

# Melt Inclusions in Minerals as a Source of Principle Petrological Information

A. V. Sobolev

*Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,  
ul. Kosygina 19, Moscow, 117975 Russia*

Received December 20, 1995

**Abstract**—Secondary ion mass spectrometry and electron microprobe studies demonstrated that melt inclusions in magnesian olivine bear evidence of the composition and formation conditions of the primary melts and their mixing products, including the initial water contents of the mantle melts. This information is partially or completely obliterated in the compositions of rocks and glasses by later processes of mixing, contamination, degassing, and crystal fractionation. The typical oceanic basalt of the Mid-Atlantic Ridge is shown to have formed through the mixing of primary melts that were derived by the critical melting of a mantle column, more than 50 km thick. The melting began in the presence of garnet and proceeded in an open system which could retain no more than 2–3 wt % melt. The mixing of the primary melts took place both in magma chambers, simultaneously with crystallization and, probably, during melt transport through the mantle. The initial concentrations of H<sub>2</sub>O in the mantle magmas of suprasubduction zones were as high as 2–3 wt %, which is significantly higher than was estimated previously. No correlation was found between the concentrations of H<sub>2</sub>O in the primary MORB magmas and those of elements with a similar incompatibility degree (La, Ce, K). This fact may indicate the continuous interaction of the melts with H<sub>2</sub>O-bearing CO<sub>2</sub>-rich fluid.

## INTRODUCTION

A unique feature of magmatic inclusions in minerals is their ability to preserve information on the instantaneous composition and evolutionary conditions of magmatic systems (e.g., Roedder, 1984), which is completely or partially obliterated from the rock or glass chemistries by the processes of mixing, crystal fractionation, degassing, and contamination of natural magmas (Sobolev, 1994). This property of inclusions results from their isolation after entrapment from the influence of the external system. The efficiency of such isolation is a function of the rate of volume diffusion through the host mineral, which in turn depends on the gradients and concentrations of an element in the mineral and its diffusion coefficients (Qin *et al.*, 1992). For those elements which are incompatible with respect to the host mineral, the capability of diffusion transport is limited and the isolation of melt inclusions from the external media is much more efficient compared to that of elements with high concentrations in the host mineral (Qin *et al.*, 1992). Thus, the most favorable aspect for inclusion studies appears to be a container phase that possesses minimum concentrations of the elements under investigation and contains major components indicating it to be nonequilibrium with the external media. Such a phase in the magmas of mantle origin is magnesian olivine, which in most cases is not equilibrated with the transporting melt with respect to Fe–Mg

distribution (Sobolev and Chaussidon, 1996), and contains trace amounts of most of the elements that characterize the melt composition. Glassy melt inclusions in these olivines are safely isolated from the external media and represent the composition of primary melts at the early stage of system crystallization for most elements, except for those which compose olivine: Mg, Si, and the elements of the Fe group (e.g., Green, 1994). The abundances of the latter in inclusions could be modified by olivine crystallization on the walls or exchange with the host mineral, but calculation or homogenization methods allow these effects to be easily corrected (Sobolev and Danyushevsky, 1994).

The goal of this work is to demonstrate how the application of the methods of melt inclusion investigations of minerals, more specifically, of olivine, enables us to obtain petrological and geochemical information which could not be gained by other methods. Two examples are considered: the reconstruction of primary melt compositions for the typical basalts of mid-oceanic ridges (MORB), and the determination of primary H<sub>2</sub>O contents in mantle melts. The results of this investigation show that melt inclusions in olivine from a particular typical MORB sample bear information on the considerable ranges of compositions and formation conditions of primary melts, whereas the abundances of H<sub>2</sub>O in melt inclusions trapped in the magnesian olivines of mantle magmas from various geodynamic set-

tings provide important information on the concentrations and behavior of H<sub>2</sub>O in mantle source regions and magmatic systems.

## METHODS OF STUDY

This work presents the results of the investigations of natural glassy inclusions in olivine phenocrysts without their preliminary homogenization. All inclusions studied are primary (Roedder, 1984) and contain glass and shrinkage bubbles. Since most of the melt inclusions in minerals experienced the crystallization of the host mineral on the inclusion walls (Roedder, 1984; Anderson, 1974), the reconstruction of their initial composition is imperative. For the inclusions under study, this procedure included the inverse simulation of olivine fractionation until equilibrium with the host mineral was attained (Sobolev and Shimizu, 1993). The model of Ford *et al.* (1983) for the olivine–melt equilibrium was used for the calculations. The fractions of different valence forms of iron in melt were calculated by the model of Kilinc *et al.* (1983) for the conditions of the quartz–fayalite–magnetite buffer. The concentrations of incompatible elements including H<sub>2</sub>O in olivine were taken to be zero. All the following considerations use the corrected compositions of trapped melts with respect to both major and trace elements.

### Major Elements

The concentrations of major elements in the inclusions and their host minerals were determined under standard conditions by a Camebax Microbeam electron microprobe at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences. The measurements were performed at a beam current of 10–30 nA and an accelerating voltage of 15 kV. Natural glass (USNM 111240/52), olivine (USNM 111312/444), and microcline (USNM 143968) (Jarosewich *et al.*, 1980) were used as standards.

### Trace Elements

Trace elements (Zr, Y, La, Ce, Nd, Sm, Eu, Dy, Er, and Yb) and Ti in inclusions were determined by secondary ion mass spectrometry on an IMS-4f ion microprobe at the Institute of Microelectronics, Russian Academy of Sciences (Yaroslavl', Russia). The energy filtering method was used for analysis (Shimizu and Hart, 1982) with the size of a primary O<sup>-</sup> beam at 20 μm, a current at 5–7 nA, and an energy offset at 50 eV, the width of the energy slit was 50 eV. Element concentrations were calculated from the ratio of respective isotopes to <sup>30</sup>Si using calibration curves for glass and clinopyroxene standards, which were analyzed by the isotope dilution method. Figure 1a shows examples of such curves. Analyses of the standards and replicate measurements of inclusions indicated the accuracy of trace element concentrations to be better than 10% for

concentrations higher than 1 ppm, better than 20% for concentrations at 0.1–1 ppm, and better than 40% for concentrations below 0.1 ppm.

### H<sub>2</sub>O

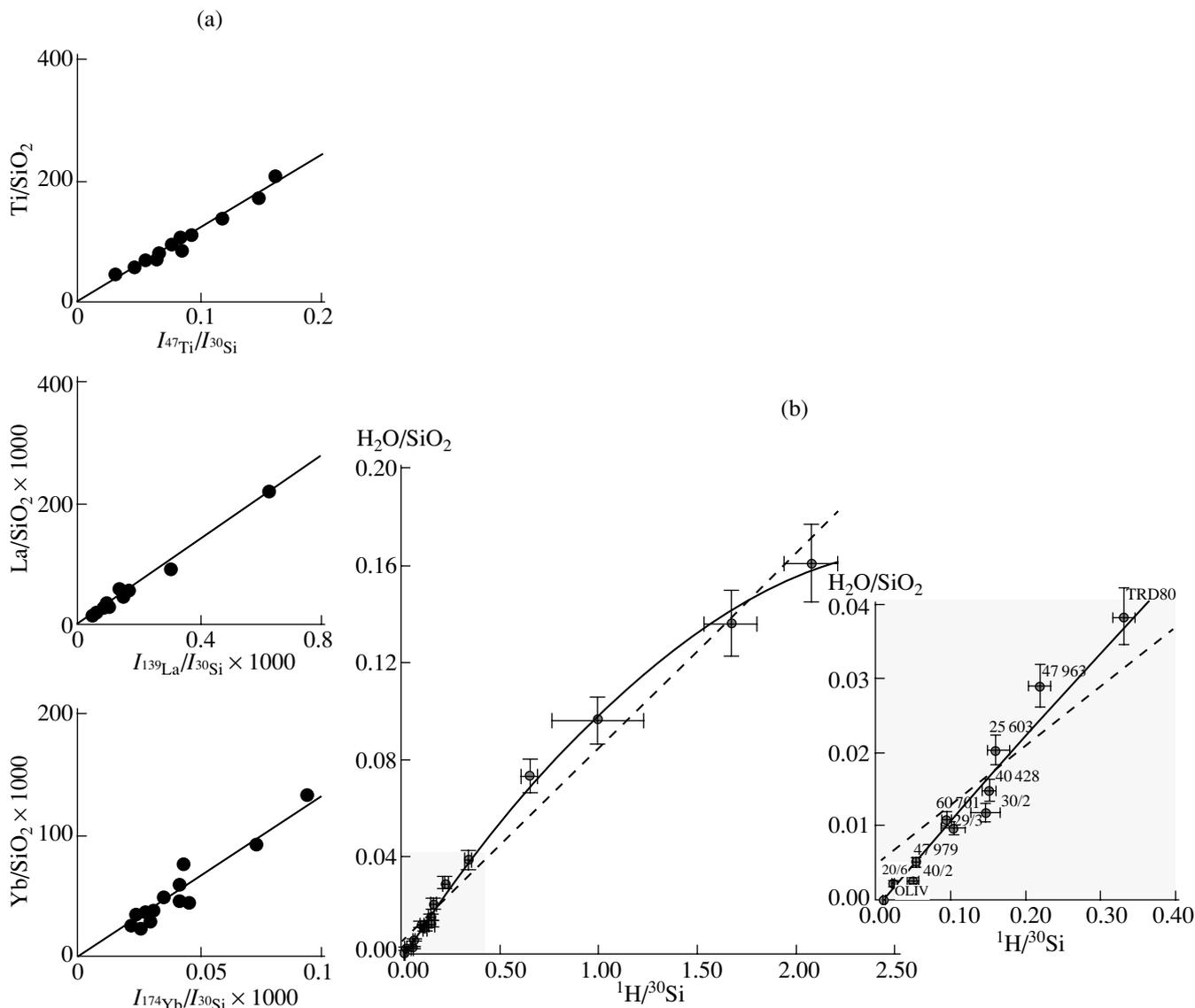
The abundances of H<sub>2</sub>O in inclusions and glasses were determined by secondary ion mass spectrometry on IMS-4f and IMS-3f ion microprobes at the Institute of Microelectronics, Russian Academy of Sciences (Yaroslavl', Russia) and Centre de Recherches Petrographiques et Geochimiques (CRPG) (Nancy, France), respectively. The analytical conditions at CRPG, France, were published elsewhere (Sobolev and Chaussidon, 1996). In Yaroslavl', H<sub>2</sub>O was determined from the mass of <sup>1</sup>H measured in the same cycle together with trace elements under the above conditions. In order to eliminate the effect of sample charging on the real shift of energy offset, it was measured and corrected automatically in the beginning of each cycle. The low background H<sub>2</sub>O level of the equipment (0.03 wt %) was provided by keeping the sample under high vacuum conditions for 2–3 days and measured on magnesian olivine.

The calibration curve (Fig. 1b) was obtained on the basis of natural glasses with H<sub>2</sub>O contents ranging from 0.1 to 4.0 wt % as was determined by infrared spectroscopy (Danyushevsky *et al.*, 1993). The calibration at higher water contents (6–10 wt %) was based on experimental glasses of ongonite composition (60–63 wt % SiO<sub>2</sub>) rich in fluorine (4.5 wt %), courtesy of V.I. Kovalenko. Figure 1b demonstrates that, in spite of the considerable compositional interval, the results for the whole set of the standard glasses may be satisfactorily fitted by a unique quadratic relation with an error of no more than 10% relative. The relative reproducibility of particular measurements normally equaled 2–5%. Thus, the integrated relative error in the H<sub>2</sub>O measurement in the inclusions was determined by the calibration precision, and was better than 10%.

## RECONSTRUCTION OF INITIAL MORB MELTS

### Problem Statement

According to modern concepts (McKenzie, 1994; McKenzie and O'Nions, 1995; Langmuir *et al.*, 1992; Kinzler and Grove, 1993, etc.), the products of mantle magmatism in all main geodynamic settings are formed by multiple mixing, contamination, and crystal fractionation of continuous series of initial mantle melts formed under a finite interval of *P–T* conditions during decompression melting in an open mantle system. The primary mantle melts are practically absent among natural glasses and rocks (O'Hara, 1995). This fact makes the determination of the compositions of primary mantle melts an important challenge, because this information alone could be used for the direct reconstruction of melting conditions and the compositions of mantle source regions. A number of authors proposed indirect approaches to this problem based on the idealized mod-



**Fig. 1.** Examples of calibration curves for the method of secondary ion mass spectrometry.

(a) Calibration curves for the determination of Ti, La, and Yb. Elements are in ppm, oxides, in wt %.  $I$  is the secondary ion intensity in counts.

(b) Calibration curve for the determination of H<sub>2</sub>O contents in glass. The inset shows the enlarged low-concentration region. The whole interval of values is satisfactorily approximated by the quadratic equation (shown by the solid line):  $Y = -0.0214X^2 + 0.12013X - 0.0012$ . The dashed line shows the linear regression, which does not satisfactorily fit the obtained data.

els of primary melt modification, for instance, assuming complete mixing and reequilibration in transport systems (e.g., Langmuir *et al.*, 1992). The present work utilizes an alternative approach based on the direct reconstruction of the compositional interval of primary melts participating in the generation of the typical oceanic basalt.

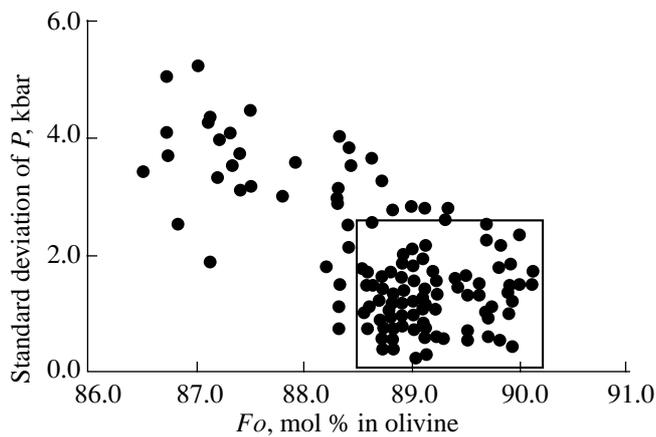
#### Study Object

The sample that we studied (649/c) is a olivine–plagioclase phryic basalt dredged in the rift valley of the Mid-Atlantic Ridge at 9°N (Sushchevskaya *et al.*, 1985).

The sample was described by Sobolev *et al.* (1988), and is of particular interest because it contains phenocrysts of unzoned magnesian olivine and is the first oceanic basalt, where the presence of ultradepleted melt inclusions in olivine was documented (Danyushevsky *et al.*, 1987; Sobolev and Shimizu, 1992, 1993).

#### Major Elements

Two independent criteria were used to identify primary melts that have been in equilibrium with the mantle source: (1) equilibrium with mantle olivine ( $Fo$  88.5–91.0) and (2) equilibrium with the olivine–orthopyrox-



**Fig. 2.** Dependence of the standard deviation in the average equilibrium pressure of melt inclusions with olivine, orthopyroxene, clinopyroxene, and an aluminous phase (spinel or plagioclase) upon the composition of host olivine. The pressures were calculated by the model of Kinzler and Grove (1992).

The rectangular field shows melt compositions assumed to be potentially primary (see text).

ene-clinopyroxene-aluminous phase (spinel or plagioclase) assemblage. The first condition is based on data on the olivine composition in abyssal peridotites (Dick, 1989). The second one implies the convergence of pressures calculated for the equilibrium of each of the four mantle phases with melt using the model of Kinzler and Grove (1992). It should be pointed out that these criteria do not allow primary melts to be differentiated from the products of their mixing because of the additivity and linearity of the considered parameters. The melts selected on the basis of these criteria will therefore be referred to as potentially primary (table).

On the basis of the major element composition of the melt, equilibrium pressure was determined for each of the four phases of the mantle association using the algorithm of Kinzler and Grove (1992), and the average value was then calculated. The equations for plagioclase lherzolite or spinel lherzolite were used for an average pressure of less than 9 kbar and more than 10 kbar, respectively. For intermediate pressures, between 9 and 10 kbar, the calculations were carried out for both associations, and a model was accepted which resulted in the lowest standard deviation of pressure estimates. Figure 2 demonstrates the standard deviation for calculated equilibrium pressure as a function of the composition of the host olivine. The standard deviation clearly increases with the decline of the forsterite mole fraction of olivine owing to the crystallization differentiation of the melt. Meanwhile, most of the melts trapped in magnesian olivine ( $Fo > 88.5$ ) yielded the standard deviation that appeared to be lower than the method accuracy (2.5 kbar) claimed by Kinzler and Grove (1992). These compositions, therefore, may be accepted as the estimates of potentially primary melts.

The compositions of these potentially primary melts are plotted in Fig. 3 against the pressure of their equi-

librium with the mantle source. This diagram reveals a considerable interval of parameters, which was not reported previously for a single sample. The pressure decline is accompanied by a significant increase of  $SiO_2$  and  $CaO$  and decrease of  $FeO$  and  $MgO$ , which agrees with the polybaric model of mantle source melting (Kinzler and Grove, 1992, 1993).

#### Rare Earth Elements

Figure 4 shows that the melt inclusions in olivines from the sample studied are characterized by extremely wide variations of LREE concentrations, considerably exceeding the range of known MORB compositions (Sobolev and Shimizu, 1993). For instance, the minimum and maximum La contents differ by a factor of 450. The majority of the inclusions (approximately 90%) are similar to the quench glass of the sample with respect to REE distribution (Fig. 4) and incompatible element ratios (Fig. 5). The remaining 10% comprise inclusions either ultradepleted or relatively enriched in the most incompatible elements. Most of these inclusions were found in magnesian olivines (Fig. 5).

#### Formation Conditions

According to previous studies (Sobolev *et al.*, 1988; Danyushevsky *et al.*, 1987), olivine phenocrysts from the considered sample crystallized together with calcium plagioclase at low pressures (1–4 kbar) and in the temperature interval of 1250–1200°C. The system was quenched in a submarine environment at a temperature of approximately 1200°C. The magnesian olivine ( $Fo$  90.5–88.5) crystallized within the first 20°C of the temperature interval. Thus, taking into account the data presented in Figs. 2 and 3, the melts from the inclusions in magnesian olivine are either primary mantle liquids or the products of their mixing, which migrated from depths of 50–10 km into intermediate reservoirs at a depth of less than 10 km, where they were trapped and isolated by liquidus olivine.

The coexistence of chemically contrasting melt inclusions in the liquidus olivine of a single sample is rather common in the products of mantle magmatism of various geodynamic settings (Sobolev and Shimizu, 1992, 1993, 1994; Sobolev, 1994; Nikogosian and Sobolev, 1995; Gurenko and Chaussidon, 1995; Portnyagin *et al.*, 1996). This phenomenon may be explained by the crystallization of phenocrysts in different parts of a magmatic system (series of magma chambers and conduits) from melts of varying composition. The chemical heterogeneity of the melt could result from magma mixing in a dynamic system. Similar concentrations of incompatible elements in most of the inclusions and in the quench glass (Figs. 4 and 5) indicate that the final product of mixing was in that case the transporting melt. The compositions of melt inclusions in the magnesian olivines (Fig. 5) suggest that the mixing may have already proceeded at the earliest stages of

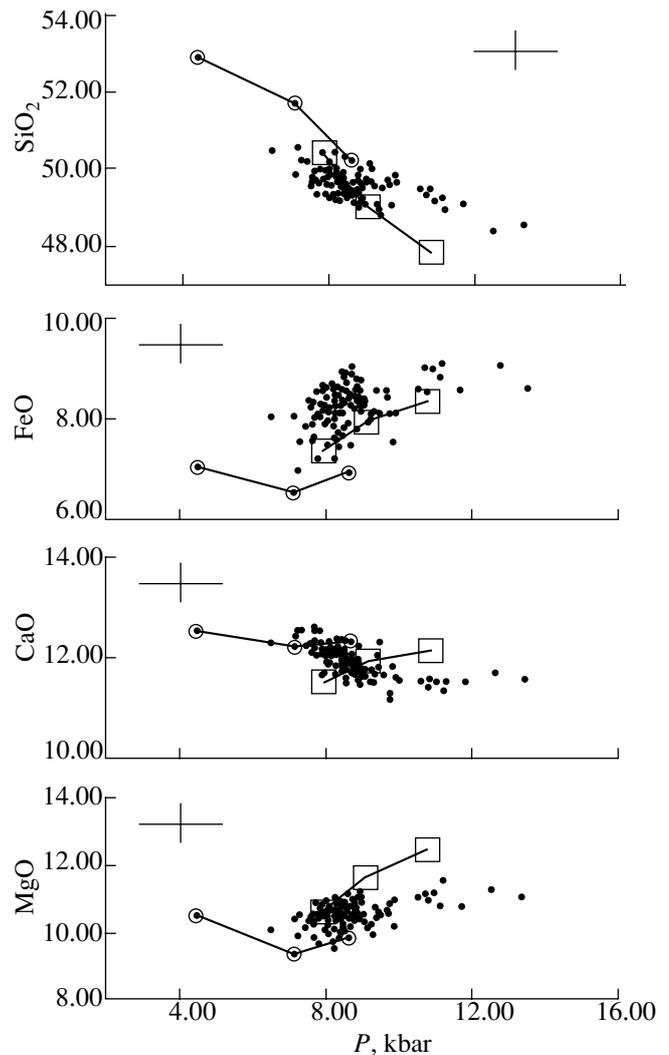
crystallization or before it in the mantle. Direct evidence on the mixing of chemically different melts coeval with the growth of a particular phenocryst of magnesian olivine (*Fo* 90) is provided by the compositions of inclusions coexisting in one grain with the ultradepleted melt inclusion [Fig. 3 and (Sobolev and Shimizu, 1992)].

The investigation of abyssal peridotites (Johnson *et al.*, 1992), cumulates of dike complex in the oceanic crust (Ross and Elthon, 1993), and melt inclusions in the olivines of oceanic basalts (Sobolev and Shimizu, 1993) demonstrated that the melting of the oceanic mantle proceeded through a mechanism similar to fractional melting. Primary melts formed in this process must display the extensive fractionation of the most incompatible elements and differ significantly from typical MORBs by both depletion and enrichment in these elements (Sobolev, 1994). These are precisely the patterns typical of approximately 10% of the inclusions in the most magnesian olivines of the sample studied (Figs. 4 and 5).

The variations of incompatible element contents in the melt inclusions may be explained in the context of the critical melting of the mantle source (Sobolev and Shimizu, 1992). The calculations demonstrated (Fig. 6a) that the abundances of REE in the ultradepleted melt inclusions are satisfactorily modeled by the melting of oceanic spinel lherzolite at a degree of melting ranging from 13 to 18%, and a fraction of melt retained in the residua, from 2 to 3%. The presence of garnet in a source material is required to explain the high Nd and Sm contents relative to heavy REE (Er, Yb) in the enriched melts. In this case, the composition of the most enriched melt may be approximated by a mixture of 60% of the melt formed by the low-degree melting of the garnet-bearing oceanic mantle and 40% of the ultradepleted melt. The fraction of melt retained by the mantle material was estimated in all models as no more than 2–3%, which indicates the high permeability of the oceanic mantle for low melt fractions and agrees with the results of previous studies (Johnson *et al.*, 1990; Sobolev and Shimizu, 1993; Sobolev, 1994). The compositions of most inclusions are satisfactorily modeled by the mixing of all primary melts formed over the entire melting interval.

Figure 6 compares the  $P$ – $T$  parameters of the formation of potentially primary melts estimated on the basis of major element compositions and the results of geochemical modeling. The obtained data are consistent with each other and with the decompression melting model of the oceanic mantle. The latter may be inferred from the following observations:

1. All the  $P$ – $T$  estimates of melt formation conditions lie within the interval of the partial melting of the mantle lherzolite and show a temperature decline with decreasing pressure.



**Fig. 3.** Composition (wt %) of potentially primary melts plotted against the pressure of equilibrium with the mantle lherzolite assemblage.

The compositions of melts trapped in the same olivine grain (*Fo* 90) are enclosed in open circles and connected by lines. Open squares show the compositions of mixed melts formed through polybaric melting approaching the fractional model [after Kinzler and Grove (1992)] at the following pressure intervals (from left to right): 15–4, 20–4, and 25–4 kbar. With respect to all elements but Fe, the compositions of most of the potentially primary melts may be interpreted to represent polybaric mixtures formed between 15–4 and 20–4 kbar. The regular enrichment in Fe could result from the presence of ferric oxide.

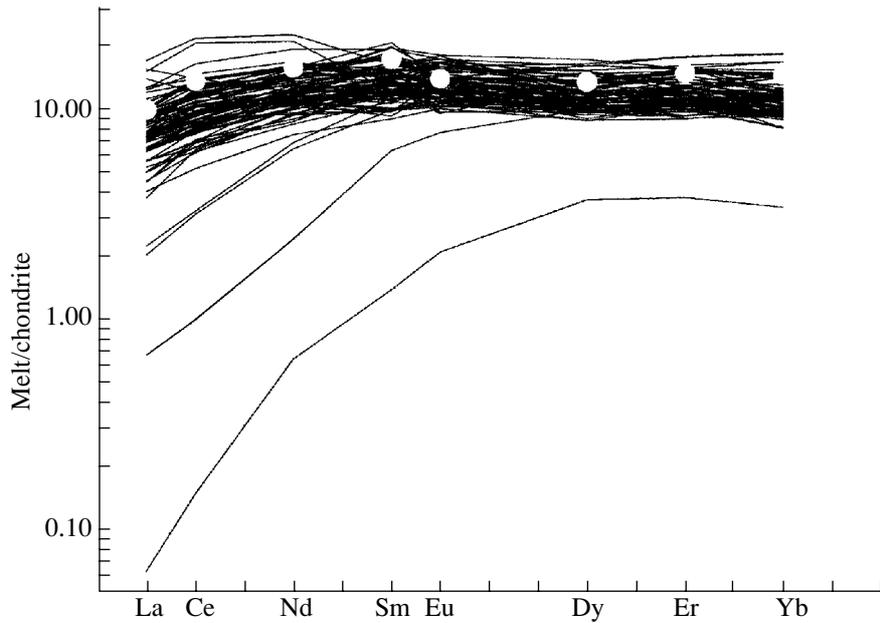
2. The minimum degrees of melting and the presence of garnet in the mantle source region were detected for the deepest melt (Fig. 6, composition 4).

3. Geochemical criteria of mixing between the deepest melt with the most shallow ultradepleted one are consistent with the fact that the estimated formation pressure of the former is not high enough to equilibrate with a garnet-bearing source (14 kbar at a required value of 22–24 kbar). The total pressure for such a mixture should be approximately 16 kbar, which agrees

Representative compositions of potentially primary melts from inclusions in the olivine of sample 649/c

Components	18/4	14/4	UDM*	36a/4	4/4	1a/4	16/4*	21/4	19/4	29/4	34/4*	27/4*	Glass
SiO <sub>2</sub> , wt %	48.8	49.67	52.9	50.15	50.16	49.63	48.52	49.85	49.65	49.84	50.1	49.64	49.7
TiO <sub>2</sub>	0.78	0.79	0.29	1	0.74	0.75	1.24	0.88	0.86	0.8	0.8	0.81	1.25
Al <sub>2</sub> O <sub>3</sub>	17.45	16.73	15.5	17.07	16.64	16.62	16.8	16.31	17.34	16.88	17.24	16.48	15.9
FeO	7.76	7.63	7.03	7.46	7.84	8.08	8.65	8.04	7.93	7.96	7.91	8.48	9.20
MnO	0.12	0.13	0.08	0.13	0.14	0.16	0.13	0.18	0.14	0.12	0.15	0.12	0.2
MgO	10.64	10.51	10.5	9.93	10.15	10.39	11.02	10.36	10.09	10.22	10.13	10.78	8.1
CaO	12.3	12.51	12.5	12.09	12.22	12.29	11.54	12.4	11.74	12.18	11.51	11.7	11.8
Na <sub>2</sub> O	2.01	1.89	1.12	1.99	1.96	1.89	1.93	1.81	2.06	1.84	2.04	1.87	2.58
K <sub>2</sub> O	0.03	0.04	0	0.08	0.05	0.06	0.07	0.06	0.1	0.05	0.02	0.02	0.1
<i>Fo</i> (olivine)	90	89.92	89.9	89.52	89.23	89.22	89.2	89.2	89.13	89.13	89.08	89.02	–
<i>P</i> <sub>avg</sub> , kbar	9.4	7.7	4.5	8.0	7.4	7.8	13.3	7.1	9.2	8.0	9.2	8.6	–
<i>P</i> std. dev.	1.5	1.8	1.0	0.7	1.3	1.6	1.3	1.6	0.3	0.7	0.8	1.2	–
<i>T</i> , °C	1287	1271	1247	1272	1268	1270	1332	1264	1282	1272	1282	1278	–
H <sub>2</sub> O	0.26	0.13	–	0.17	0.17	0.26	0.17	0.20	0.18	0.20	0.25	0.19	0.15
Ti	5064	5045	1722	5645	4623	4802	8231	5467	5439	4675	4872	4812	6743
Y	14.7	17.0	10.2	15.1	15.0	16.3	14.6	17.5	15.0	15.0	14.3	14.4	22.3
Zr	47.9	47.9	2.9	53.7	46.1	47.1	98.6	54.3	55.6	49.7	22.6	6.4	67.5
La	1.65	1.78	0.015	2.08	1.97	2.30	4.03	2.53	2.57	1.96	0.50	0.16	2.56
Ce	5.94	6.06	0.09	6.69	6.27	7.50	13.45	7.49	7.85	6.47	2.10	0.53	8.12
Nd	5.29	5.33	0.30	6.32	5.29	5.28	9.91	5.32	5.96	5.46	2.87	0.91	7.28
Sm	1.99	2.02	0.21	2.04	2.04	2.04	2.17	2.10	2.00	1.81	1.73	0.84	2.71
Eu	0.63	0.67	0.12	0.65	0.58	0.63	0.77	0.65	0.68	0.60	0.61	0.41	0.82
Dy	2.48	2.94	0.93	2.51	2.52	3.20	2.28	2.65	2.65	2.49	2.58	2.28	3.78
Er	1.41	1.62	0.62	1.43	1.36	1.70	1.67	1.68	1.50	1.43	1.37	1.18	2.20
Yb	1.53	1.77	0.57	1.65	1.48	1.83	1.56	1.69	1.45	1.63	1.63	1.50	2.41

Note: Trace elements (ppm) and H<sub>2</sub>O (wt %) were determined by secondary ion mass spectrometry. *Fo* (olivine)—composition of host olivine; *P*<sub>avg</sub> and *T* are the pressure (average of four values for olivine, orthopyroxene, clinopyroxene, and an aluminous phase) and temperature of equilibrium with mantle lherzolite calculated by the model of Kinzler and Grove (1992). *P* std. dev. is the standard deviation of pressure estimates. UDM is the inclusion described by Sobolev and Shimizu (1993). Glass is the quench glass of the sample. Asterisks mark the compositions that approach real primary melts modeled in Fig. 6a. Dashes—not determined.



**Fig. 4.** Normalized REE distributions for melt inclusions in olivine of the studied sample.

Open circles show the composition of quench glass from the sample. The data of Sobolev and Shimizu (1994) were used in addition to the results of this work.

Here and in the following diagrams, REE are normalized to the chondrite composition after Anders and Greves (1989).

with the pressure estimate within the claimed precision of the method (Kinzler and Grove, 1992).

4. The highest degrees of melting were determined for the most shallow melt (Fig. 6, composition 1).

5. The majority of the melts may be interpreted as products of the mixing of primary melts on the basis of both geochemical and petrological modeling (Fig. 6, composition 6).

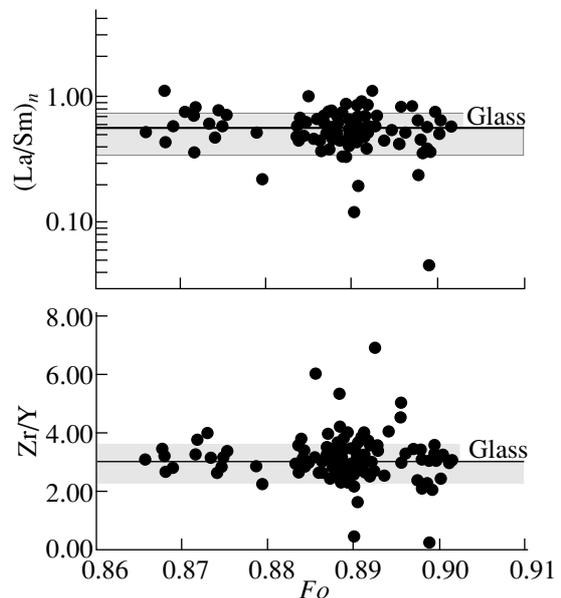
Thus, the obtained result indicates that melt inclusions in olivine phenocrysts from a single MORB sample bear information on melting conditions in a mantle column, approximately 60 km thick, and demonstrates the efficient mixing of the primary melts during the stage of shallow-level crystallization and, probably, under mantle conditions as well.

## INITIAL H<sub>2</sub>O CONTENTS OF MANTLE MAGMAS

### *Problem Statement*

The determination of volatiles, and especially water, in mantle magmas and their source regions is an important petrological task (e.g., Sobolev, 1973; Thompson, 1992). Currently, the main approach to this problem is the investigation of natural glasses in the products of submarine eruptions [see the reviews of Michael (1995) and Jambon (1994)]. However, the processes of degassing and contamination could significantly change the chemistry of mantle melts by increasing or decreasing H<sub>2</sub>O abundances (Kyser *et al.*, 1986; Sobolev and Chaussidon, 1996). In this case, inclusions of melt in

the early crystalline phases may provide more reliable information on the initial H<sub>2</sub>O contents of the magmas (Sisson and Layne, 1993; Sobolev and Chaussidon, 1996) owing to the isolation effect, as was discussed in the introduction.



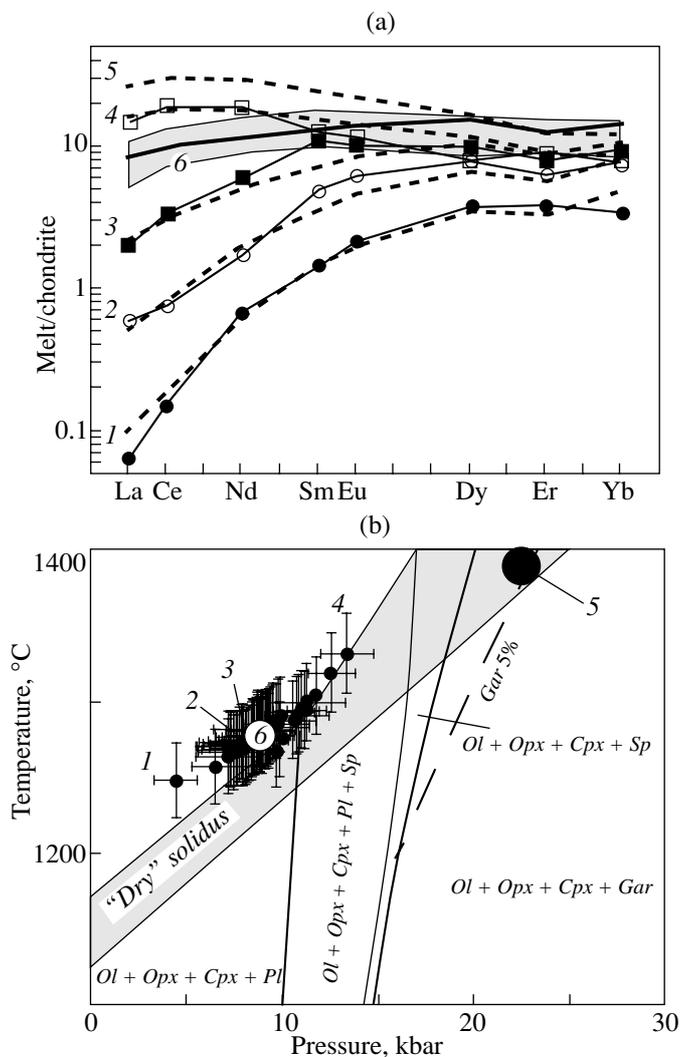
**Fig. 5.** Correlations between the ratios of incompatible elements in melt inclusions and the composition of the host olivine.

The solid line shows the composition of quench glass from the sample. The shaded area is the field of compositions whose departure from the glass composition does not exceed the analytical uncertainty. Also used are data from (Sobolev and Shimizu, 1994).

## Study Objects

In addition to the above-described sample, primitive MORBs were studied from the Mid-Atlantic Ridge, at 12°–14° and 36°N, and the Siqueiros Fracture Zone of the East Pacific Rise. The primitive magmas of subduction-related zones were studied on the example of *island-arc tholeiites* of the Troodos ophiolites (Cyprus), Hunter

Fracture Zone (Pacific Ocean), *calc-alkaline magmas* of the Klyuchevskoi Volcano (Kamchatka), *boninites* of the Tonga Trench, Hunter Fracture zone, Bonin Island, Papua New Guinea (Pacific Ocean), and Troodos and Mamonia ophiolite complexes (Cyprus). These objects are described in more detail by Sobolev and Chaussidon (1996).



**Fig. 6.** Results of geochemical and petrological modeling.

(a) Normalized REE concentrations in the anomalous melt inclusions and the results of their modeling. The symbols show real compositions, the dashed lines are the models of critical melting after Sobolev and Shimizu (1992) and Gurenko and Chaussidon (1995). 1—17.5% melting, 2.3% melt in the residua; 2—15% melting, 2.5% melt in the residua; 3—13% melting, 3% melt in the residua; 4—mixture of 60% melt, formed in equilibrium with garnet (4%) at 4% melting, and 2.3% melt in the residua (composition 5) and 40% melt of composition 1; 6—product of mixing of all melt portions formed in the interval of critical melting up to 17.5% with 2.3% melt retained in the residua. The shaded area shows the field of typical melt compositions (Fig. 4).

(b) Formation conditions of the primary melts.

Phase boundaries for the mantle source of MORB are shown according to the experimental results of Falloon and Green (1988), Thompson (1992), and calculations by the model of Sobolev and Babeyko (1994) for composition MPY-87 (Falloon and Green, 1988). The  $P$ – $T$  conditions of potentially primary melts equilibration with the lherzolite association were calculated by the model of Kinzler and Grove (1992). The solid circle shows the assumed conditions of lherzolite melting with 4 wt % garnet [calculated by the model of Sobolev and Babeyko (1994)]. *Ol*—olivine, *Opx*—orthopyroxene, *Cpx*—clinopyroxene, *Pl*—plagioclase, *Sp*—spinel, *Gar*—garnet.

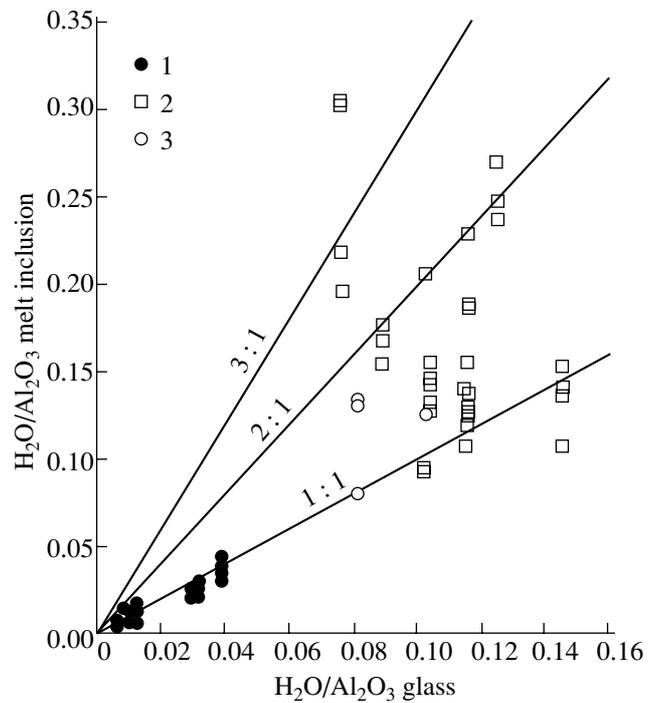
### Effect of Degassing on the H<sub>2</sub>O Content of Melt

The relative abundances of H<sub>2</sub>O in melt inclusions from olivine phenocrysts and in quench glasses from the same samples are compared in Fig. 7. In all the MORB samples, the H<sub>2</sub>O concentrations of inclusions are similar to those of glasses, indicating the negligible influence of degassing on the melt composition. This is consistent with the evidence of the H<sub>2</sub>O-undersaturated character of MORB melts (Jambon, 1994). In contrast, the significant enrichment of inclusions in H<sub>2</sub>O as compared to glasses was observed in the mantle magmas of suprasubduction zones. This fact indicates a significant water loss due to magma degassing in this geodynamic environment, and is consistent with the evidence for the presence of a water-bearing fluid phase in them (Sobolev and Danyushevsky, 1994).

### H<sub>2</sub>O in Primary Mantle Melts

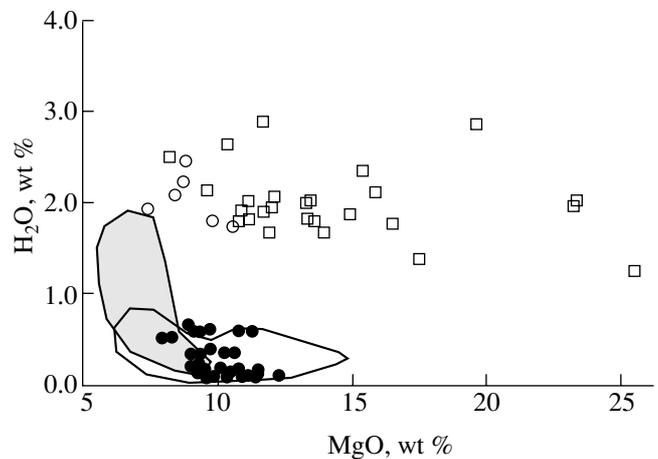
**Suprasubduction settings.** The highest water contents were found in the mantle magmas formed above a subducted slab, as shown in Fig. 8. Taking into account the effect of crystal fractionation on increasing the concentration of H<sub>2</sub>O in the residual melt, we may conclude that the maximum H<sub>2</sub>O contents of melt inclusions from suprasubduction magmas significantly (by a factor of 2–3) exceed those of quench glasses. This implies that the values published earlier for the water flux in island-arc systems based on glass compositions (Thompson, 1992) are appreciably underestimated: compare the value of 1 wt % used by Thompson for a water content in magma and 2–3 wt % obtained in this work. This, in turn, results in revising the balance between subducted and recycled water, and suggests that most of the water entrained in a subduction zone could be recovered in an igneous processes, a possibility rejected by Thompson (1992).

**Mid-ocean ridges.** The H<sub>2</sub>O abundances of the mantle magmas of mid-ocean ridges are significantly lower than those of the magmas of suprasubduction zones, and agree with the estimates based on quench glasses. However, another result unexpectedly appeared after studying melt inclusions demonstrating independent behavior of H<sub>2</sub>O and elements with similar degrees of incompatibility (K, La, Ce) (Fig. 9), which were not detected in quench glasses. The regular relationships between the concentrations of water, K, La, and Ce reported for MORB glasses in a number of previous studies [see the review of Michael (1995)] were not observed in the inclusions with extreme abundances of incompatible elements. Roughly constant H<sub>2</sub>O contents were measured in melt inclusions from the same samples from a number of the world's regions, in spite of the considerable variations of incompatible element contents. Such water behavior cannot be explained by melting processes or variations in the composition of mantle source regions, because the partition coefficients of water and the mentioned incompatible ele-



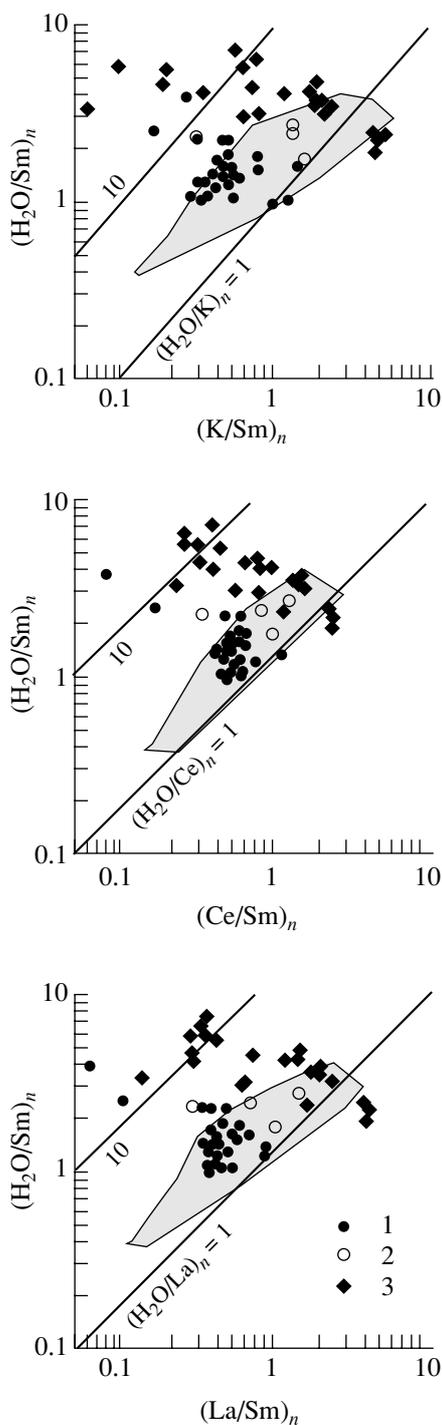
**Fig. 7.** Correlation between the H<sub>2</sub>O concentrations in the melt inclusions from olivine phenocrysts and in glasses from the same samples.

1—basalts of mid-ocean ridges; 2—boninites; and 3— island arc tholeiites. To eliminate the effect of olivine and clinopyroxene fractionation, the concentrations of H<sub>2</sub>O are normalized to Al<sub>2</sub>O<sub>3</sub> contents. The lines show constant ratios of H<sub>2</sub>O contents in the inclusions and glasses. The data of this work and of Sobolev and Chaussidon (1996) are plotted.



**Fig. 8.** H<sub>2</sub>O and MgO contents in the melt inclusions from magnesian olivines.

See Fig. 7 for symbol explanations. The shaded area shows the compositions of Cenozoic glasses from suprasubduction zone environments, the empty field shows modern basalts from mid-ocean ridges and ocean islands (Sobolev and Chaussidon, 1996). Only maximum H<sub>2</sub>O contents in each sample are plotted for the magmas of suprasubduction zones. The data from this work and Sobolev and Chaussidon (1996) are plotted.



**Fig. 9.** Comparative geochemical behavior of  $\text{H}_2\text{O}$  and elements similar in the degree of incompatibility with respect to melts for glasses and inclusions from MORB.

1–3—melt inclusions in olivine from the basalts of the Mid-Atlantic Ridge: 1—region at  $9^\circ\text{N}$  (table); 2—FAMOUS region (author's unpublished data); 3—region at  $14^\circ\text{--}15^\circ\text{N}$  (unpublished data, courtesy of O.P. Tsameryan, Vernadsky Institute of Geochemistry and Analytical Chemistry). All ratios are chondrite-normalized after Anders and Greves (1989). The contents of  $\text{H}_2\text{O}$  and K were normalized to 85 and 83 ppm, respectively. The shaded fields are the compositions of MORB glasses after Michael (1995).

ments between melt and crystal phases are similar (Michael, 1995). The observed phenomenon may be supposed to result from the buffering of the  $\text{H}_2\text{O}$  content in the mantle magmas of mid-ocean ridges by a water-bearing phase, essentially free from other incompatible elements. This phase may be represented by a  $\text{CO}_2$ -rich fluid, whose presence was ascertained by magmatic fluid inclusions found in the phenocrysts of all studied MORB samples (Sobolev *et al.*, 1988; and author's unpublished data).

## CONCLUSION

1. The application of secondary ion mass spectrometry and electron microprobe analysis demonstrated that melt inclusions in magnesian olivine are capable of preserving information on the composition and formation conditions of the primary melts and the products of their mixing, as well as on the initial  $\text{H}_2\text{O}$  contents of the mantle melts. This information is completely or partially obliterated from the compositions of rocks and glasses by the processes of mixing, contamination, degassing, and crystallization differentiation.

2. It was shown that the typical oceanic basalt of the Mid-Atlantic Ridge formed through the mixing of primary melts generated by the critical melting of a mantle column, more than 50 km thick. The melting commenced in the presence of garnet and proceeded in an open system which could retain no more than 2–3 wt % melt. Primary melts were mixed in magma chambers during crystallization and, probably, also during their transport through the mantle.

3. The initial  $\text{H}_2\text{O}$  contents of suprasubduction zone magmas are no less than 2–3 wt %, which exceeds the previous estimates by a factor of 2–3.

4. No correlation was found in the primary MORB magmas between the concentrations of  $\text{H}_2\text{O}$  and elements with a similar degree of incompatibility (La, Ce, K), which may be indicative of the continuous interaction of melts with a water-bearing carbon dioxide fluid.

## ACKNOWLEDGMENTS

The author thanks S.A. Simakin (Institute of Microelectronics, Russian Academy of Sciences, Yaroslavl') and N.N. Kononkova (Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences) for ion and electron microprobe analyses, respectively. N. Shimizu (WHOI, USA) and M. Chaussidon (CRPG, France) greatly influenced the author's concepts of the use of secondary ion mass spectrometry. This work was supported by the International Science Foundation, grants no. MNN000 and MNN300 and the Russian Foundation for Basic Research, projects no. 93-05-8895 and 96-05-66014.

## REFERENCES

- Anders, E. and Grevesse, N., Abundance of the Element: Meteoritic and Solar, *Geochim. Cosmochim. Acta*, 1989, vol. 53, pp. 197–214.
- Anderson, A.T., Evidence for Picritic, Volatile-rich Magma beneath Mt. Shasta, California, *J. Petrol.*, 1974, vol. 15, pp. 243–267.
- Danyushevsky, L.V., Falloon, T.J., Sobolev, A.V., *et al.*, The H<sub>2</sub>O Content of Basalt Glasses from Southwest Pacific Back-Arc Basins, *Earth Planet. Sci. Lett.*, 1993, vol. 117, pp. 347–362.
- Danyushevsky, L.V., Sobolev, A.V., and Dmitriev, L.V., Orthopyroxene-bearing Low-Titanium Tholeiites: A New Type of Ocean Ridge Tholeiites, *Dokl. Akad. Nauk SSSR*, 1987, vol. 292, no. 6, pp. 1449–1452.
- Dick, H.J.B., Abyssal Peridotites, Very Slow Spreading Ridges and Ocean Ridge Magmatism, *Geol. Soc. Spec. Publ., London*, 1989, pp. 71–105.
- Falloon, T.J. and Green, D.H., Anhydrous Partial Melting of Peridotite from 8 to 35 kbar and the Petrogenesis of MORB, *J. Petrol.*, 1988, vol. 29, Special Lithosphere Issue, pp. 379–414.
- Ford, C.E., Russel, D.G., Graven, J.A., *et al.*, Olivine–Liquid Equilibria: Temperature, Pressure and Composition Dependence of the Crystal / Liquid Cation Partition Coefficients for Mg, Fe<sup>2+</sup>, Ca and Mn, *J. Petrol.*, 1983, vol. 24, pp. 256–265.
- Green, T.H., Experimental Studies of Trace Element Partitioning Applicable to Igneous Petrogenesis—Sedona 16 Years Later, *Chem. Geol.*, 1994, vol. 117, pp. 1–36.
- Gurenko, A.A. and Chaussidon, M., Enriched and Depleted Primitive Melts Included in Olivine from Icelandic Tholeiites: Origin by Continuous Melting of a Single Mantle Column, *Geochim. Cosmochim. Acta*, 1995, vol. 59, no. 14, pp. 2905–2917.
- Jambon, A., Earth Degassing and Large-Scale Geochemical Cycling of Volatile Elements, *Volatiles in Magmas, Rev. Mineral.*, Washington, DC: Mineral. Soc. Am., 1994, vol. 30, pp. 479–517.
- Jarosewich, E.J., Nelen, J.A., and Norberg, J.A., Reference Samples for Electron Microprobe Analysis, *Geostand. Newsl.*, 1980, vol. 4, pp. 43–47.
- Johnson, K.T.M., Dick, H.J.B., and Shimizu, N., Melting in the Oceanic Upper Mantle: An Ion Microprobe Study of Diopsides in Abyssal Peridotites, *J. Geophys. Res.*, 1990, vol. 95, pp. 2661–2678.
- Kilinc, A., Carmichael, I.S.E., Rivers, M.L., and Sack, R.O., The Ferric–Ferrous Ratio of Natural Silicate Liquids Equilibrated in Air, *Contrib. Mineral. Petrol.*, 1983, vol. 83, pp. 136–140.
- Kinzler, R.J. and Grove, T.L., Corrections and Further Discussion of the Primary Magmas of Mid-Ocean Ridge Basalts, 1 and 2, *J. Geophys. Res.*, 1993, vol. 98, no. B12, pp. 22 339–22 347.
- Kinzler, R.J. and Grove, T.L., Primary Magmas of Mid-Ocean Ridge Basalts. 1. Experiments and Methods, *J. Geophys. Res.*, 1992, vol. 97, no. B5, pp. 6885–6906.
- Kyser, K.T., Cameron, W.E., and Nisbet, E.G., Boninite Petrogenesis and Alteration History: Constraints from Stable Isotope Composition of Boninites from Cape Vogel, New Caledonia and Cyprus, *Contrib. Mineral. Petrol.*, 1986, vol. 93, pp. 222–226.
- Langmuir, C.H., Klein, E.M., and Plank, T., Petrological Systematics of Mid-Ocean Ridge Basalts: Constraints on Melt Generation beneath Ocean Ridges, *Mantle Flow and Melt Generation at Mid-Ocean Ridges*, Washington, DC: AGU, 1992, pp. 183–280.
- McKenzie, D., Melt Movement in the Mantle, *Mineral. Mag.*, 1994, vol. 58A, pp. 585–586.
- McKenzie, D. and O’Nions, R.K., The Source Regions of Ocean Island Basalts, *J. Petrol.*, 1995, vol. 36, no. 1, pp. 133–159.
- Michael, P., Regionally Distinctive Sources of Depleted MORB: Evidence from Trace Elements and H<sub>2</sub>O, *Earth Planet. Sci. Lett.*, 1995, vol. 131, pp. 301–320.
- Nikogosian, I.K. and Sobolev, A.V., Geochemical Heterogeneity of Primary Melts in the Hawaii Plume: Evidence from Melt Inclusion Study, *5th Zonenshain Conf. Plate Tectonics*, Moscow: IO RAN–GEOMAR, 1995, pp. 18–19.
- O’Hara, M.J., Trace Element Geochemical Effects of Integrated Melt Extraction and “Shaped” Melting Regimes, *J. Petrol.*, 1995, vol. 36, no. 4, pp. 1111–1132.
- Portnyagin, M.V., Magakyan, R., and Schmincke, H.-U., Geochemical Diversity of Primitive Boninite Magmas from the Study of Magmatic Inclusions in Highly Magnesian Olivine from the Lavas of Southwestern Cyprus, *Petrologiya*, 1996, vol. 4, no. 3.
- Qin, Z., Lu, F., and Anderson, J.A.T., Diffuse Reequilibration of Melt and Fluid Inclusions, *Am. Mineral.*, 1992, vol. 77, pp. 565–576.
- Roedder, E., *Fluid Inclusions*, Mineral. Soc. Am., 1984.
- Ross, K. and Elthon, D., Cumulates from Strongly Depleted Mid-Ocean-Ridge Basalt, *Nature*, 1993, vol. 365, no. 6449, pp. 826–829.
- Shimizu, N., and Hart, S.R., Applications of the Ion Microprobe to Geochemistry and Cosmochemistry, *Ann. Rev. Earth Planet. Sci.*, 1982, vol. 10, pp. 482–526.
- Sisson, T.W. and Layne, G.D., H<sub>2</sub>O in Basalt and Basaltic Andesite Glass Inclusions from Four Subduction-related Volcanoes, *Earth Planet. Sci. Lett.*, 1993, vol. 117, nos. 3–4, pp. 619–635.
- Sobolev, A.V., Permeability of the Oceanic Mantle and Non-linearity in the Processes of Its Melting, *Nelineinaya geodinamika* (Nonlinear Geodynamics), Moscow: Nauka, 1994, pp. 54–67.
- Sobolev, V.S., *Stroenie verkhnei mantii i sposoby obrazovaniya magm* (Structure of the Upper Mantle and Mechanisms of Magma Formation), XIII Vernadsky Lecture, Moscow: Nauka, 1973.
- Sobolev, S.V. and Babeyko, A.Yu., Modelling of Mineralogical Composition, Density and Elastic Wave Velocities in the Unhydrostatic Rocks, *Surv. Geophys.*, 1994, vol. 15, pp. 515–544.
- Sobolev, A.V. and Chaussidon, M., H<sub>2</sub>O Concentrations in Primary Melts from Island Arcs and Mid-Ocean Ridges: Implications for H<sub>2</sub>O Storage and Recycling in the Mantle, *Earth Planet. Sci. Lett.*, 1996, vol. 137, pp. 45–55.

- Sobolev, A.V. and Danyushevsky, L.V., Petrology and Geochemistry of Boninites from the North Termination of the Tonga Trench: Constraints on the Generation Conditions of Primary High-Ca Boninite Magmas, *J. Petrol.*, 1994, vol. 35, no. 5, pp. 1183–1211.
- Sobolev, A.V., Danyushevsky, L.V., Dmitriev, L.V., *et al.*, High-Alumina Magnesian Tholeiite: A Primary Melt of Mid-Ocean Ridge Basalts, *Geokhimiya*, 1988, no. 10, pp. 1522–1528.
- Sobolev, A.V. and Shimizu, N., The Origin of Typical NMORB: The Evidence from a Melt Inclusion Study, *Mineral. Mag.*, 1994, vol. 58A, pp. 862–863.
- Sobolev, A.V. and Shimizu, N., Ultradepleted Melts and the Permeability of the Oceanic Mantle, *Dokl. Ross. Akad. Nauk*, 1992, vol. 326, no. 2, pp. 354–360.
- Sobolev, A.V. and Shimizu, N., Ultra-Depleted Primary Melt Included in an Olivine from the Mid-Atlantic Ridge, *Nature*, 1993, vol. 363, no. 6425, pp. 151–154.
- Sushchevskaya, N.M., Gevorkyan, V.Kh., Kononkova, N.N., *et al.*, Petrogenesis of Tholeiitic Magmas at 8°–10°N of the Mid-Atlantic Ridge, *Geokhimiya*, 1985, no. 7, pp. 953–961.
- Thompson, A.B., Water in the Earth's Upper Mantle, *Nature*, 1992, vol. 358, pp. 295–302.