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Methods of Local Analysis for Study of Carbon in Silicates: Nuclear Microprobe Analysis and Secondary Ion Mass Spectrometry

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Abstract—New approaches are proposed to analyze the content, distribution, and diffusion of carbon in silicates using nuclear microprobe analysis and secondary-ion mass spectrometry (SIMS). Techniques based on the nuclear reaction $^{12}C(d,p)^{13}C$ were developed to determine the coefficients of radiation-enhanced carbon diffusion in olivine at 300–370 K and deuteron doses that are comparable in terms of defect formation with those of α-particles generated by the decay of uranium and thorium isotopes for ~400 Ma (olivine age). The coefficients of thermal (D_{th}) and radiation-enhanced (D_{rad}) carbon diffusion in synthetic forsterite were compared to those of natural olivines from alkaline basalt nodule (Shevaryn Tsaram volcano, Mongolia). It is demonstrated that the diffusion coefficients strongly depends on the migration mechanisms of carbon atoms in crystals. The developed techniques and software package for SIMS determination of carbon distribution in silicates allowed us to study simultaneously the carbon and hydrogen distribution in a glass vein of the Chelyabinsk meteorite. The possible presence of hydrocarbons in the studied silicate glass of meteorite is suggested.

Keywords: carbon, hydrogen, silicates, nuclear microanalysis, secondary ion mass spectrometry (SIMS)

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INTRODUCTION

The isotope composition, speciation, redox state of carbon in the Earth's rocks, and the global carbon cycle represent the fundamental geochemical problem, because carbon is one of the most important and unique chemical elements of our planet. Carbon is the major gas-forming element and actively involved in the redox reactions in the Earth's interior, i.e., its presence determines the fluid and redox mode of the Earth's interior. This problem has been studied for over 60 years and described in numerous publications (huge amount of literature), for instance, in the last review "Carbon in Earth" (Ed. by Hazen et al., 2013). The solution of this problem is tightly related to the development of methods of carbon determination in silicates and its distribution in different geochemical objects, which are characterized by complex phase and chemical composition. In these objects, carbon occurs in different species and compounds in the coexisting phases. The bulk determination of carbon is based on the vacuum extraction in combination with manometric and mass-spectrometric methods. These methods are described in different reviews (Hauri et al., 2002 and reference therein, for instance, Ihinger et al., 1994). The advantage of these methods is the possibility of determining the bulk content of carbon in the rock and its isotopic composition, with simultaneous determination of other volatiles, for instance, H_2O. At the same time, this method requires large amount of starting material (few hundreds of mg) for accurate carbon determination. Other disadvantages are the problem of removal of absorbed CO_2 at low carbon content (at ppm level) as well as analytical difficulties in determination of carbon contribution from different coexisting phases. For instance, a large amount (few hundreds of mg) of these glasses carefully handpicked under a binocular microscope is required for determination of carbon in volcanic and ocean-floor glasses. Methods of local analysis have recently received the wide application in determining the carbon in diverse coexisting phases of the rock. The development of this method having the low detection limit and high resolution is one of the top priority directions in the modern analytical geochemistry. Such methods of local analysis as autoradiography, methods of nuclear reactions, IR spectroscopy, X-ray microprobe, combination scattering spectroscopy (Raman spectroscopy), and secondary-ion mass-spectrometry became widely used for measurement of carbon in diverse magmatic silicates.

This paper considers new original approaches to the determination of carbon, study of its distribution and diffusion in silicates using methods of nuclear reactions and secondary ion mass spectrometry (SIMS).

Nuclear Microprobe Analysis

Carbon is incompatible element in the crystal lattice of oxides and silicates. In the mid-1980, the presence of carbon in atomic state in the crystals of oxides and rock-forming minerals has been hotly debated. These discussions were based on the works of Freund et al. (Freund et al., 1977, 1978, 1980; Wengeler et al., 1982; Kathrein et al., 1983), who demonstrated the ability of carbon to be dissolved in significant amounts (up to 1000 ppm) in the crystal lattice of oxides and silicates. Based on the above publications, Galimov (1984) proposed that the enrichment of reduced carbon in light isotope ^{12}C in rock is related to its dissolution in crystal in atomic zero-valent species, which corresponds to the beta factor equal unity. Later works (Shilobreeva et al., 1987; Mathez et al., 1987; Tsong et al., 1987; Tingle and Green, 1987; Tingle et al., 1988; Minaev et al., 1995; Keppler et al., 2003; Ni and Keppler, 2013; Rosental et al., 2015) showed the lower solubility of carbon in crystal lattice and possibility of its dissolution in form of C^{4+} (Shcheka et al., 2006). In this relation, the question of content and speciation of carbon dissolved in silicates remains controversial.

Another controversial question is the high mobility of carbon in silicates. Using nuclear $^{12}C(d,p)^{13}C$ reaction analysis and X-ray photoelectron spectroscopy, it was demonstrated (Freund et al., 1982; Oberheuser et al., 1983) that the carbon diffusion coefficient in MgO and olivine crystals was $D \sim 10^{-10}$ cm^2/s at temperature $T \sim 370$ K and carbon content of 0.03—0.1 wt %. However, later studies (Mathez et al., 1987; Tsong et al., 1987) using the same methods in combination with secondary-ion mass spectrometry and Auger electron spectroscopy did not confirmed the results of the works (Freund et al., 1982; Oberheuser et al., 1983) on the carbon diffusion in <2 μm layers within a temperature range of 78—723 K. It was noted (Kuzmin et al., 1998; Shilobreeva et al., 2000) that the disagreement between the results could be caused by radiation impact of both natural (magmatic) rocks and ion probes on the carbon-rich surface layers of crystals during analysis, which may lead to the acceleration of diffusion. Radiation acceleration of the diffusion occurs either during irradiation and heating, or during heating after irradiation (Vavilov et al., 1981). These processes were observed by Freund et al. (1982) but were not mentioned by Mathez et al. (1987) and Tsong et al. (1987), which caused disagreement in obtained results. In work (Oberheuser et al., 1983), significant diffusion of carbon was observed in layers ≤2.5 μm during in situ experiments with neutron dose of 5×10^{15} cm^{-2} at $E = 1.05$ MeV. Calculation of vacancy concentrations using TRIM-90 software showed that a dose of ~10^{14} cm^{-2} is sufficient to cause carbon diffusion under α-particles irradiation (Kuzmin et al., 1998). According to (Kuzmin et al., 1998) precisely this dose may be obtained by natural crystals with age of ~400 Ma due to uranium and thorium isotope decay.

The study of in situ radiation-enhanced diffusion on α-particle beams is complicated due to the absence of appropriate nuclear reaction. Therefore, in this work we also applied reaction $^{12}C(d,p)^{13}C$ for studying migration ability of carbon in olivines at $T \sim 300$—370 K. Irradiation and measurements were performed using deuteron beam of 1.43-MeV electrostatic accelerator EG-2 (INR RAS) 1.5 × 1.5 mm^2 in size. The detector was covered by a thin (4 μm thick) aluminum-coated Mylar film to reduce the integral loading from deuterons scattered in sample. This film practically has no effect on the detector (25 keV) and the high-energy part of backscattered deuteron spectrum. The back-scattered spectra were used to control the reference sample and radiation dose during analysis. Magnesium targets and thin films SiO_2/Si were used for band identification and energy calibration. Processing of spectra and obtaining depth concentrations profiles were carried out using integrated BEAM EXPERT software (Kogan et al., 1994), which does not require reference samples. Measured concentration profiles at depths of 0.3—1.5 μm were approximated by Gaussians, the parameters of which were used to determine the diffusion coefficients.

Olivine sample ~ 3 mm across from nodule in the Shevaryn Tsaram alkaline basalt (Mongolia) without preliminary surface treatment was cyclically irradiated with deuterons with doses 100 μC (2.8×10^{16} cm^{-2}). The measurements were performed between irradiation, with a decrease of beam current by ten times. The irradiation and measurement lasted for ~1000 s. After the third cycle, a 30-min pause was made to estimate the inverse (opposite to the concentration gradient) carbon diffusion. Maximum temperature of sample during irradiation was 100°C. Proton spectra of reaction $^{12}C(d,p)^{13}C$ prior to irradiation (1) and after third irradiation (4) and next 30-min pause (5) are shown in Figs. 1 and 2 as examples. Carbon concentration profiles obtained from proton spectra for all four irradiation cycles and pause are shown in Figs. 3 and 4. The dose of the last irradiation was increased to 250 μC. During recovery of concentration profiles using BEAM EXPERT, the background of associated reactions (d,p) on Mg and Si isotopes was automatically taken into account. In order to test the validity of the Fick law application for calculation of diffusion coefficients, the integral carbon contents were determined in the top 1.5 μm layer for all measured spectra. All results are given in Table 1.

As seen from Table 1, obtained data show satisfactory agreement with Fick law (integral content of carbon remains practically unchangeable within measurement error), while concentration profiles (Figs. 3, 4) are well described by the Gaussian distribution. The coefficients of the radiation-enhanced diffusion calculated from distribution data are shown in Table 2 and fall in the range of D_{rad} 1.2—1.8 × 10^{-12} cm^2/s.

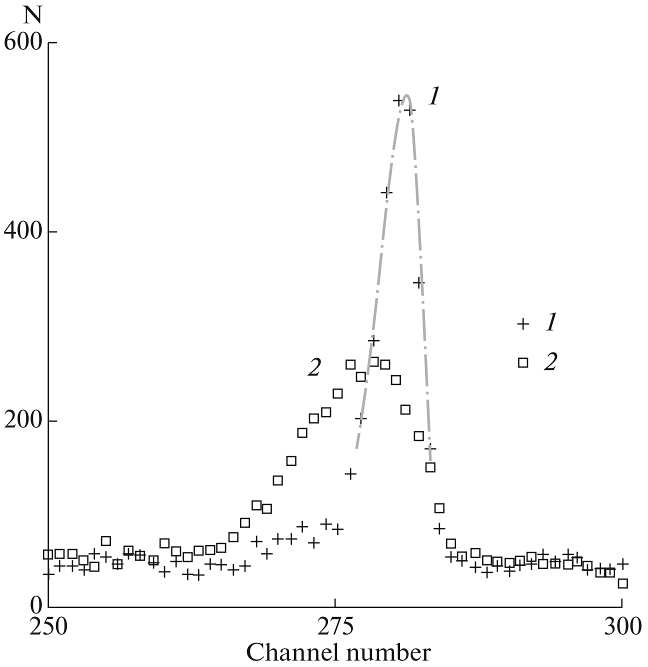

Fig. 1. Energetic proton spectra of the reaction $^{12}C(d, p)^{13}C$ (spectra nos. 1, 2 are presented in Table 1). N is the counts per channel.

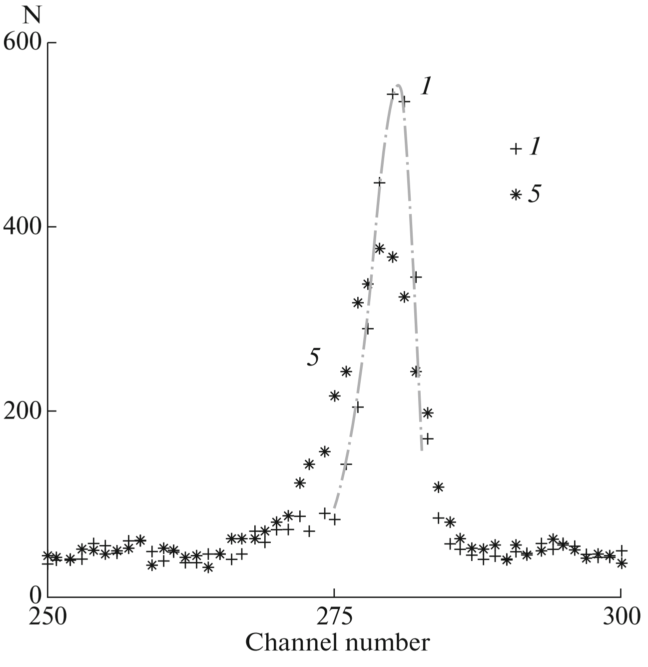

Fig. 2. Energetic proton spectra of the reaction $^{12}C(d, p)^{13}C$ (spectra nos. 1, 5 are presented in Table 1). N is the counts per channel.

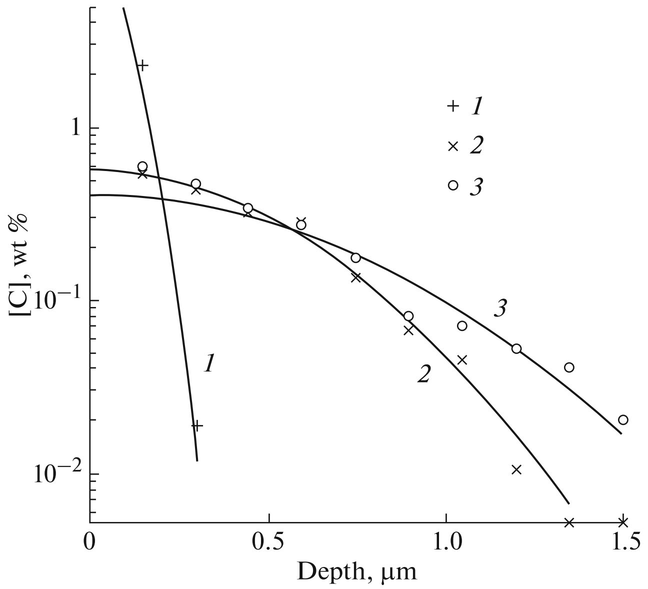

Fig. 3. Profiles of carbon concentrations obtained from energetic proton spectra of the reaction $^{12}C(d, p)^{13}C$ (spectra nos. 1, 2, 3 are presented in Table 1).

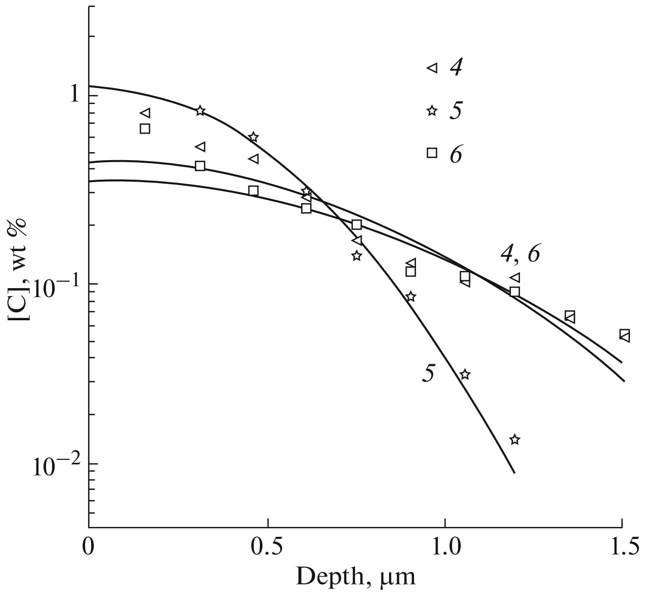

Fig. 4. Carbon concentration profiles obtained from energetic proton spectra of the reaction $^{12}C(d, p)^{13}C$ (spectra nos. 4, 5, 6 are presented in Table 1).

Obtained diffusion coefficients are two orders of magnitude lower than values obtained in (Freund et al., 1982; Oberheuser et al., 1983). Such a divergence may be caused by the difference in the preparation of sample surface before experiment, the low accuracy of spectrum processing, and the difference in the deuteron beam parameters. The possibility of radiation-enhanced diffusion in works (Freund et al., 1982; Oberheuser et al., 1983) has not been considered at all.

Table 1. Results of determination of the carbon content in the surface crystal of olivine.

NN spectrum	Irrradiation dose, μC	Total irradiation dose, μC	Integral content, μg/cm^2
1	Prior to irradiation	0	1.54
2	100	100	1.29
3	100	200	1.26
4	100	300	1.37
5	After a 30-minute pause	300	1.59
6	250	550	1.43

Table 2. Diffusion coefficients D of carbon from measured spectra

Spectra N	1	2	3	4	5	6
Diffusion coefficient D, 10^{-12} cm^2/s	1.8	1.4	1.4	1.2	Inverse diffusion after 30-min pause	1.2

In our case, unlike (Freund et al., 1982; Oberheuser et al., 1983), the surface was not subjected to mechanical or chemical treatment; the number of defects was maximal and corresponded to the natural conditions. Since surface defects (dislocations, mirofissures, etc.) serve as sinks for impurity atoms, the irradiation impact may cause atom migration in opposite directions, which retards the radiation-enhanced diffusion. This assumption is confirmed by the opposite carbon diffusion (Figs. 2, 3) to the crystal surface. Shilobreeva and Kuzmin (2003) assumed that such diffusion is caused by gettering with crystal surface as a getter. This process may be explained by the presence of carbon in the intergranular space of meteorites owing to the segregation on crystal surface caused by gettering in the response to weakening of the intensity of α-radiation after formation of the Solar System.

Thus, our experiments showed that carbon diffusion in olivine was radiation $^{12}C(d,p)^{13}C$ in nature, rather than thermal, as supported by (Freund et al., 1982; Oberheuser et al., 1983), because all above mentioned studies were based on the same technique of nuclear reaction $^{12}C(d,p)^{13}C$.

We studied experimentally the thermal diffusion of carbon in forsterite crystals (Shilobreeva et al., 2000; Shilobreeva and Kuzmin, 2003). After polyenergetic ion implantation of carbon in crystals (0.25 wt %), the samples were annealed in air at a temperature of 1100 K for an hour and then kept at room temperature for 190 days. The depth profiles of carbon concentration in forsterite were measured by secondary ion mass spectrometry using a Cameca IMS-4F. The value of thermal diffusion coefficient in forsterite crystals was $D_{\rm th} = 1 \times 10^{-15}$ cm^2/s at 1100 K (Shilobreeva et al., 2000), and decreased to $D_{\rm th} < 6 \times 10^{-20}$ cm^2/s at 300 K. Thus obtained coefficient of radiation-enhanced diffusion in olivine ($D_{\rm rad} = 1.6 \times 10^{-12}$ cm^2/s at 300 K) was more than ~ seven orders of magnitude higher than the thermal diffusion coefficient. These data allow the comparison of thermal and radiation-enhanced carbon diffusion in olivine.

Based on the study of carbon diffusion in olivine crystals, Shilobreeva and Kuzmin (2003) hypothesized a radiation nature of carbon migration in natural olivine crystals from meteorites and assumed a vacancy mechanism for the radiation-enhanced carbon diffusion.

Secondary-Ion Mass Spectrometry

Secondary-ion mass spectrometry (SIMS), the microprobe method, is widely applied in studying the carbon geochemistry. The surface of analyzed samples is bombarded by primary ions (Xe^+, Cs^+, Ga^+, O^+ etc.), which leads to sputtering of atoms and molecules both in neutral and charged state. SIMS method is based on this phenomenon of the formation of charged particles (secondary ions) and their subsequent mass spectrometric measurement. Theoretical principles of SIMS have been described in (Stephan, 2001; Werner, 2003; Senoner and Unger, 2012; Kuznetsov, 2010; Lebedev, 2013).

The SIMS method is widely used for solution of such geochemical problems as determination of concentration of chemical elements (including volatile carbon, hydrogen, fluorine, chlorine, sulfur, and others) in different phases (glasses, melt inclusions, etc.) in the rocks of different genesis (Portnyagin et al., 2007; Mironov et al., 2015; Plechov et al., 2015). SIMS method is also applied for experimental determination of solubility of water and carbon-bearing gases in silicate melts at high and elevated temperatures and pressures (Pan et al.1991; Thibault et al., 1994; Brooker et al., 1999; Behrens et al., 2004; Dasgupta et al., 2013; Ardia et al., 2013; Li et al., 2015), for determination of C and H partition coefficients between silicate and metallic phases (Li et al., 2015), melts and crystals (Rosental et al., 2015), as well as for study of carbon diffusion in silicates (Farquhar et al., 1999; Shilobreeva et al., 2000.)

We would like to mention also the works where low carbon concentrations were locally determined using SIMS method. These works consider the following fundamental problems: distribution of volatiles in the "atmosphere—magma" "ocean—core" system as applied to the evolution of the Martian atmosphere on the basis of experimental study of CH_4 solubility in Fe-free basaltic melt (Ardia et al., 2013); the determination of carbon partition coefficients between Fe-rich alloy and silicate melts $\left(D_{\mathrm{C}}^{\mathrm{metal/silicate}}\right)$ and between silicate melts and minerals (Li et al., 2015, Rosental et al., 2015); determination of volatile solubility in the C—O—H system in the reduced silicate melts (Li et al., 2015); the measurement of carbon content in melt inclusions in minerals of different genesis (Nekrylov, 2015; Plechov et al., 2015).

Besides advantage, SIMS also has a significant disadvantage in quantitative measurements. This disadvantage is a strong matrix effect: the dependence of the ionization coefficient of the sputtered atoms on the surrounding atoms in a solid (Drozdov et al., 2011). Reference samples are required to solve this problem. The preparation of the reference samples is laborious and difficult procedure, especially for multicomponent silicate glasses. Mass spectrometer is usually calibrated by the measurement of $^{12}C/^{30}Si$ and $^{13}C/^{56}Fe$ intensities depending on the carbon content in the reference sample. The carbon content also should be determined in the analyzed samples, which are close in composition to the reference sample. In this case, the selection and preparation of the reference samples represent a difficult problem.

To solve this problem we proposed a new method of quantitative SIMS measurement of the carbon ionization coefficient in silicate glasses. This method is based on the calculation of the carbon sputtering coefficients during bombardment of the surface by primary ions (Cs^+, O^+) using SIMS analysis.

In this work, the carbon sputtering coefficients in samples of silicate glasses analyzed by SIMS method (Hauri, 2002; Dasgupta et al., 2013; Ardia et al., 2013; Nekrylov et al., 2015) were calculated using SRIM2013 software package (Ziegler, 1995). In the works (Hauri, 2002; Dasgupta et al., 2013; Ardia et al., 2013; Nekrylov, 2015), analyses were carried out using Cameca IMS 4f, Cameca IMS 6f, and Cameca IMS 1280 mass spectrometers. In order to estimate the matrix effect on the carbon ionization coefficient, we proposed to apply the NBO/T parameter (Mysen, 1987; Shildt et al., 2015), which characterizes the structure and composition of the silicate matrix. The application of this parameter is limited by amorphous matrices, which are silicate glasses. The linear dependence of parameter $\beta_i^{\pm}/I_i^{\mathrm{reg}}$ ($\beta_i^{\pm}$—ionization coefficient of carbon, I_i^{reg}—the secondary ion current of carbon) on NBO/T for the above considered experimental literature data is shown in Fig. 5. Obtained dependences factually represent the calibration plots for the determination of ionization coefficient, and further, for the quantitative assessment of carbon concentration in unknown sample for given SIMS device and experimental conditions. Unlike calibrations previously applied in works (Hauri, 2002; Dasgupta et al., 2013; Ardia et al., 2013), our method makes it possible to obtain dependence of $\beta_i^{\pm}/I_i^{\mathrm{reg}}$ parameter in the wider compositional range of silicate glasses. The slopes of obtained straight lines for experiments with primary Cs^+ for different instruments coincide within an error and equals -3.1 ± 0.2 (Fig. 5), in contrast to the experiments with primary O^+ ions for which the slope is -5.9. Such difference is presumably determined by the nature of the primary beam, which in turn, affects the carbon sputtering from the surface of silicate glasses.

In this work, we developed a method of SIMS study of carbon and performed a calibration of Cameca IMS 4f (Lukin Institute of Physical Problems, Zelenograd) in order to study carbon in the glass vein of the Chelyabinsk meteorite. Special attention was given to the preparation of the surface of meteorite sample for analysis. The sample was ground and polished using carbon-free powders. In addition, its surface was etched with argon ions with energy of 5keV, $I_a = 60$ μA and slope angle 55° for 20 hours. In order to remove carbon pollution from the surface and fissures, the sample was also etched with oxygen plasma for 10 minutes. The studies were carried out on a Cameca IMS-4f. Cs^+ ions with the energy of 10 keV were used as a primary beam for analysis. The density of ion beam current was 30 μA/cm^2. The incidence angle of the primary beam relative to the normal was 25° at impact energy of 14.5 keV. Since the studied object is excellent isolator, the charge of the sample surface was compensated using a normal-incidence electron gun. In addition, the sample was covered by a thin gold layer (~10 nm) to remove charge. Mass spectral resolution $\Delta m/m = 5000$ was used to solve the interference problems. Maps of element distribution were compiled in a dynamic mode (DTS). A spatial resolution was determined by the microscopic field and accounted for 5 μm at a raster of 250 × 250 micron. Secondary particles were detected using secondary ion multiplier SEV217. As a result, we obtained numerical arrays for secondary ion current intensities of carbon (ion number per second) in the points with coordinates (X, Y) for each ionic image (layer). The secondary ion current intensities were obtained not only for carbon, but also for hydrogen. During analysis, the sample was studied to a depth of 65 μm. 1134 ion images (layers 250 × 250 μm in size) were obtained for depth distribution of carbon. An example of ion image of ^{12}C distribution in the glass vein in the sample of the Chelyabinsk meteorite is shown in Fig. 6a.

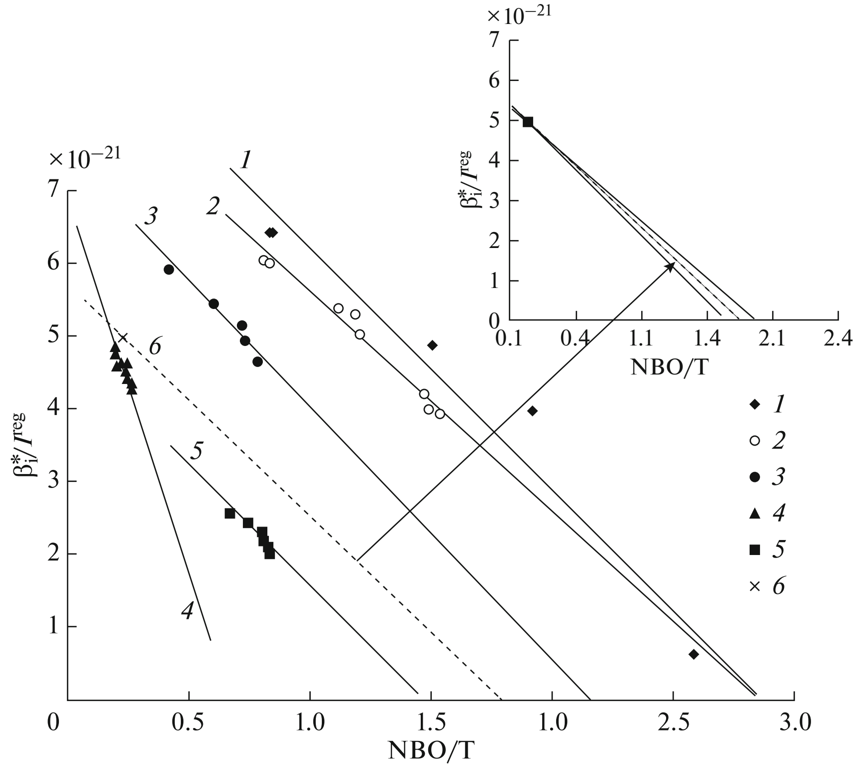

Fig. 5. Dependence of $\beta_i^{\pm}/I_i^{\text{reg}}$ parameter on NBO/T characterizing the structure and composition of matrix. The calculations were performed for experimental data by Dasgupta et al., 2013 (*1*), Hauri, 2002 (*2*), Chi H. et al., 2014 (*3*), Nekrylov et al., 2015 (*4*), Ardia et al., 2013 (*5*), and Chelyabisk meteorite (*6*). Obtained dependences are described by the following equations: (*1*) $y = -3.1x + 9.3$, $R^2 = 0.96$; (*2*) $y = -2.9x + 8.6$, $R^2 = 0.96$; (*3*) $y = -3.2x + 7.3$, $R^2 = 0.95$; (*4*) $y = -3.3x + 4.8$, $R^2 = 0.92$; (*5*) $-5.9x + 5.9$, $R^2 = 0.82$ according to Bronsky et al., 2016.

Cameca IMS-4f was calibrated using above described method based on the estimation of the ionization factor and sputtering coefficient of carbon during SIMS analysis. The procedure of estimate is described in detail in (Bronsky and Shilobreeva, 2016). Obtained calibration dependence for used Cameca IMS-4f device is shown in Fig. 5 (dashed line).

The measured intensities of secondary ion current of carbon (as well as hydrogen) were statistically processed using new software developed using C# algorithm. This software provides statistical processing of the great body of SIMS output data (over 1000 files with more than 30000 intensity values in each). SIMS analysis is accompanied by the loss and some distortion of signal, which is related to specifics of the instrument (for instance, the drop of resistance in a dynamic mode of analysis). To remove these errors, a function of trilinear interpolation of results over the entire analysis volume with possibility of subsequent smoothing was implemented in the developed software. Figure 6b shows an example of starting and recovered profile of carbon distribution with depth in the glass sample of the Chelyabinsk meteorite.

The developed technique was used to construct the distribution profiles of intensity signals for ^{1}H and ^{12}C versus sample depth in points with maximum and minimum values (Figs. 7c, 7d). To estimate the ^{12}C contents (Fig. 7d) with depth in recovered profile, the total and average intensities of the secondary ion current of carbon were calculated over the entire analyzed volume ($I_{\text{tot}} = 9.2 \times 10^9$, $I_{\text{av}} = 23620$). The average intensity of the secondary ion current of carbon was compared with the average carbon content of 205 ppm in the glass-like vein of the Chelyabinsk meteorite (Pillinger et al., 2013). The recalculation coefficient of the intensity of secondary ion current of carbon in ppm was calculated to be 0.009 ($205/I_{\text{av}}$).

Data array of the intensities of secondary ion currents obtained by us during analysis of silicate glass from the Chelyabinsk meteorite were used to present them as a 3-D image.

Widely applied imaging mass spectrometry provides not only qualitative and quantitative, but also spatial information on sample (Lebedev, 2013).

The imaging technique was used to obtain the spatial distribution of carbon and hydrogen in silicate glass sample of the Chelyabinsk meteorite. For this purpose, we developed a MatLab script to compile the 3D distribution of analyzed elements on the basis of obtained data array. Imaging of the results was performed using

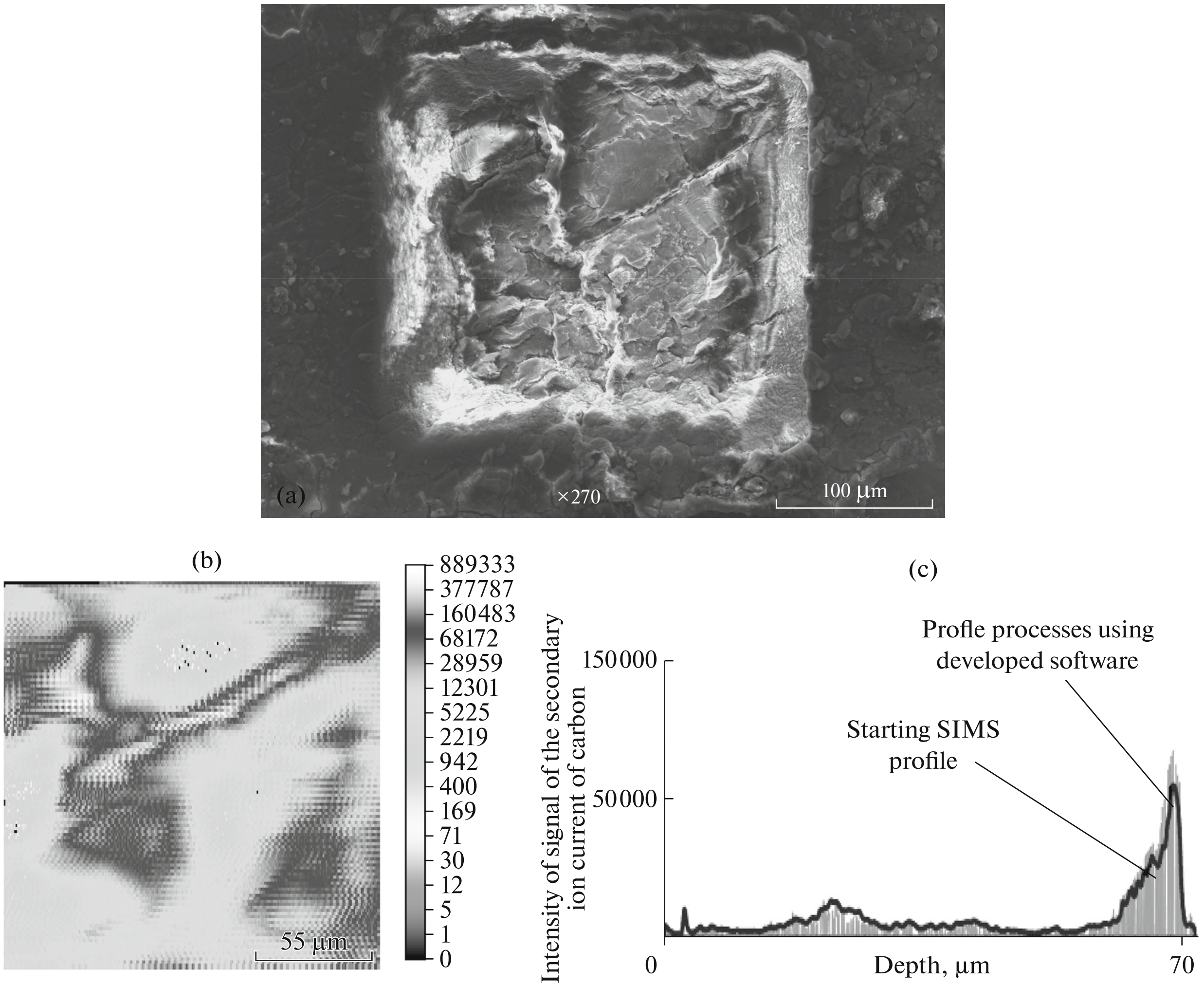

Fig. 6. Analyzed region and ion images on the crater floor (65 μm) of glass vein of the Chelyabinsk meteorite obtained by SIMS method (a) analyzed region; (b) example of ion image of ^{12}C distribution, (c) carbon distribution over the entire analyzed depth from sample surface to the crater floor.

GNUplot software. Using analysis of silicate glass of the Chelyabinsk meteorite as an example, 3D distribution of ^1H, ^{12}C was plotted in two regions of the studied sample analyzed to a depth of 20 (Fig. 8) and 65 μm (Fig. 9), their spatial correlation was analyzed, and the ratios of secondary ion current intensities $^1H/^{12}C$ were calculated (Figs. 8, 9). The developed technique of imaging of isotope distribution in sample allowed simultaneous study of carbon and hydrogen in meteorite.

It is shown (Fig. 9) that the ratios of secondary ion current intensities $^1H/^{12}C$ in 95% correlation region of ^1H, ^{12}C are less than 0.2 and lie within the range of 0.05–0.2. The spatial correlation ^1H, ^{12}C and calculated ratio of the intensities of secondary ion currents in these regions may indicate the presence of hydrocarbons in a sample of silicate glass of the Chelyabinsk meteorite. The presence of hydrocarbons in the heterogeneous samples of the Chelyabinsk meteorite has been confirmed in (Romanovskaya, 2013) by simultaneous spectrofluorimetry.

Thus, the developed software package and SIMS method were used to demonstrate the spatial distribution of ^1H and ^{12}C in the analyzed silicate glass sample from the Chelyabinsk meteorite. The regions of spatial correlation of carbon and hydrogen and their absence were identified. The ratios of the intensities of the secondary ion current $^1H/^{12}C$ were estimated and the presence of hydrocarbon in the studied meteorite was assumed. However, obtained results require further study using spectroscopic methods.

CONCLUSIONS

Original technique was developed to determine the carbon diffusion coefficients in silicate crystals using energetic proton spectra of nuclear reaction $^{12}C(d,p)^{13}C$. The radiation-enhanced carbon diffusion

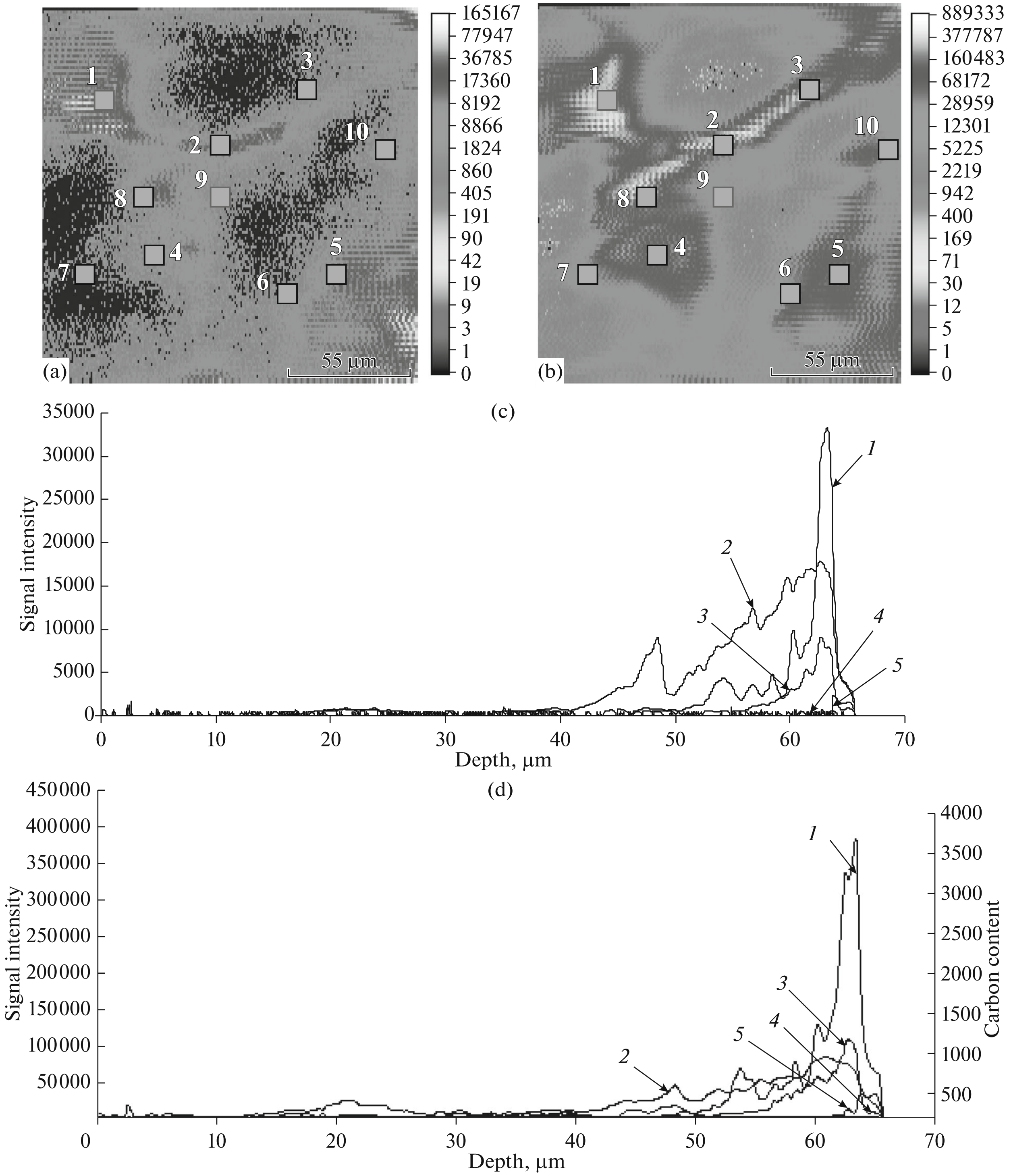

Fig. 7. Ion images ^{1}H (a) and ^{12}C (b) (with distinguished analysis spots) in glass vein obtained by SIMS method at a depth around 65 μm, and profiles of the distribution of the secondary ion current intensities ^{1}H (c), ^{12}C (d) in selected spots. Calculated carbon content is shown in (d).

was studied in natural olivines crystals from the Shevaryn Tsaram alkaline basalts at deuteron doses comparable in terms of defect formation with alpha-particle doses produced by decay of natural uranium and thorium isotopes during ~400 Ma (olivine age).

The coefficients of thermal (D_{th}) and radiation-enhanced (D_{rad}) carbon diffusion in the crystals of synthetic forsterite were compared with those of natural olivine from nodule of alkaline basalt (Shevaryn Tsaram, Mongolia). The results showed the high

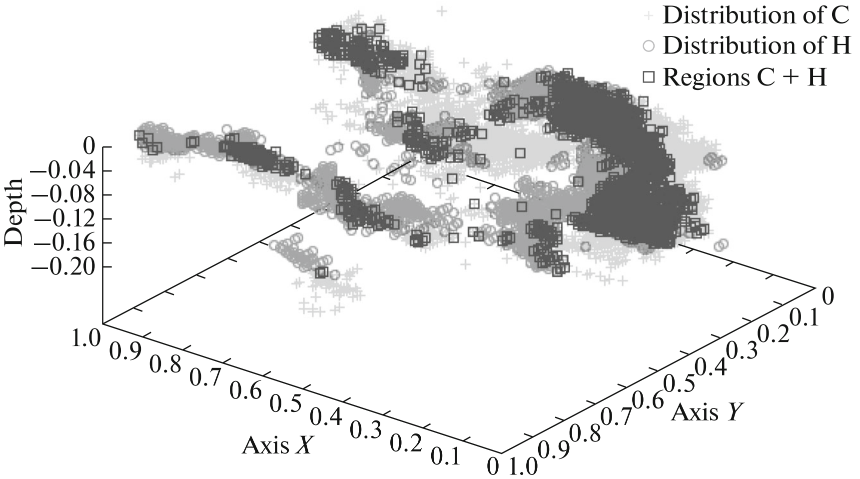

Fig. 8. Distribution of carbon (+) and hydrogen (o) (carbon and hydrogen correlation regions – □) in the sample of the Chelyabinsk meteorite obtained by SIMS method with depth. Axes *X*, *Y* correspond to the coordinates of the analyzed region (ion images) 250 × 250 µm, where 0 corresponds to 0 µm, while 1—250 µm. Axis *Z* corresponds to a depth of around 20 µm, where –0.1 corresponds to a depth of 10 µm.

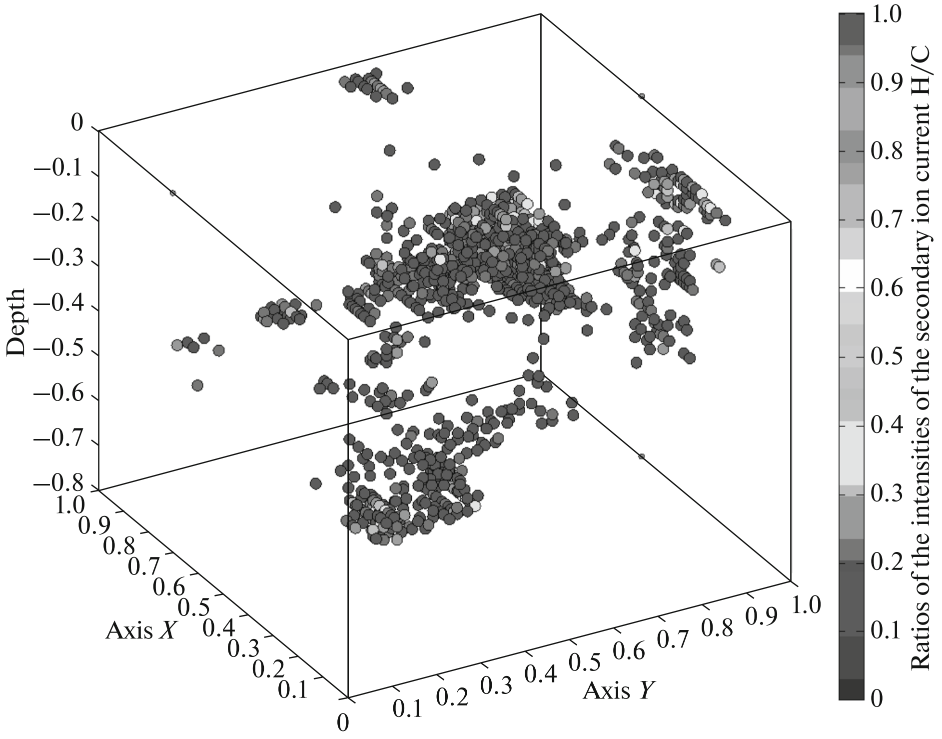

Fig. 9. Region of spatial correlation of ^{1}H and ^{12}C in sample of the Chelyabinsk meteorite and ratios of the intensities of the secondary ion currents ^{1}H/^{12}C. Axes *X*, *Y* correspond to the coordinates of analyzed region (ion image) 250 × 250 µm, where 0 corresponds to 0 µm, while 1, to 250 µm. Axis *Z* corresponds to analysis depth around 65 µm, where –0.1 corresponds to a depth of 10 µm. Scale corresponds to the value of ^{1}H/^{12}C concentration ratio.

dependence of the diffusion coefficients on the migration mechanisms (interstitial and vacancy) of carbon atoms in crystals: $D_{\text{th}} = 1 \times 10^{-15}$ cm^2/s (1100 K, 1 bar) and $D_{\text{rad}} = 1.6 \times 10^{-12}$ cm^2/s (300–370 K, deuteron irradiation dose at energy of 1.4 MeV – 2.8×10^{16} at/cm^{-2}). Since vacancies are generated both during growth of natural crystals at high pressure and during their natural α-radiation from decay of uranium and thorium isotopes that are contained in alkaline basalt, the high carbon concentrations in olivines of ~0.01–0.0001 wt % become possible.

Developed techniques and software package for SIMS study of carbon in silicates allowed simultaneous study of carbon and hydrogen distribution in the glass vein of the Chelyabinsk meteorite. The possible presence of hydrocarbons in studied silicate glass is suggested.

The considered methods of carbon study in silicates are characterized by high accuracy, sensitivity, and resolution and represent microprobe methods, which allow the determination of content, distribution, and diffusion of carbon in silicate samples. Data obtained by these methods are unique and cannot be obtained by other techniques.

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REFERENCES

P. Ardia, M. M. Hirschmann, A. C. Withers, and B. D. Stanley, "Solubility of CH_4 in a synthetic basaltic melt, with applications to atmosphere–magma ocean–core partitioning of volatiles and to the evolution of the Martian atmosphere," Geochim. Cosmochim. Acta. **114**, 52–71 (2013).

H. Behrens, S. Ohlhorst, F. Holtz, and M. Champenois, "CO_2 solubility in dacitic melts equilibrated with H_2OCO_2 fluids: implications for modeling the solubility of CO_2 in silicic melts," Geochim. Cosmochim Acta **68**, 4687–4703 (2004).

V. S. Bronskii, and S. N. Shilobreeva, "Method of estimation of the ionization factor of carbon on an example of analyses of silicate by secondary ion mass spectrometry (SIMS)," J. Anal. Chem. **71**, 1033–1040 (2016).

R. A. Brooker, S. C. Kohn, J. R. Holloway, P. F. McMillan, and M. R. Carroll, "Solubility, speciation and dissolution mechanisms for CO_2 in melts on the $NaAlO_2$–SiO_2 join," Geochim. Cosmochim Acta **63**, 3549–3565 (1999).

Carbon in Earth, Ed. by R. M. Hazen, A. P. Jones, and J. A. Baross, Rev. Mineral. Geochem. **75**, (2013).

H. Chi, R. Dasgupta, M. Duncan, and N. Shimizu "Magma ocean depth and oxygen fugacity in the early Earth — implications for biochemistry," Geochim. Cosmochim. Acta **129**, 447 (2014).

R. Dasgupta, H. Chi, N. Shimizu, A. S. Buono, and D. Walker, "Carbon solution and partitioning between metallic and silicate melts in a shallow magma ocean: implications for the origin and distribution of terrestrial carbon," Geochim. Cosmochim. Acta **102**, 191–212 (2013).

N. M. Drozdov, Yu. N. Drozdov, V. N. Polkovnikov, S. D. Starikov, and P. A. Yunin, "A new alternative to secondary CsM^+ ions for depth profiling of multilayer metal structures by secondary ion mass spectrometry," Techn. Phys. Lett. **1** (24), 46–50 (2013).

C. A. Farquhar, Dickinson, and M. Bruce, "Prophylactic potential of pentosan polysulphate in transmissible spongiform encephalopathies," Lancet **353**, 117 (1999).

F. Freund, "Hydrogen and carbon in solid solution in oxides and silicates," Phys. Chem. Miner. **15**, 1–18 (1987).

F. Freund, G. Debras, and G. Demortier, "Carbon content of high–purity alkaline earth oxide single crystals grown by arc fusion," Amer. Ceram. Soc. **61** (9–10), 429–434 (1978).

F. Freund, G. Debras, and G. Demortier, "Carbon content of magnesium oxide single crystals grown by the arc fusion method," J. Cryst. Growth, **38**, 277–280 (1977).

F. Freund, H. Kathrein, R. Knobel, G. Oberheuser, H. Wengeler, G. Demortier, and H. J. Heinen, "Depth profiling measurement of atomic carbon dissolved in oxides and silicates," Nucl. Instrum. Methods **197,** 27–36 (1982).

F. Freund, H. W. Kathrein, H. Knobel, R., and H. J. Heinen, "Carbon in solid solution in forsterite; a key to the untraceable nature of reduced carbon in terrestrial and cosmogenic rocks," Geochim. Cosmochim. Acta **44**, 1319–1334 (1980).

E. M. Galimov, "Isotopic variations of diamond and their relation with diamond formation, Geokhimiya, No. **8**, 1091–1117 (1984).

E. Hauri, "SIMS analysis of volatiles in silicate glasses, 2: isotopes and abundances in Hawaiian melt inclusions," Chem. Geol. **183**, 115–141 (2002).

P. Ihinger, R. L. Hervig, and P. F. McMillan, "Analytical methods for volatiles in glasses," Mineral. Soc. Am. Rev. Mineral. **30** (2), 67–121 (1994).

Kathrein, H. H. Gonska, and F. Freund, "Subsurface segregation and diffusion of carbon in magnesium oxide," Appl. Phys. A, **30** (1), 33–41 (1983).

H. Keppler, M. Wiedenbeck, and S. S. Shcheka "Carbon solubility in olivine and the mode of carbon storage in the Earth's mantle," Nature **424**, 414–416 (2003).

D. L. Kogan, A. M. Kazantsev, and L. E. Kuzmin, "BEAM EXPERT–integrated software for nuclear analysis," Nucl. Instrum. Methods **88**, 495 (1994).

L. E. Kuzmin, S. N. Shilobreeva, A. M. Kazantsev, and V. M. Minaev, "Radiation–Accelerated carbon diffusion in olivine crystals," Kratk. Soobshch. Fiz. FIAN, **9**, 12–17 (1998).

V. M. Kuznetsov, *Modern Methods of Study of the Solid Surface: Photoelectron Spectroscopy and Diffraction, STM Microscopy* (Inst. Tverd. Tela UrO AN RAN, 2010) [in Russian].

A. T. Lebedev, *Mass–Spectrometer for Analysis of Environmental Objects* (Moscow, Tekhnosera, 2013) [in Russian].

Y. Li, R. Dasgupta, and K. Tsuno, "The effects of sulfur, silicon, water, and oxygen fugacity on carbon solubility and partitioning in Fe–rich alloy and silicate melt systems at 3 GPa and 1600°C: implications for core–mantle differentiation and degassing of magma oceans and reduced planetary mantles," Earth Planet. Sci. Lett. **415**, 54–66 (2015).

E. A. Mathez, J. D. Black, J. Berry, M. Hollander, and C. Maggiore, "Carbon in olivine: results from nuclear reaction analysis, J. Geophys. Res. **92**, 3500 (1987).

V. M. Minaev, S. N. Shilobreeva, and A. A. Kadik, "Activation method for determination the carbon content of natural crystals," J. Radioanal. Nucl. Chem. **189**, 1, 147–155 (1995).

N. Mironov, M. Portnyagin, R. Botcharnikov, A. Gurenko, K. Hoernle, and F. Holtz, "Quantification of the CO_2 budget and H_2O–CO_2 systematics in subduction–zone magmas through the experimental hydration of melt inclusions in olivine at high H_2O pressure," Earth Planet. Sci. Lett. **425**, 1–11 (2015).

B. O. Mysen, "Magmatic silicate melts: relations between bulk composition, structure and properties," in *Magmatic Processes: Physicochemical Principles,* Ed. by B. O. Mysen, Geochem. Soc. Spec. Publ., No. 1, 375–400 (1987).

N. A. Nekrylov, Candidate's Dissertation in Geology and Mineralogy (Moscow, 2015).

H. Ni, and H. Keppler, "Carbon in silicate melts," Rev. Mineral. Geochem. **75**, 251–287 (2013).

G. Oberheuser, H. Ksthrein, G. Demotier, and F. Freund, "Carbon in olivine single crystals analyzed by the 12 C(d, p) 13 C method and by photoelectron spectroscopy," Nucl. Instrum. Methods. **47**, 1117–1129 (1983).

V. Pan, J. R. Holloway, and R. L. Hervig, "The pressure and temperature dependence of carbon dioxide solubility in tholeiitic basalt melts," Geochim. Cosmochim. Acta **55**, 1587–1595 (1991).

C. T. Pillinger, R. C. Greenwood, D. Johnson, M. J. Gibson, A. G. Tindle, A. B. Verchovsky, A. I. Buikin, I. A. Franchi, and M. M. Grady, "Light element geochemistry of the Chelyabinsk meteorite," Geochem. Int. **51** (7), 540–548 (2013).

P. Plechov, J. Blundy, N. Nekrylov, E. Melekhova, V. Shherbakov, and M. S. Tikhonova, "Petrology and volatile content of magmas erupted from Tolbachik volcano, Kamchatka, 2012–2013," J. Volcanol. Geotherm. Res. **307**, 182–189 (2015).

M. Portnyagin, K. Hoernle, P. Plechov, N. Mironov, and S. Khubunaya, "Constraints on mantle melting and composition and nature of slabcomponents in volcanic arcs from volatiles (H_2O, S, Cl, F) and trace elements in melt inclusions from the Kamchatka Arc," Earth Planet. Sci. Lett. **255**, 53–69 (2007).

G. I. Romanovskaya, "Analysis of selected samples of the Chelyabinsk Meteorite for organic compounds by synchronous spectrofluorimetry," Geochem. Int. **51** (7), 590–592 (2013).

A. Rosenthal, E. H. Hauri, and M. M. Hirschmann, "Experimental determination of C, F, and H partitioning between mantle minerals and carbonated basalt, CO_2/Ba and CO_2/Nb systematics of partial melting, and the CO_2 contents of basaltic source regions," Earth Planet. Sci. Lett. **412**. 77–87 (2015).

M. Senoner and W. E. S. Unger, "SIMS imaging of the nanoworld: applications in science and technology," J. Anal. At. Spectrom. **27**, 1050 (2012).

S. S. Shcheka, M. Wiedenbeck, D. Frost, and H. Keppler, "Carbon solubility in mantle minerals," Earth Planet. Sci. Lett. **245**, 30–42 (2006).

A. V. Shildt, A. A. Ariskin, and V. B. Polyakov, "Degree of polymerization of silicate melts as alternative to NBO/T parameter," in *Proceedings of All–Russian Annual Seminar on Experimental Mineralogy, Petrology, and Geochemistry VESEMBG-2015* (Moscow, 2015), p. 134 [in Russian].

S. N. Shilobreeva, A. A. Kadik, V. M. Minaev, S. S. Kazakov, and L. E. Kuzmin, "Carbon determination in deep–seated natural olivine crystals," Dokl. Akad. Nauk SSSR, **297** (2), 457–461 (1987).

S. N. Shilobreeva, and L. E. Kuz'min, "Modeling of carbon migration in meteorite olivines influenced by ionizing radiation," Solar Syst. Res. **37** (2), 144–149 (2003).

S. N. Shilobreeva, L. E. Kuz'min, and A. M. Kazantsev, "Nuclear reaction and SIMS studies of carbon diffusion in olivines," Nucl. Instrum. Methods Phys. Res. B. **161**, 797–800 (2000).

T. Stephan, "TOF–SIMS in cosmochemistry," Planet. Space Sci. **49**, 859–906 (2001).

Y. Thibault, and J. R. Holloway, "Solubility of CO_2 in a Ca–rich leucitite: effects of pressure, temperature, and oxygen fugacity," Contrib. Mineral. Petrol. **116**, 216–224 (1994).

T. N. Tingle and H. W. Green, "Carbon solubility in olivine–implications for upper mantle evolution," Geology **15**, 324–326 (1987).

T. N. Tingle and M. F. Hochella, "Formation of reduced carbonaceous matter in basalts and xenoliths: reaction of C–O–H gases on olivine crack surfaces," Geochim. Cosmochim. Acta **57**. 3245–3249 (1993).

T. N. Tingle, H. W. Green, and A. A. Finnerty, "Experiments and observations bearing on the solubility and diffusivity of carbon in olivine," J. Geophys. Res. **93**, 15289–15304 (1988).

I. S. Tsong, T. U. Knipping, C. M. Loxton, C. W. Magee, and G. W. Arnold, "Carbon on surfaces of magnesium and olivine single crystals. diffusion from the bulk or surface oxide contamination?" Phys. Chem Mineral. **12**, 261–270 (1985).

V. S. Vavilov, A. E. Kiv, and O. R. Neyazova, *Mechanisms of Defect Formation and Migration in Semiconductors* (Nauka, Moscow, 1981) [in Russian].

H. R. Wengeler, Knobel, H. Kathrein, and F. Freund, "Atomic carbon in magnesium oxide single crystals – depth profiling, temperature and time–dependent behavior," J. Phys Chem Solids **43**, 59–71 (1982).

H. W. Werner, "SIMS: from research to production control," Surf. Interface Anal. **35**, 859–879 (2003).

J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Matter.* (Pergamon, New York, 1985), pp. 93–129.

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