Engineering of experiment

Chertkova N.V., Spivak A.V., Zakharchenko E.S., Safonov O.G. Applicability of ammonia borane as a hydrogen source in diamond anvil cell experiments. *UDC 552.11*

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Abstract. Ammonia borane (NH_3BH_3) is used in experimental petrology as a laboratory source of hydrogen, boron, and nitrogen. In the present study, the thermal decomposition of this compound was investigated up to 300 °C in a diamond anvil cell using Raman spectroscopy. The obtained results demonstrated that ammonia borane can be effectively used to generate hydrogen in the working volume of the cell at temperatures as low as approximately 200 °C. However, the formation of numerous bubbles significantly deteriorates visual monitoring and the quality of Raman spectra. Thus, the use of this compound to create a reducing environment in a diamond anvil cell is associated with a decline in the quality of optical imaging and spectroscopic analysis.

Keywords: *experiment; diamond anvil cell; ammonia borane; hydrogen; reducing conditions; optical spectroscopy*

Creating reducing conditions in a diamond anvil cell (DAC) is important for studying phase relationships under mantle-relevant conditions, as well as for the synthesis of new materials (Sokol et al., 2020; Boehler, 2005). The main methods for achieving such conditions include loading with reducing agents (Machida et al., 2010), in situ generation of hydrogen through chemical reactions (Wang and Chou, 2023), the use of oxygen fugacity buffers (McCubbin et al., 2014), and the addition of carbon- or hydrogen-containing components (Peña-Alvarez et al., 2021).

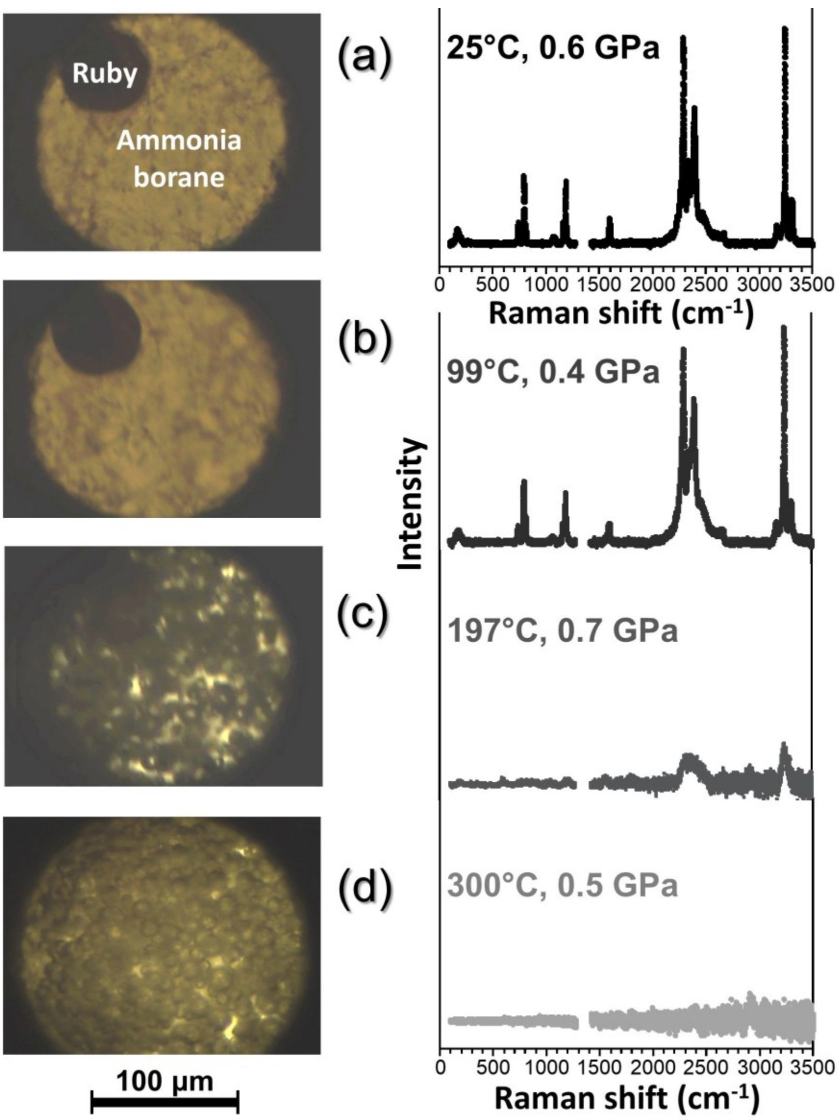

Fig. 1. Microphotographs of the sample chamber containing the sample and pressure marker, and Raman spectra acquired at the corresponding temperatures and pressures (after baseline correction).

Ammonia borane (NH_3BH_3) is a promising hydrogen-containing material whose properties are being actively studied in experiments using diamond anvil cells. Due to hydrogen release upon heating, it is of interest as a potential reagent for forming a reducing environment directly during experiments. In this context, the present study investigates the thermal decomposition of ammonia borane in order to evaluate its potential use as a hydrogen source in high-pressure diamond anvil cell apparatuses.

The experiments were carried out in a piston-cylinder type diamond anvil cell with external heating at the Mantle Laboratory of the D.S. Korzhinskii Institute of Experimental Mineralogy, Russian Academy of Sciences. Crystalline ammonia borane synthesized according to the method described by Antonov et al. (Antonov et al., 2017) was used as the starting material; it was loaded into the cell together with a ruby microcrystal serving as a pressure marker. During the experiments, the cell with a cooling unit was placed under an optical microscope equipped with a digital camera and connected to a Raman spectroscopy system. During heating, the sample was monitored visually, and spectroscopic analysis was also performed. Raman spectra were collected in backscattering geometry using a solid-state continuous-wave laser with a wavelength of 532 nm.

Microphotographs of the working chamber with the sample and pressure marker, as well as Raman spectra collected from the central part of the sample during the experiment, are shown in Figure 1. The release of molecular hydrogen began at 146 °C; at 195 °C, the formation of H_2 globules was observed throughout the entire volume. Hydrogen continued to be actively released up to 300 °C and was detected in the quenched experimental products.

At room temperature and a pressure of 0.6 GPa, ammonia borane is a crystalline compound whose Raman spectrum exhibits characteristic bands at ~788 cm^{-1} (B–N stretching vibrations), ~1186 cm^{-1} (B–H bending), ~1595 cm^{-1} (N–H bending), in the 2280-2335 cm^{-1} region (B–H stretching), and 3240-3310 cm^{-1} region (N–H stretching) (Hess et al., 2008) (Fig. 1a). At a temperature of 195 °C, intense hydrogen release began throughout the entire sample volume. In the Raman spectrum recorded at 197 °C, a significant decrease in the intensity of NH_3BH_3 molecular vibrational bands was observed (Fig. 1c). At 300 °C, Raman bands in the 2280-2380 cm^{-1} and 3240-3310 cm^{-1} ranges were no longer detected (Fig. 1d), which was accompanied by a substantial deterioration in spectral quality and suppression of the useful signal by background emission.

A comparison of optical images obtained at different temperatures shows that when hydrogen is released, visual access is blocked, and the boundaries of the various phases (in this case, the sample and the pressure marker, ruby) become poorly distinguishable. As hydrogen accumulates in a significant volume within the sample chamber, the ruby microcrystal is no longer visible in optical images (Fig. 1d).

The obtained results show that ammonia borane can be effectively used for hydrogen generation in the working volume of the cell at temperatures of 195-300 °C. However, the formation of numerous bubbles significantly limits visual control and degrades the quality of Raman spectra. Thus, the use of this compound for creating a reducing environment in high-pressure diamond anvil cell experiments is associated with deterioration in the quality of optical images and reduced analytical capability for sample characterization.

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Krivolutskaya N.A. Melt inclusions in minerals from intrusive rocks: to the methodology of the study. *GRNTI 38.33.17*

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Abstract. The study of melt inclusions in rock-forming minerals from intrusive rocks is discussed, using the example of melt inclusions in olivine from ore-bearing massifs in the Norilsk region. The process of the inclusions' heating and producing high-Mg olivine and orthopyroxene within them is described. Their formation is attributed to the difference in cooling rates between the rocks in nature and the experimental conditions. These results are often misinterpreted as the actual composition of the original melt, which can lead to errors in interpretation.

***Keywords**: melt inclusions, olivine, temperature of homogenization, parental melts, intrusions*

Introduction. Composition of parental magmas for igneous rocks is extremely important for understanding their origin in petrology, geodynamics, and ore genesis. Various methods are used to get concentrations of major and trace elements in magmas, for example, rock compositions for homogeneous geological bodies and weighted average composition for differentiated intrusions. However, rocks often undergo secondary alterations changing their original composition that do not allow to accurately determine the composition of the parental magma. In the case of effusive rocks, fresh quenched glasses and melt inclusions in rock-forming minerals can be used to assess volatile component content as well. These techniques have become possible due to the development of modern analytical methods for the last few decades (Redder, 1987; Sobolev, 1996). They are also used in the study of intrusive rocks, although the nature of their crystallization rarely leads to the formation of melt inclusions in rock-forming minerals in general, and is suitable for experimental work in particular. These studies require special care both in conducting experiments and interpreting the results. Our experience shows that serious mistakes often occur both in the first and second stages, so the number of works on intrusive rocks is much less than those on effusive rocks. This article will share the results of our work on inclusions in olivine from ore-bearing rocks in the Norilsk region, which may help future researchers avoid making mistakes in their own work.

Objects and methods of the study. As objects for research, we selected samples from ore-bearing intrusions in the Norilsk region (Talnakh, Kharayelakh, Norilsky1, Maslovsky) in the northwestern part of the Siberian platform. These samples consist of picritic gabbros-dolerites containing disseminated PGE-Cu-Ni sulfide ore. The rocks contain early liquidus olivine, which reflect the composition of the parental melt to the greatest extent. We made transparently polished plates from these rocks to study the inclusions. The inclusions were viewed under an Olympus microscope. They were homogenized in a Sobolev-Slutsky chamber (1984), a muffle furnace and a vertical furnace with controlled oxygen fugacity. Inclusions have been studied before and after experiments using an electron microscope, electron and ion microprobes (GEOHI RAS, YAF ITHIAN RAS; analysts N.N.Kononkova, S.G.Simakin, E.V.Potapov).

Results. One of the most important questions on genesis of ore-bearing intrusions is a parental magma composition which formed the Norilsk deposits. Is it close to other magmas of the Siberian province? In particular, does it contain high concentrations of volatile components as suggested by some researchers (Distler et al., 1999; Barnes et al., 2017). For our study, we selected olivine which dominates in the picritic gabbro-dolerite (60-70 vol.%). These rocks also contain plagioclase (15-20 vol.%) and clinopyroxene (10-15 vol.%). Subordinate minerals include orthopyroxenes and chromspinels (Ryabov et al., 2014, Krivolutskaya et al., 2024).

The process of inclusions' study and the results obtained at each stage are described below step by step.

1. Study of magmatic inclusions using an optical microscope and microprobe analysis before the experimental work.

There are three types of magmatic inclusions in olivine (Figs.1,2) i.e., melt, fluid, and crystalline. Melt inclusions could be divided into the groups: glassy (glass + bubble), partially crystallized (glass+bubble+solid phases, mostly, titanomagnetite, orthopyroxene), and completely crystallized. The composition of glasses and individual phases was analyzed using an electron microprobe (Table 1).

Glass inclusions (Fig. 1a) are typically small in size (5–25 microns) and rounded shape, with a very acidic composition (up to 70% SiO_2) due to crystallization olivine from the trapped melt on the host-mineral walls. However, these newly formed phases have a more ferruginous composition compared to the host mineral and are clearly visible in reflected electrons (Fig.3a,b). The second feature of naturally quenched glasses is their very low calcium oxide concentration, which varies from 0.2% to 0.7% by weight. This can be attributed to the diffusion of calcium from inclusions into the host mineral, it is confirmed by the presence of orthopyroxene as a daughter phase instead of clinopyroxene which dominates in the rocks (Fig.1,3b). Thus, the composition of trapped melt at T=20°C does not correspond to its primary composition.

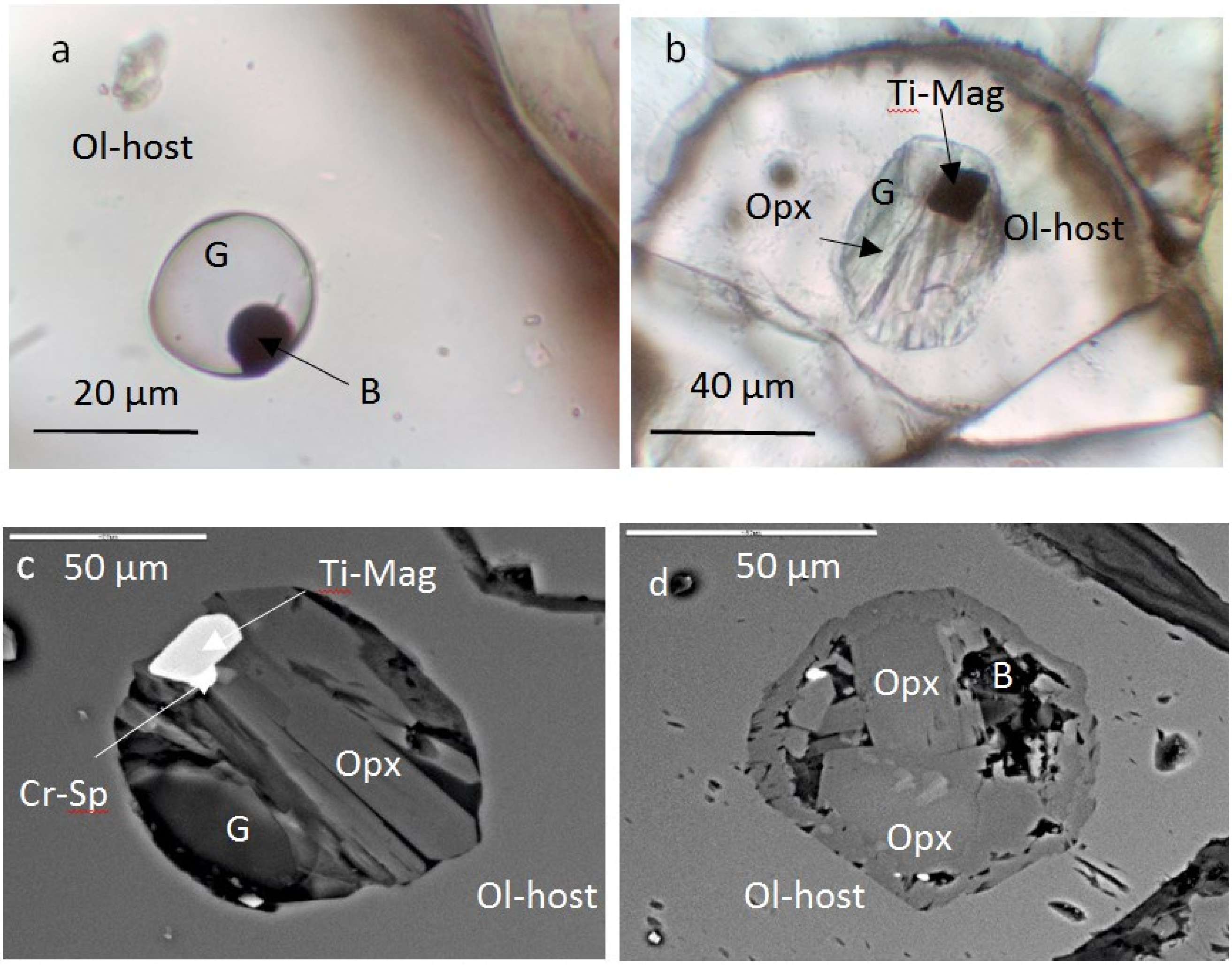

Fig.1. Melt inclusions in olivine from picritic gabbro-dolerite of the Norilsk 1 intrusion.

a, b – inclusions in transmission light: a – glass, b – partially crystallized; c, d – BSE images. Here and in Figs. 2,3: B – bubble, G – glass, Ti-Mag – titanomagnetite, Opx – orhopyroxene, Ol-host – olivine grain with inclusion, Cr-Sp – cromium spinel.

2. The process of homogenization of melt inclusions.

To reconstruct the composition of the original melt, the source of the mineral, it is necessary to reverse the cooling process by heating the inclusions to achieve a uniform glass. The temperature at which this process is completed, known as the homogenization temperature (T_{hom}). It was determined by heating individual inclusions in a Sobolev-Slutsky chamber (Sobolev, Slutsky, 1984), closely monitoring the process and using native gold placed in the chamber alongside the sample to measure the temperature (Sobolev, Krivolutskaya, 2009). Initially, we followed the method described by A.V. Sobolev for basalt (1996). It includes raising the temperature from 20^{o}C up to T_{hom} for 20–25 minutes and keeping the sample at this temperature no more than 5 minutes to avoid loss of volatile components from the melt. Then the inclusion is quickly quenched, they were mounted in capsules and polished until the inclusion was brought to the surface. Thus, 15 inclusions were prepared. When viewing the heated inclusions under a microscope, their heterogeneous structure was revealed: in addition to glass and a small bubble, they contained various amounts of olivine crystals (in rare cases, orthopyroxene), which turned out to be magnesium than the host olivine (Table 1) ($Fo_{86.7}$ compared with $Fo_{80.1}$).

Table 1. Composition of olivine in Fig. 3a (wt.%)

Mineral	SiO_2	MgO	MnO	CaO	FeO	NiO	Fo,mol.%
ol-host.	36,84	44,38	0,28	0,15	18,88	0,18	80,7
Ol-2	42,16	41,98	0,21	0,59	11,42	0,21	86,7
Ol-1	36,68	44,03	0,36	0,16	17,33	0,15	81,9

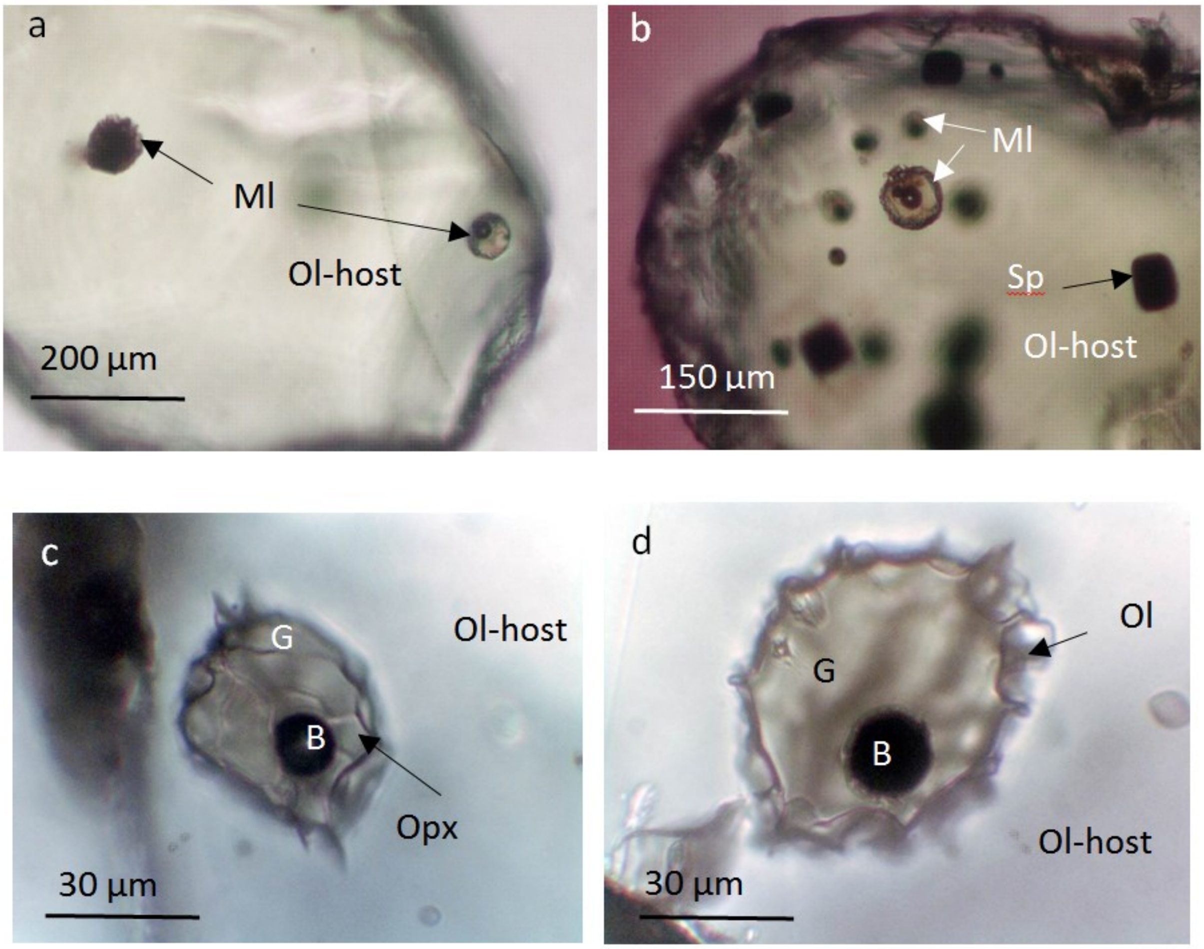

Fig.2. Melt inclusions (MI) in transmission light after heating at T=1250°C. Ol – olivine in melt inclusion.

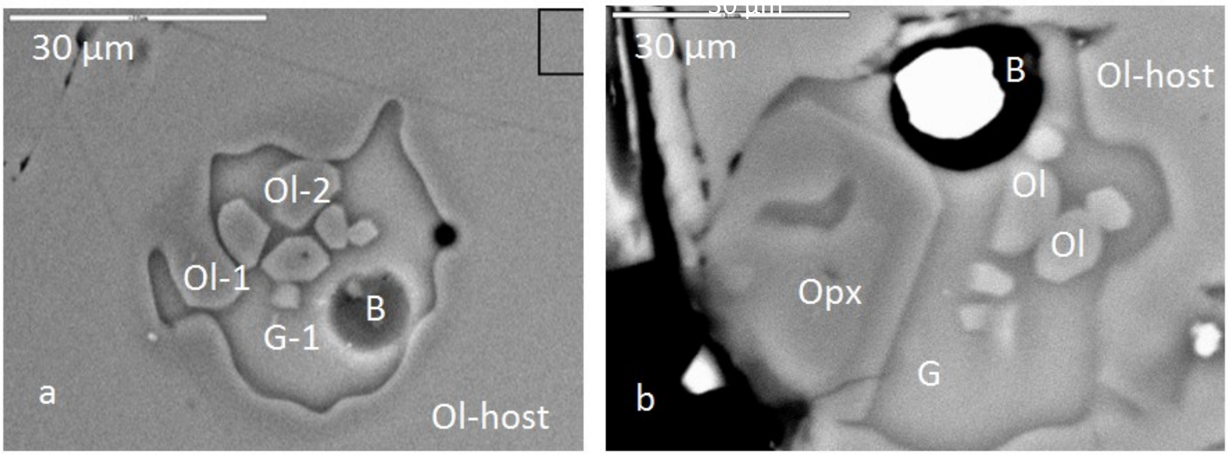

Fig.3. BSE images of quenched melt inclusions in olivine from the picritic gabbro-dolerite of the Norilsk 1 intrusion. After (Krivolutskaya et al., 2024).

The glass composition (G-1 in Fig.3a) is also characterized by high levels of silica and low levels of calcium (wt.%): 54.2 SiO_2, 1.55 TiO_2, 10.88 Al_2O_3, 8.26 FeO, 0.15 MnO, 9.46 MgO, 3.18 CaO, 1.90 Na_2O, 1.09 K_2O,0.35 P_2O_5, 0.15 S, 0.1 Cl.

Next, we conducted numerous experiments aimed at producing homogeneous glasses. Initially, the inclusions were kept at homogenization temperature for a long period of time (1-2 hours), but it was not possible to produce homogeneous glass. Secondly, we heated the inclusions at higher temperature than the temperature of homogenization (*T*hom), which reaches *T*=1450 °C. This sometimes reduced the number of crystals, but we still did not obtain homogeneous glass. Thirdly, we took a slow approach (4-5 hours) to the homogenization temperature between 1100 and 1200 °C, as a result of which we obtained homogeneous glasses that were close to the composition of the rocks, especially after calculation to their equilibrium with host olivine (Petrolog-3, Danyushevsky, Plechov, 2011) (Table 2). Naturally, the content of volatile components in these samples did not correspond to their initial levels, as they had been lost during the long experiment.

Table 2. Compositions of melt inclusions (wt.%) in olivine from picritic gabbro-dolerite of the Maslovsky deposit after long heating

	Fo	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	S
1)	80,1	50,92	1,81	10,22	14,54	0,28	5,98	9,36	3,22	0,33	1,70	0,60	0,08
2)	80,1	50,94	1,99	10,56	14,20	0,28	5,56	9,37	3,03	0,34	1,63	0,62	0,04

Recalculated to Ol-host

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	**FeO_{tot}**	MnO	MgO	CaO
1)	49,83	1,58	8,93	2,13	13,84	15,76	0,25	10,67	8,18
2)	49,90	1,72	9,15	2,07	13,80	15,66	0,24	10,68	8,12

	Na_2O	K_2O	P_2O_5	Cl	S
1)	2,81	0,29	1,49	0,53	0,07
2)	2,62	0,29	1,41	0,53	0,04

Discussion and Conclusions. In recent years, numerous papers have been published on the topic of melt inclusions in minerals of intrusive rock. These works include studies of inclusions in chromium spinel from gabbro of the Norilsk 1 massif (Chayka et al., 2020a,b) and olivine from the Bushveld massif (Solovova et al., 2021). The results of these studies are similar to those obtained in our experiments, showing olivine inclusions within spinel crystals and an acidic composition of the glass phase. The authors attribute this result to local assimilation of host rock by melt (Chayka et al., 2020a) or other processes, while ignoring the discrepancy between melt composition and rock composition.

In fact, the slow cooling of intrusive rocks leads to a process where melts trapped during crystallization are intensively exchanged with the host mineral, which, in turn, with the parental melt. The latter factor cannot be taken into account in the experiment. Despite this, it does not appear to have a significant effect on the final composition of the melt. With prolonged heating of the inclusion, it is still possible to reconstruct the exchange process between the inclusion and the host mineral to obtain accurate results on the composition of the original melt. Therefore, when working with inclusions in intrusive rock minerals, it is essential to constantly monitor the results obtained at each stage and especially during interpretation.

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