C
along the capsule length (50 mm). Thus, the container
with a sample, 7–10 mm high, was situated in the zone
practically free of any temperature gradient. The ther-
mocouples were calibrated against the melting temper-
atures of pure gold, and the accuracy of temperature
measurement was ±7°C. In addition, the temperature
gradient along the capsule was controlled by melting of
gold foil.

At high temperatures, no hydrogen loss was
observed through the 3-mm-thick walls of tungsten or
rhenium reactors (Bezmen, 1989, 1992). Hence, hydro-
gen fugacity was invariant during the whole experi-

Thermodynamic parameters of the experiments

Sample no.	Starting material	P, kbar	T, °C	$-\log f_{O_2}$	$-\log f_{S_2}$	X_{H_2O}	X_{H_2}	X_{CO_2}	X_{CO}	X_{CH_4}	X_{H_2S}	X_{HCl}	Duration, h
1	*Ol-Pl* bronzitite	4	1350	9.9	3.71	0.310	0.20	0.077	0.190	0.218	0.003	–	96
2	*An-Opx*	4	1250	11.09	1.80	0.284	0.20	0.032	0.080	0.350	0.050	–	72
3	*An-Opx*	3	1250	10.77	0.27	0.200	0.10	0.113	0.190	0.070	0.320	–	72
4	*An*-gabbro–ilmenite	4	1250	13.43	–	0.027	0.28	0.005	0.005	0.687	–	–	72
5	Ijolite–urtite–apatite	2	1200	11.12	–	0.252	0.10	0.273	0.319	0.056	–	–	72
6	"	2	1150	11.61	–	0.304	0.10	0.274	0.250	0.073	–	–	48
7	"	4	1250	11.00	–	0.319	0.20	0.041	0.090	0.350	–	–	72
8	Anorthosite–granite	4	1200	11.17*	–	0.667	0.25	0.007	0.009	0.065	–	–	10
9	Anorthosite–bronzitite	3	1250	10.95**	–	0.406	0.25	0.067	0.036	0.107	–	0.18***	12

* Fe–FeO, Ni indicator of f_{O_2} (Bezmen and Suk, 1990).

** Mo–MoO₂ buffer.

*** Calculated from the ratio of chlorine (2.73 wt %) and water (0.85 wt %) in the apatite indicator (Bezmen, 1992).

ment. The fugacities of other gases in the system H–O–C–S were calculated from reaction between them (Bezmen, 1992a, 1992b; Bezmen *et al.*, 1994).

After the experiment, the charge was represented by a column of glass or material partially crystallized during quenching, 3–5 mm in diameter and 5–8 mm high, which showed a convex meniscus in vitreous carbon crucibles and a concave meniscus in metal crucibles. The charge was sectioned into two parts, which were used for preparation of thin sections for optical examination and polished sections for the analysis on a Camebax electron microprobe.

The experiments were performed at temperature and water partial pressure above the liquidus. Hydrogen fugacity and proportions of other gases were selected in such a way as to model the natural conditions of particular massifs, which were estimated from direct investigations of oxygen fugacity or composition of gas inclusions in minerals. In some experiments, layering was not observed under experimental parameters. In such cases, temperature or pressure were changed and the critical gas composition was selected again.

RESULTS OF THE EXPERIMENTAL MODELING OF LIQUID-STATE MELT LAYERING

Experimental Modeling of Ultrabasic Magma Differentiation

Our previous work (Bezmen and Suk, 1983; Bezmen, 1992a, 1992b; Bezmen and Elevich, 1998) was focused primarily on the basic–ultrabasic superliquidus layering, which was obtained for basic melts of various compositions at their interaction with complex hydrogen-bearing fluids under redox conditions approaching those of natural environments. In this paper, we present

experimental results on the layering of ultrabasic melt chemically corresponding to the basal zones of stratiform massifs. In this part of the section, the major role is played by dunite and olivine bronzitite with minor plagioclase. The average composition of the basal zone is close to plagioclase-bearing olivine bronzitite. Glass of the following composition was synthesized as a starting material for this experiment (wt %): SiO_2 = 49.10; TiO_2 = 0.20; Al_2O_3 = 7.56; Fe_2O_3 = 9.48; FeO = 5.36; MnO = 0.16; MgO = 22.79; CaO = 4.52; K_2O = 0.11; and Na_2O = 0.71. The experiment was carried out under gas pressure of the system H–O–C–S at 4 kbar and 1350°C. The mole fraction of hydrogen in the experiment was controlled by an argon–hydrogen mixture at X_{H_2} = 0.2. The fugacities of other gases (table, sample 1) were calculated taking into account the presence of elemental carbon, which was used as a crucible material, and composition of pyrrhotite melt. It was suggested that the experimental parameters were close to the conditions of formation of the Bushveld intrusion. The rocks of the Bushveld complex are characterized by the presence of abundant elemental carbon with a mantle isotope signature (Touysinhthiphonexay *et al.*, 1984; Elliott *et al.*, 1982). Gas–liquid inclusions in the minerals contain reduced gases including CH_4 (Ballhaus and Stumpfl, 1985). The experimental oxygen fugacity was close to the natural value (Elliott *et al.*, 1982).

Under the pressure of hydrogen-bearing fluid in the absence of temperature gradient, the initial melt exhibits layering with the separation of a zone in the upper part of the crucible chemically similar to dunite (Fig. 3). The superliquidus temperature was confirmed by experiments with pure water pressure ($P_{H_2O} = P_{tot} =$
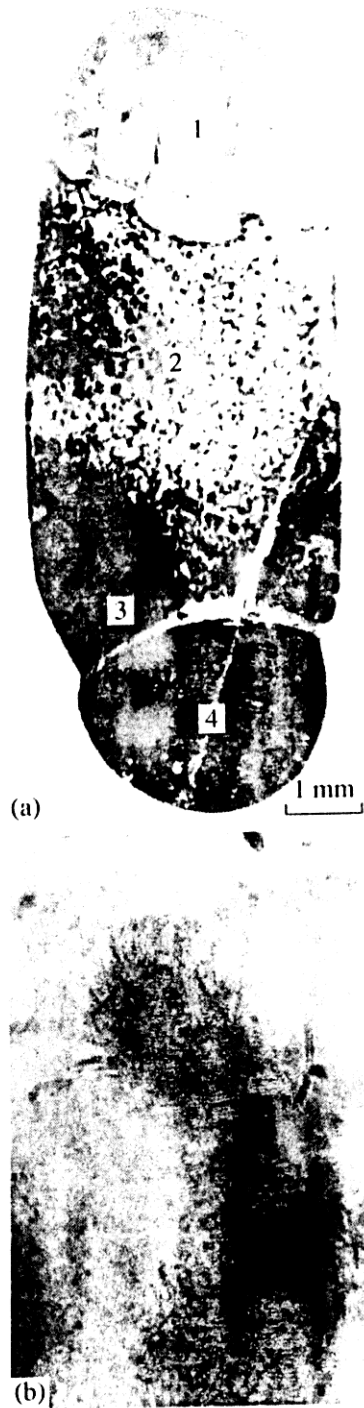
1200 bar) equal to water partial pressure in the mixture (X_{H_2O} = 0.310; table, sample 1). The peridotite zone is composed of large (up to 1 mm) euhedral olivine grains, which crystallized during quenching, almost without interstitial liquid between them. The average composition of this zone (scanned with a defocused 100 μm beam) is the following (wt %): SiO_2 = 42.76; TiO_2 = 0.2; Al_2O_3 = 4.20; FeO = 17.41; MnO = 0.21; MgO = 32.69; CaO = 2.14; Na_2O = 0.44; and K_2O = 0.07. After four-day exposure, liquid layering developed in the lower zone in a form of spherical aggregates (Fig. 3b) concentrated in the lower part of the sample. The resulting liquid is enriched in bronzite (wt %): SiO_2 = 51.09; TiO_2 = 0.2; Al_2O_3 = 9.37; FeO = 15.13; MnO = 0.15; MgO = 18.36; CaO = 4.71; Na_2O = 0.84; and K_2O = 0.17 (Fig. 3a). The matrix melt is represented by transparent glass similar in composition to plagioclase bronzitite (wt %): SiO_2 = 50.80; TiO_2 = 0.20; Al_2O_3 = 9.99; FeO = 14.34; MnO = 0.15; MgO = 17.61; CaO = 5.78; Na_2O = 0.95; and K_2O = 0.18. After quenching, the X-ray amorphous spheroids show a fibrous texture (Fig. 3b). This is not liquid immiscibility, because there is no interface boundary (Fig. 3b).

In our previous experiments on the layering of basalt magmas (Bezmen and Suk, 1983; Bezmen, 1992), more basic liquids accumulated in the lower portions of the samples. In contrast, in the present experiment, fluid-bearing dunitic melt was accumulated in the upper part of the capsule. It is conceivable that the high chemical affinity of light volatile components to mafic elements (Marakushev and Perchuk, 1972) promoted in the absence of temperature gradient the accumulation of fluid-bearing ultrabasic (in the silicate constituent) liquid in the upper part of the sample. Similar relationships with the concentration of heavy minerals in the upper parts of layers are often observed in natural massifs (Campbell, 1978).

Fig. 3. Layering of *Ol–Pl* bronzitite under H–C–O–S fluid pressure at 1350°C and 4 kbar (X_{H_2} = 0.2) at an experimental duration of four days.
(a) Photomicrograph of the sample: (1) peridotite of the upper zone crystallized during quenching; (2) *Pl* bronzitite matrix of the lower zone (glass); (3) accumulation of bronzite-rich melt (b) in the lower part of the sample; (4) pyrrhotite melt crystallized during quenching (indicator of sulfur and H_2S fugacity).
(b) Fine dispersed linear aggregates (magnification 1000) in quenched liquid enriched in bronzite.

Superliquidus Formation of Chromitite Melts

Chromite ores occur in varying proportion with ultrabasic rocks in massifs and reflect their magmatic heterogeneity related to liquid-state differentiation. They form individual thick layers and piles of massive, often monomineral rocks or intercalate rhythmically with mafic–ultramafic rocks (dunite, pyroxenite, occasionally anorthosite). In general, the type of mineralization changes from chromite in dunite–harzburgite ophiolite associations to chromite–platinum-group metal (native) in dunite–clinopyroxenite associations of rift zones and chromite–platinum-group metal (sulfide) in the stratiform magmatism of platforms.

The experiments on the liquid-state separation of chromite from silicate melt in the presence of sulfide platinum-bearing liquid was carried out at 1250°C under H–O–C–S fluid pressure. The conditions of these experiments are shown in the table (samples 2 and 3).
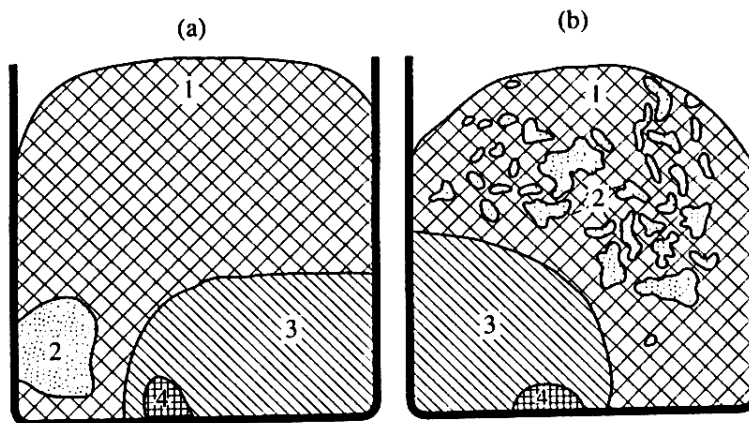
(a)   (b)

Fig. 4. Results of experimental superliquidus separation of anorthite-bronzitite melt into (1) silicate and (2) chromitite liquids at 1250°C. The sample contains (3) sulfide melt (indicator of sulfur fugacity) and (4) platinum-group metal phase.
(a) $P = 4$ kbar, $X_{H_2} = 0.2$; (b) $P = 3$ kbar, $X_{H_2} = 0.1$.

The starting material was represented by homogeneous glass of an anorthite–orthopyroxene composition, $An_{80}Ab_{20}$ (30 wt %)–$En_{75}Fs_{25}$ (70 wt %) with an initial content of Cr_2O_3 of 0.5 wt %, which is similar to the bulk composition of the Merensky reef of the Bushveld complex. The experiments were performed in vitreous carbon crucibles, i.e., at carbon activity equal to one. Pyrrhotite was used as an indicator of sulfur fugacity.

Figure 4 shows the results of a three-days' experiment. Chromitite liquid (17.85 wt % Cr_2O_3) crystallized during quenching in the lower part of the crucible (Fig. 4a) or formed irregular segregations (3.87 wt % Cr_2O_3) randomly distributed throughout the silicate column (Fig. 4b). It is enriched in sulfur (0.8 wt %) relative to the silicate melt (0.1–0.2 wt %). The chromitite melts are also rich in platinum-group elements and gold. However, the partition coefficients of these elements between silicate and chromitite liquids according to the data of neutron activation analysis (Bezmen, 1992; Bezmen et al., 1994) are lower by several orders of magnitude ($K_D = n \times 10^{-2}$) than for sulfide–silicate partitioning ($K_D = 10^{-3}$– 10^{-5}).

Experimental Modeling of Ilmenite Ore Formation in Gabbro–Anorthosite Massifs

The separation of ore liquids of an ilmenite-dominated composition was experimentally modeled using a preliminary prepared glass consisting of 67 wt % of anorthite gabbro from the Novomirgorod Massif (Ukrainian shield) and ilmenite (33 wt %). The glass was obtained at 1600°C in a vacuum furnace. It contained needles of quench ilmenite, and was finely ground together with apatite (5 wt %) in a jasper mortar. A charge of 210 mg was pressed into a vitreous carbon crucible, which was loaded into a platinum capsule, 7 mm in diameter. Then, 150 mg of acid solution (0.25 wt % HF, 0.25 wt % HCl, 0.15 wt % H_3PO_4, and 0.15 wt % H_3BO_3) and 50 mg of paraffin, C_nH_{n+2} were

loaded into the capsule. The capsule was welded shut and inserted into a tungsten reactor (Fig. 2). The experiments were performed at $P = 4$ kbar and $T = 1250°C$ in a strongly reducing environment (Fig. 1). Methane and hydrogen were the major fluid components (table, sample 4). The composition of fluid phase (table, sample 4) was controlled by the known mole fraction of hydrogen and the presence of carbon, which was used as a crucible material. During three days, the melt interacted with fluid and separated into three zones (Fig. 5): (I) ilmenite, (II) rutile, and (III) anorthite gabbro. An essentially monomineral ilmenite zone formed in the upper part of the capsule. It should be pointed out that, despite low oxygen fugacity (Fig. 1), there was no metallic iron in the experiment, because its activity in the melt was significantly lower than one.

In the anorthosite massifs of the Ukrainian shield, lenses of rocks with vertical layering often occur among anorthosite. Their layering is represented by a sequential change from leucocratic rocks to more melanocratic (up to peridotite) from bottom to top in the section. Massive ilmenite or titanomagnetite ores are confined to the latter (Kudinova, 1987; Tarasenko, 1987). The massifs were formed under reducing conditions, which is suggested by the occurrence of rocks with euhedral graphite phenocrysts. The theory of crystallization differentiation does not provide a mechanism for the formation of monomineral rocks at high porosity of cumulates and the confinement of heavy minerals to the upper parts of the sections of massifs. These facts are easily explained by the hypothesis of liquid-state differentiation, which is supported by the experiments. The fluid-rich liquid of an ilmenite composition is enriched in low-density components and. accumulated in the upper part of the sample as an almost monomineral layer.
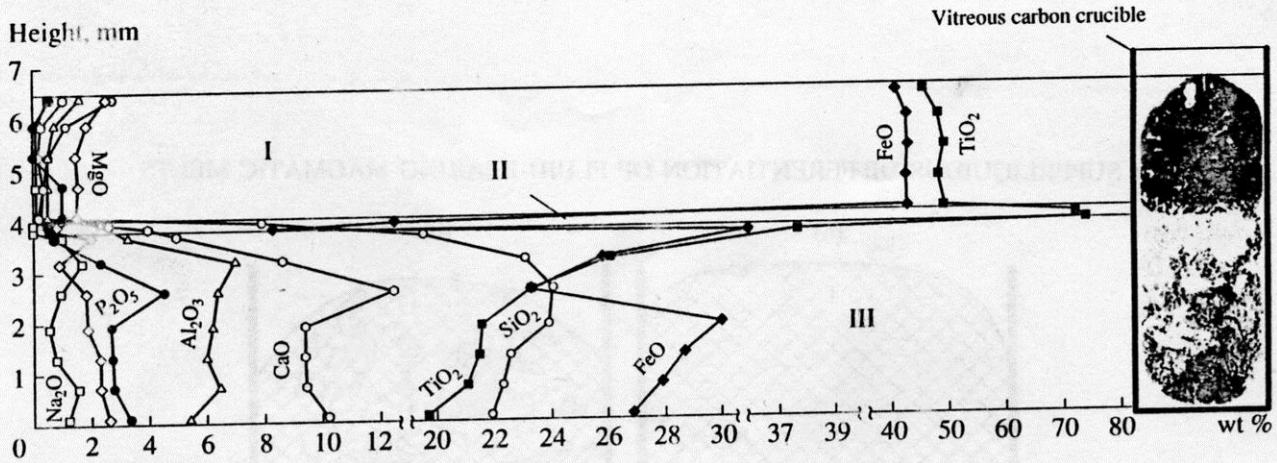
Fig. 5. Influence of hydrogen–methane-dominated fluid on the differentiation of ilmenite–anorthosite melt under strongly reducing conditions.
Zones: (I) ilmenite; (II) rutile; and (III) gabbro.

Modeling of the Liquid-State Formation of the Khibiny Apatite Ores

Another example of the liquid-state separation of ores is illustrated by the experimental modeling of apatite mineralization in the Khibiny alkaline massif. It is known that apatite ores are denser than host ijolite–urtite rocks and occur in the upper part of the horizon. According to various authors, the total pressure of the formation of the massif was 2–5 kbar and the temperature of intruding melt was 1100–1350°C (Zyryanov and Kozyreva, 1981). The presence of large amounts of hydrogen, methane, and carbon monoxide in gas–liquid inclusions in minerals from various rocks of the massif suggests a reducing regime of volatile components. The redox conditions were calculated from the analysis of gas phase released at high temperature from apatite (Karzhavin et al., 1975; Suk, 1990). The calculated oxygen fugacity was within the wüstite stability field (Fig. 1). The experiments were carried out at $P =$ 2 kbar, $T = 1150°C$ and 1200°C (table, samples 5, 6) and at 4 kbar and 1250°C (table, sample 7). The proportions of gases in the fluid phase of the H–C–O system were controlled by hydrogen fugacity and the presence of carbon, which was used as a crucible material. The starting material was represented by columns of homogeneous glass, which was preliminary synthesized at a water pressure of 1.5 kbar. Melt composition corresponded to the average composition of the ijolite–urtite horizon (Zak et al., 1972) with 10 wt % of apatite: $SiO_2 = 41.24$, $TiO_2 = 2.11$, $Al_2O_3 = 18.1$, $FeO = 7.37$, $MnO = 0.18$, $MgO = 2.0$, $CaO = 11.15$, $Na_2O = 8.30$, $K_2O = 4.78$, and $P_2O_5 = 4.35$ wt %. 150 mg of acid solution of HF (2 wt %) and HCl (2 wt %) was poured into the capsule.

In the experimental series at 2 kbar, 1200°C, and three-day duration, the fluid-bearing phosphate–silicate liquid was separated into three zones, which showed cryptic and contrasting layering. Apatite-rich melt accumulated in the upper part of the sample (Fig. 6a). In this experiment, all the zones were composed of glass without any quench crystals. There were also no interface boundaries between the melts, which are characteristic of liquid immiscibility. The boundary between zones I and II (Fig. 6a) is traced by gas phase released during quenching from the fluid richer upper zones of melt as small gas inclusions. The boundary between zones II and III was defined by different characters of cryptic layering, which resulted in the accumulation of the urtite component between the zones. Thus, in addition to the accumulation of apatite-rich liquid in the upper part of the sample, there is cryptic layering of the ijolite–urtite type.

The experimental design was then complicated in order to reproduce rhythmic layering. The material was initially kept for two days at 1200°C and then temperature was reduced to 1150°C and the experiment continued for two more days. This resulted in the appearance of a fundamentally new type of layering: in addition to further apatite accumulation in the upper part of the sample, melt of a nepheline syenite composition formed as a thin layer at the base of the capsule (Fig. 6b). Similar to other experiments on liquid layering, the general regularity was manifested of more contrasting separation of melts in experiments with longer duration.

An increase in total pressure up to 4 kbar at a temperature of 1250°C and a mole fraction of hydrogen of 0.2 resulted in more contrasting layering into two zones. The upper zone is enriched in apatite ($SiO_2 = 30.96$, $TiO_2 = 1.63$, $Al_2O_3 = 13.75$, $FeO = 2.95$, $MnO = 0.12$, $MgO = 1.47$, $CaO = 20.12$, $Na_2O = 7.61$, $K_2O = 4.09$, and $P_2O_5 = 17.28$ wt %), and its volatile content was so high that even isobaric quenching resulted in significant contraction. The high content of fluid in melt promoted its crystallization and formation of quench needle and dendritic crystals of apatite and
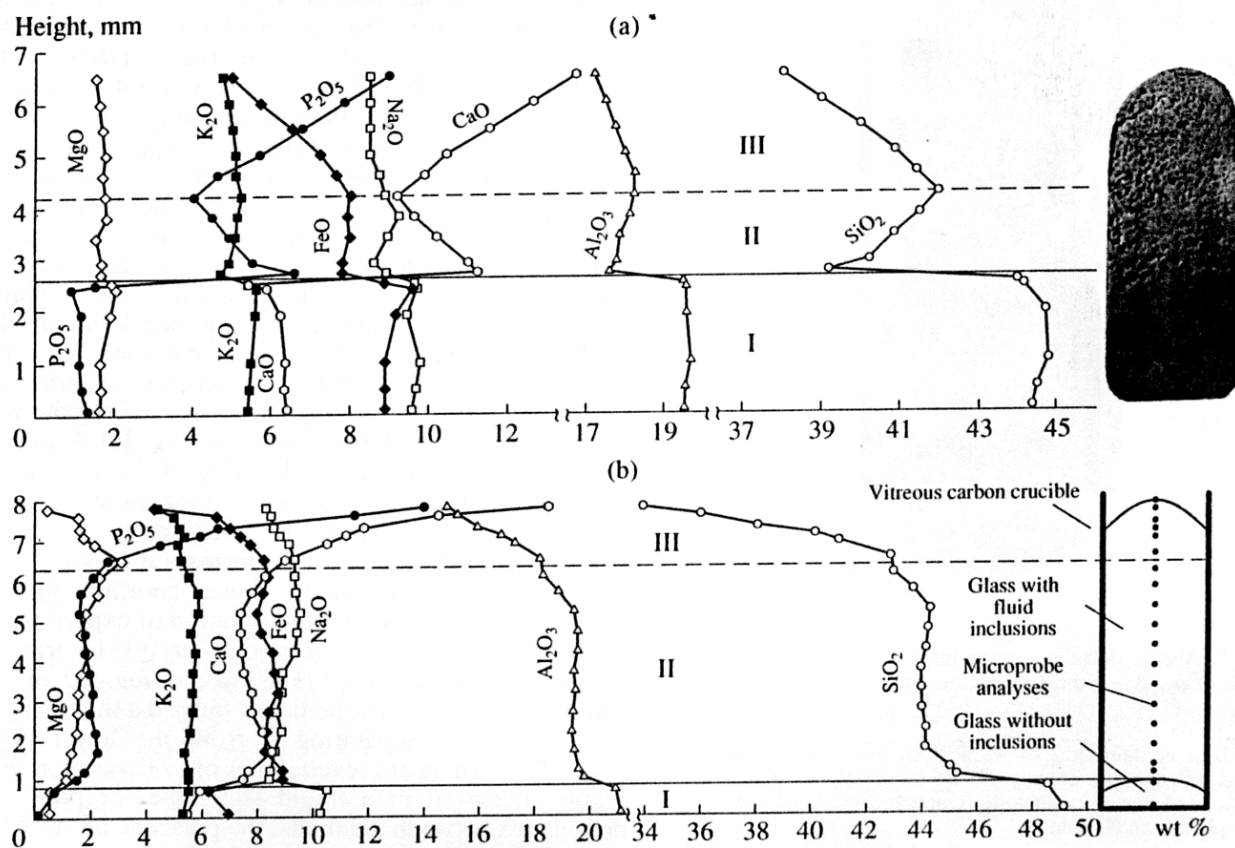
Fig. 6. Experimental modeling of the genesis of apatite ores from the Khibiny alkaline massif (Kola Peninsula). Development of cryptic and contrasting superliquidus layering at the interaction of apatite-bearing alkaline melt with H–C–O fluid at a total pressure of 2 kbar.

(a) Results of an experiment at 1200°C and a duration of 72 h: (I) zone with low phosphorus content without cryptic layering; (II) zone with a decrease in apatite content with increasing distance from the bottom of the sample; and (III) zone of apatite accumulation in the upper part of the sample. (b) An experiment at 1200°C and 48 h with subsequent drop of temperature to 1150°C and 48 h exposure: (I) nepheline syenite layer; (II) zone of weak cryptic layering; and (III) ore zones of extensive apatite accumulation in the upper part of the sample.

sphene (Fig. 7). The lower zone is composed of glass of the following composition (wt %): SiO_2 = 46.14, TiO_2 = 2.08, Al_2O_3 = 19.23, FeO = 6.58, MnO = 0.19, MgO = 2.33, CaO = 5.70, Na_2O = 9.75, K_2O = 5.72, and P_2O_5 = 2.19. Thus, in this experimental series, similar to that described above, the heavier mineral apatite under thermodynamic conditions approaching natural ones was accumulated as a lighter fluid-bearing liquid in the upper part of the sample, which is in full accord with the geologic structure of the apatite–ijolite–urtite horizon of the Khibiny alkaline massif (Zak et al., 1972). Furthermore, the apatite ores are often brecciated. Ore melts are richest in fluid components and, hence, they crystallized after the solidification of the host rocks. Presumably, the accumulation and subsequent explosive release of fluids were responsible for the formation of areas of brecciated ores.

The experimental investigation suggests that methane played a significant role in the differentiation processes. Its high fugacity was prerequisite for the accumulation in the upper parts of samples of more basic (in

silicate component) or fluid-containing ore melts (Figs. 3, 5–7).

A POSSIBLE MECHANISM OF SUPERLIQUIDUS MELT LAYERING

It is usually thought that layering in magmatic melts is a consequence of heat and mass transfer owing to thermal and chemical gradients. In such a case, concentration and heat convection cells (D–D type) are formed, which results in magmatic stratification (Frenkel', 1995). As was noted above, a careful control demonstrated the complete absence of temperature gradients in our experiments. Chemical gradients could result either from a temperature gradient or mass fluxes of components. Let us suppose that despite the absence of temperature gradients, there was a flux of hydrogen owing to some reason. Then, a question emerges as to the mechanism of mass transfer of major elements having constant valency. Similar to water, hydrogen dissolves in melt as OH^- species and molecular water

Fig. 7. Abrupt decrease of apatite-rich melt volume as a result of degassing during isobaric quenching ($P = 4$ kbar, $T = 1250°C$, H–C–O fluid, $X_{H_2} = 0.2$, and duration of 72 h).

(1) Glass containing 2.19 wt % P_2O_5 and (2) glass with higher phosphorus content (17.28 wt % P_2O_5) partially crystallized during quenching. Quench crystals of apatite and sphene can be seen.

(Bezmen *et al.*, 1991). According to experimental data, water migration does not cause mass transfer of other elements (Chekhmir *et al.*, 1991). Similarly, hydrogen in the presence of water cannot lead to mass transfer of rock-forming or ore components. Bezmen (1992) demonstrated that the reaction of ferric iron reduction proceeded within a few hours and also did not cause melt heterogeneity. Moreover, the majority of experimental samples reported in this work contained no Fe^{3+}. If mass transfer had been the consequence of hydrogen influence, an increase of its mole fraction in the melt would have resulted in a more strong effect. It was experimentally established that differentiation occurred at certain values of hydrogen fugacity in the fluid. For instance, in a two-day experiment with apatite-bearing ijolite–urtite melts at a hydrogen mole fraction in fluid of 0.05, only weak cryptic layering was observed; at a mole fraction of 0.1, the layering is shown in Fig. 6; and at a mole fraction of 0.3, there was no differentiation in glass at all. Moreover, the interval of hydrogen fugacity favorable for layering depends on temperature and pressure: at high temperature, layering did not occur at

any value of hydrogen fugacity in the experiment. Thus, it can be stated that the values of intensive thermodynamic parameters were held constant in our experiments.

The goal of this work was the experimental modeling of layering processes in particular geologic objects. Because of this, the systems approach was not used for the investigation of the nature of layering. Nevertheless, many types of layering were traced in time. At the experimental modeling of layering in ultrabasic liquid, small (less than 1 µm) star-shaped quench olivine crystals were observed in the glass in the upper part of the sample obtained at short duration (5 h). Zoning developed in longer experiments: initially (24 h), two zones formed with a diffuse boundary and weakly contrasting compositions; then (two days), the contrast increased and the boundary took the form of a meniscus separating crystallized during quenching peridotite of the upper zone and plagioclase bronzitite of the lower zone represented by transparent glass. In longer experiments (up to four days), a third layer enriched in bronzite was formed at the base of the lower zone (Fig. 3a). A similar picture was observed at the layering of ilmenite–anorthite gabbro. Experiments with varying duration (from three hours to three days) demonstrated that, without any temperature gradient, the formation of the upper ilmenite rutile zone and the lower anorthite gabbro zones occurred. At increasing duration of experiments, the zones developed independently. Cryptic layering in the form of an anorthite-rich layer developed in the lower zone (Fig. 5). Rutile liquid formed a thin layer in the upper zone separating it from the lower zone (Figs. 5, 8). There are several lines of evidence that separation occurred in a liquid state: the sharpness of boundaries between the melts, the presence of menisci, and drops of anorthite gabbro in the ilmenite zone, which in turn contained drops of ilmenite (Fig. 9). The formation of melts of ultrabasic, chromitite, apatite, ilmenite and rutile compositions at 1250–1350°C seems to be impossible, but these facts have been experimentally established. The fluid constituent of melts, which degasses at the crystallization during quenching, is of primary importance in this process. The cryptic layering in glasses formation of compositionally contrasting zones without the participation of immiscible liquid drops, and investigation of the dynamics of layering as a function of experimental time suggest that melt differentiation occurred at a macromolecular level.

The thermodynamic description of silicate melts usually relies on the assumption of a quasi-crystalline structure (Berman and Brown, 1987; Ghiorso, 1987), i.e., that there are chemical bonds typical of compounds in a crystal state (Seifert *et al.*, 1981). However, in solids, particles are strictly fixed in certain states, whereas melt is characterized by continuous renewal of particles or fluctuations. Belov (1955) inferred on the basis of thermodynamic calculations that silicate glass must be considered as a combination of silicon–oxygen com-
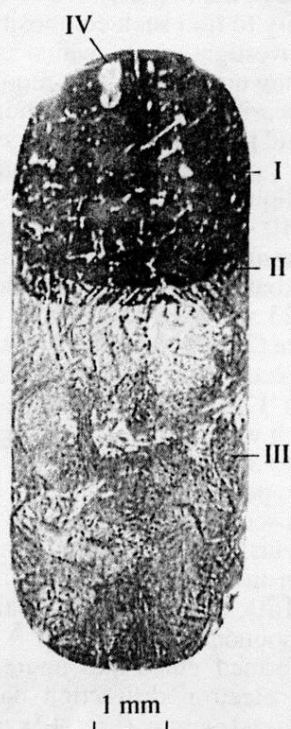
Fig. 9. A drop of anorthite gabbro (*Gb*) with quench crystals of apatite in the ilmenite layer (Fig. 8, IV) containing in turn a drop of ilmenite liquid (*Ilm*). Magnification ×90.

Fig. 8. Photomicrograph of layered ilmenite gabbro obtained under strongly reduced conditions (table, sample 4).

Three layers are distinguished: (I) ilmenite; (II) rutile; and (III) anorthite gabbro. The liquid-state nature of layering is supported by the presence of menisci, sharp boundaries between layers, and retention of (IV) drops of anorthite gabbro in the ilmenite layer (Fig. 9).
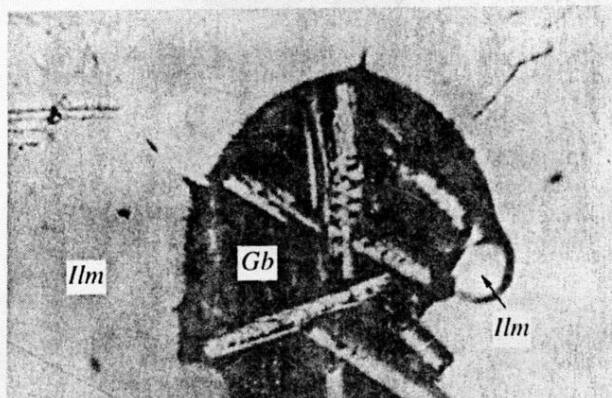
plexes of variable composition and structure. The results of extensive studies of properties and structures of silicate glasses by direct analytical methods (electron microscopy, low-angle X-ray dispersion, cryoscopic, and ultrasonic methods) demonstrated that melts displayed a strongly manifested microheterogeneous structure (Vatolin and Pastukhov, 1980; Porai-Koshits, 1988). In accord with the thermodynamics of irreversible processes, the formation of heterogeneities is related to the development of ordered fluctuating structures, clusters. They can exchange particles and energy with the parental melt, i.e., they are open systems with respect to the melt. The exchange could result in a decrease in the entropy of clusters. This leads to the appearance of nonequilibrium states with high degrees of ordering, which are known as dissipative structures (Glensdorff and Prigogine, 1971).

At constant pressure, two factors affecting cluster formation in melts are temperature and degree of depolymerization, which depends on the character of bonds between ions. At high temperature, the kinetic energy of heat movement of atoms is higher than the potential energy of their interaction, which prevents cluster formation. The experimental investigation demonstrated that at high temperatures, about 200°C above liquidus,

no liquid layering occurred at any value of hydrogen fugacity. A decrease in temperature results in higher probability of formation and larger size of clusters. Moreover, the degree of silicate melt depolymerization is affected by the dissolution of volatile, salt, and other components. Hydrogen and reduced gases exert special influence on the melt, because they reduce the effective valency of silicon in silicon–oxygen tetrahedra (Bezmen, 1992). Depolymerization is accompanied by an increase of water solubility in silicate melts in the presence of hydrogen (Bezmen *et al.*, 1991) and a decrease of liquidus temperature (Bezmen *et al.*, 1998, 1999).

Specially designed experiments demonstrated that separated ultrabasic or ore melts, which were formed at certain *T*, *P*, and composition of fluid phase owing to cluster gravitation, did not melt under the same conditions. This indicates, firstly, that the liquids were separated without the participation of liquid immiscibility processes and, secondly, the formation of clusters occurred under conditions sufficiently far from equilibrium at the proportion of fluid components higher than a certain critical value of one of the parameters, hydrogen fugacity in our case. Thus, clusters and the parent melt continuously exchange particles or groups of particles, whose number and mutual position vary. Clusters cannot exist without melt. In accord with the thermodynamics of irreversible processes (Glensdorff and Prigogine, 1971), if microscopic phenomena occur cooperatively (consistently), from a great number of fluctuating clusters, only a few groups are realized. They probably can move gravitationally in the melt. In such a case, in the course of a steady-state irreversible process, a self-organizing structure forms, which can exist infinitely.

In accord with the chemistry of high-molecular compounds (Strepikheev and Derivitskaya, 1976), fluid-free silicate melts are network polymers. Such melts are characterized by high viscosity and show no

Fig. 10. Separation of anorthosite-rich melt in the upper part of the sample.
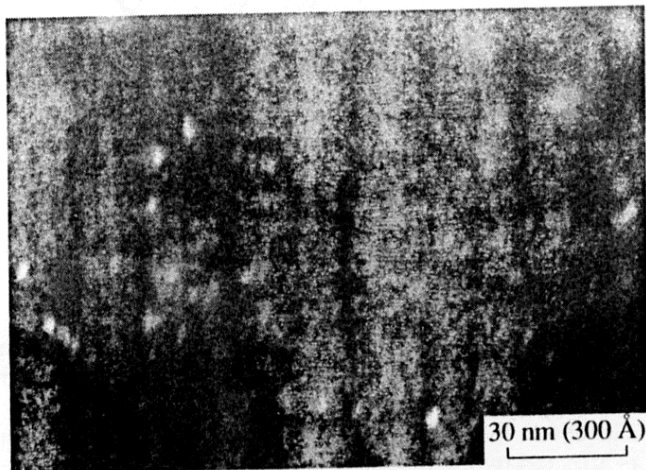The thermodynamic parameters of the experiment are shown in the table (sample 7).

30 nm (300 Å)

Fig. 11. Transmission electron microscope image of glass from the sample shown in Fig. 10, magnification ×16000. The supposed cluster cores are 6 nm (60 Å) in size and show spherical shapes with diffuse outlines.

liquid layering. Furthermore, clusters forming and decomposing in them owing to fluctuations have limited life-time of an order of 10^{-9}–10^{-14} s (Kalashnikov, 1990).

Recent *in situ* studies of fluid-bearing metal systems showed that clusters were a transitional state of matter between liquid and crystal (Stace, 1988). They have a layered structure, which is presented in the jellium model (Cohen and Knight, 1990) as an ordered core and an envelope composed of ligands: OH^-, Cl^-, F^-, CO, CO_2, Cr_2O_3, P_2O_5, etc. (Schmid, 1985; Cohen and Knight, 1990), which provide cluster stability in time (Tredoux *et al.*, 1995). It was shown (Schmid, 1985) that this is a mobile system with a pseudocrystalline core and liquid-like envelope, which is characterized by continuous energy and matter exchange between the core and the envelope and between the fluid envelope and the parental melt. Perhaps, a similar process in fluid–silicate melt is governed by different characters of bonds in aluminosilicate and silicate complexes. Of course, the existence of clusters could be unquestion-

ably proved by *in situ* observations, which is not practicable in high-pressure apparatuses. However, we attempted to analyze the quenched melts obtained in our experiments by transmission electron microscopy.

Since fluid-bearing and highly depolymerized liquids crystallize in the majority of cases during cooling, it was necessary to find such compositions for electron microscope investigation, in which cluster would be preserved during quenching. This requirement was met by anorthite-bearing granite and orthopyroxenite melts affected by fluid pressure for short time intervals, insufficient for the gravitational separation of clusters and formation of liquids of contrasting compositions (10–15 h). Figure 10 shows a photomicrograph of a layered anorthosite–granite sample obtained at a H–C–O fluid pressure of 4 kbar (table, sample 8). The initial material consisted of 23 wt % of anorthosite and 73 wt % of granite. Apatite (2 wt %) and NaCl (2 wt %) were added into the fluid phase. The 10-h exposure of the homogeneous glass at 1200°C and 4 kbar resulted in cryptic layering, which was manifested in the accumulation of anorthite (up to 3 wt % in excess of the initial composition) in the upper part of the sample. The transmission electron microscopic investigation of the initial glass showed no inclusions of gas bubbles or zones of heterogeneity. After the experiment, examination at a magnification of 16000 revealed spherical heterogeneities with diffuse boundaries, 6 nm (60 Å) in size. Sometimes, they formed chain-like aggregates (Fig. 11). According to electron diffraction data, they have a monocrystalline structure (Fig. 12) and an anorthite composition. The inclusions show no regular crystal faces, and it can be supposed that they are ordered cores of anorthite-composition clusters, which were preserved during quenching. For control, a fluid-saturated glass was also investigated, which was obtained under a pure water pressure of 2 kbar at 1200°C. No inclusions were found in this glass.

Another example is presented in Fig. 13b. This image was obtained under a magnification of 10000 and shows a glass produced at the layering of An (30 mol %)–$En_{80}Fs_{20}$ (70 mol %) melt (Fig. 13a) at $P = 3$ kbar and $T = 1250$°C under fluid pressure of the system H–C–O–Cl (table, sample 9). The experimental duration was 12 h. Oxygen fugacity was controlled by the Mo–MoO_3 buffer mixture, and HCl fugacity was calculated from the composition of apatite, which was placed in a separate capsule, 3 mm in diameter. The image reveal spheroid inclusions, up to 10 nm in size. Electron diffraction data suggests that they have the anorthite composition and form linear aggregates.

The cluster must be a sufficiently stable system in order to resist diffusion. Probably, fluid components depolymerize the melt promoting cluster formation and stabilize clusters in time. In addition, under the pressure of mixed hydrogen-bearing gases, whose proportions are close to those of magma-related fluid, necessary conditions (degree of polymerization and viscos-

ity) are attained for the gravitational movement of clusters and their aggregates. The material presented in this paper supports this supposition.

ROLE OF LIQUID-STATE CLUSTER DIFFERENTIATION AT THE FORMATION OF IGNEOUS COMPLEXES

A number of researchers attached much importance to the ionic gravitational mechanism of magma differentiation, especially for the explanation of compositional changes in lavas that come to the surface during volcanic eruptions (Zavaritskii, 1944; Piip, 1947). The fact that a single genetic series of modern volcanic differentiates is often represented by holohyaline rocks suggests that the components of the melt were separated in a liquid state. The presence of both sharp and gradual transitions between magmas could result from cryptic and contrasting liquid layering, which occurred in a deep-seated magma reservoir. Ion gravitation cannot be an efficient mechanism of silicate melt separation (Kadik, 1963). It requires larger particles, which could resist diffusion and move under the influence of gravitation forces. Our extensive experimental data, both previously published (Bezmen, 1992a, 1992b; Bezmen and Suk, 1983; Bezmen and Elevich, 1998; Fed'kin et al., 1999; Bezmen et al., 1999) and presented in this paper, suggest that clusters could be such particles (Bezmen, 1994).

The analysis of the presented material clearly demonstrates that even a simple sedimentation model of cluster separation without convection phenomena is sufficient to explain the relationships observed in igneous complexes. It is important to point out that the effect of separation is manifested in the gradient-free temperature field. As the thermal conductivity of rocks is low, the realization of temperature gradient in a magma chamber sufficient for the formation of convection cells is hardly possible. McBirney (1985) showed for the magmas of the Skaergaard massif that a temperature gradient of 12°C per one meter of melt was necessary for the development of D–D convection stratification. Because of this, Irvine et al. (1983) explained the formation of convection stratification by injections of fresh hotter magma portions, which is not supported by geological data.

The gravitation-driven movement of clusters in melts could result initially in the formation of cryptic layering manifested in a gradual change in the composition of melt with height and, then, contrasting layering with the separation of layers of different compositions (Fig. 6). Let us consider as an example the evolution of the Munro Lake layered sill in the Abitibi region of Canada, which was described in detail by MacRae (1969), who provided the analyses and thicknesses of layers in rhythmically layered units (Fig. 14). The analyses were plotted on a special petrochemical diagram, which was proposed by Bezmen (1992) and Bezmen and Elevich (1998) for the investigation of the evolu-
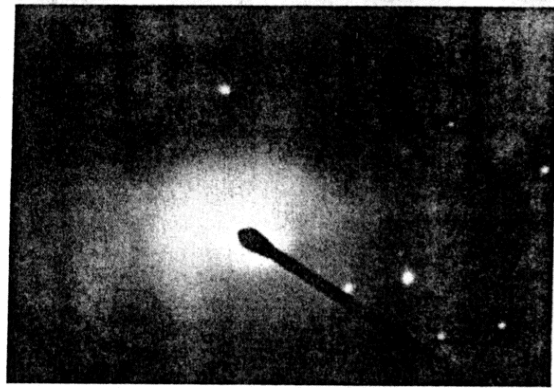

Fig. 12. Electron diffraction pattern of glass (Fig. 11) with inclusions of the anorthite composition. The supposed cores of clusters show ordered monocrystalline structures.
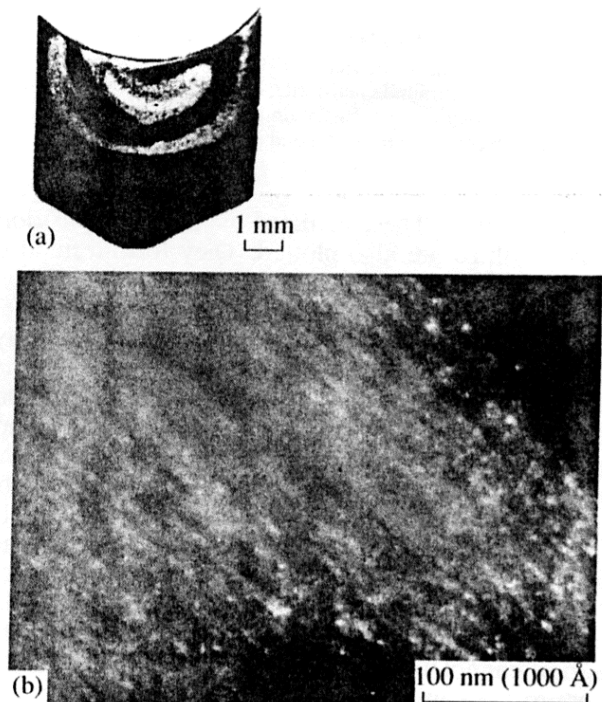

(a) 1 mm

(b) 100 nm (1000 Å)

Fig. 13. Formation of clusters aggregates of a linear structure.

(a) Rhythmically layered sample of the anorthite–bronzite composition (table, sample 8).

(b) Photomicrograph of an arbitrary area under a magnification of ×10000.

tion of igneous complexes. In this diagram, data points record almost all normative minerals. Peridotite and pyroxenite layers form rhythms in the lower part of the sill section (connected by tie-lines in the diagram). Upward in the section, the thickness of peridotite layers decreases and that of pyroxenite, increases. The upper part of the massif is composed of melanocratic and leu-
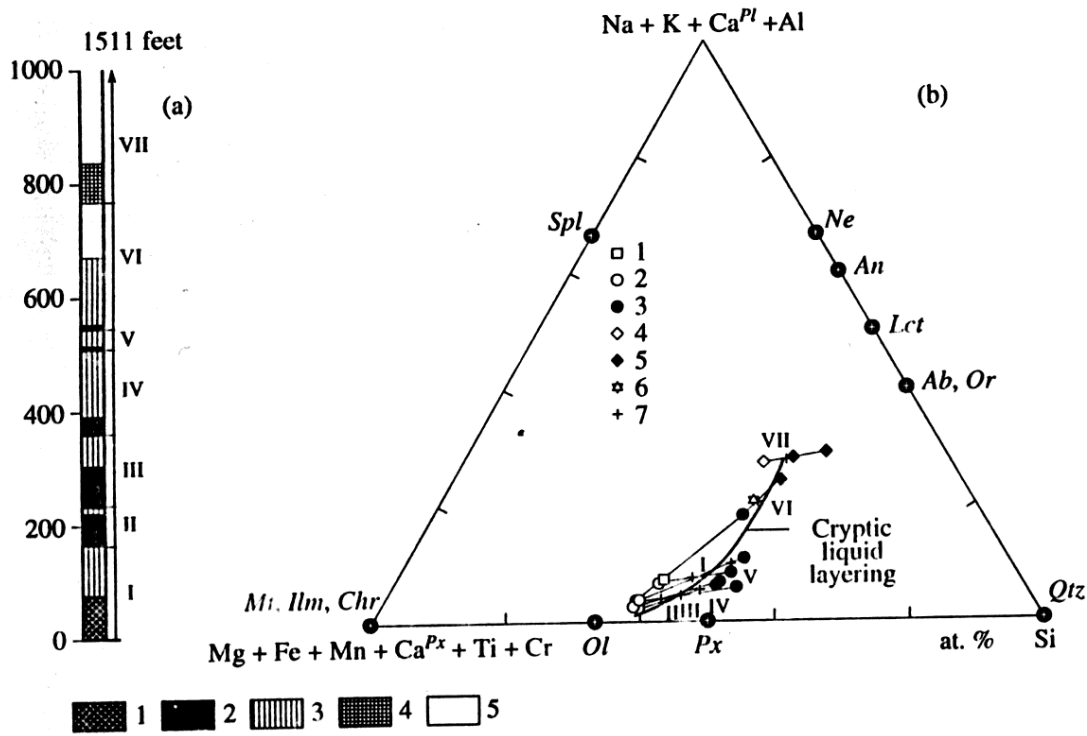
Fig. 14. Relationships between cryptic and contrasting layering in the Munro Lake differentiated sill, Abitibi, Canada. (a) Cross-section of the massif (McRae, 1969). Roman numerals denote rhythms. (b) Petrochemical diagram for the rocks of the massif. (1) Hornblende peridotite; (2) peridotite; (3) clinopyroxenite; (4) melanocratic gabbro; (5) leucocratic gabbro; (6) weighted mean composition of primary undifferentiated melt; and (7) average compositions of rhythms shown in the section. Symbols in Fig. 14b correspond to the legend of Fig. 14a.

cocratic gabbro. The calculated average compositions of the rhythms are also plotted. They form a trend of primary basic–ultrabasic liquid differentiation. Probably, along this trend, cryptic and, then, contrasting melt layering proceeded. Two zones were formed initially: the upper gabbro-dominated and the lower peridotitic. Subsequently, these zones evolved independently with the appearance of rhythmic intercalation of melanocratic gabbro and leucocratic gabbro and peridotite and pyroxenite. The formation of rhythmic patterns can be easily explained by the superliquidus convection stratification, which arises owing to density gradients. A particularly important factor is hydrogen migration, which is the most mobile element in nature. It should be emphasized that the rock relationships shown in the diagram cannot be explained by crystal settling. The latter process would have resulted in fundamentally different differentiation paths.

In layered massifs, the chemically most basic layers may occur in any part of the section or rhythms. For instance, in the Bushveld complex, South Africa (Buchanan, 1975) and Ioko-Dovyren massif, Transbaikalia (Kislov, 1998), dunite layers with the most basic compositions of minerals were found in lower but not in the lowest parts of the sections. In the dunite–clinopyroxenite massifs of the Ural platinum-bearing belt, dunite occurs either in middle or upper portions of sec-

tions. In the Panskii massif (Kola Peninsula), olivine-bearing rocks occur in the upper portion of the critical platinum-bearing zone (Latypov et al., 1999). The Noril'sk nickel-bearing massifs contain upper picritic horizons with high platinum-group metal contents (Distler et al., 1999). Many researchers related such relationships in the sections of massifs with injections of additional melt portions into the magma chamber (Irvine et al., 1983). However, this is not consistent with a number of specific characteristics of the geologic and petrochemical structure of the massifs, for example, the absence of numerous magma conduits, similarity in the structure of massifs, which are situated tens and even hundreds of kilometers apart (e.g., Pechenga intrusions in the Kola Peninsula and ophiolitic complexes of the Lesser Caucasus, etc.). Furthermore, such massifs are usually as if "inserted" into the host rocks. This is characteristic of even the thickest of them, for example, Bushveld (South Africa), Stillwater (USA), and Skaergaard (Greenland). This suggests that they were formed through the magmatic replacement of enclosing sequences.

Very often, zones of thinly layered contrasting rocks occur among weakly differentiated part of the sections. It is likely that the crystallization of underlying rocks released fluids, which moved into the upper levels and were dissolved in the melt at a certain level. Layers and

lenses (often mineralized) were formed in the magmas when the necessary (critical) fluid content was attained.

The process of crystallization differentiation passes prolonged temperature history. In accord with a decrease in the free energy of the system, small crystals must dissolve and large crystals, grow, especially at the convection mixing of melts. Consequently, rocks forming through crystallization differentiation must show strongly heterogranular textures. This was clearly illustrated by the experiments of Bowen (1915). The crystallization of separated melts occurs at small temperature changes (for monomineral melts, by a few degrees). During rapid crystallization, the rocks acquire fine-grained and homogranular textures. Such structures are typical of the majority of rocks in layered massifs.

At volatile loss and cooling, cluster (macromolecular) differentiation directly passes into crystal fractionation, which disguises the effect of liquid-state magma evolution, because clusters may be chemically identical to silicate and ore minerals (Fig. 12). Owing to their high mobility, clusters are capable of concentrating large amounts of ore components in accord with the laws of thermodynamic distribution. Moreover, clusters having fluid–silicate and fluid–oxide structures concentrate fluid components, which may separate during melt crystallization and generate ore-bearing solutions.

Thus, many characteristic features of the evolution of differentiated complexes, such as cryptic layering, rhythmic patterns in layered sections, selective concentration of ore components by melts, generation of fine-grained and homogranular textures, concentration of dense minerals in the upper portions of massifs, formation of monomineral rocks and massive ores could result from liquid-state cluster differentiation.

ACKNOWLEDGMENTS

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