Variations of isotopic compositions and elemental ratios of C, N, He and Ar in fluid inclusions from MORB chilled glasses based on the results of stepwise crushing

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A great number of investigations has been devoted to study of fluid inclusions in mantle rocks and minerals. Most of them aimed to investigate the petrologic characteristics, such as P-T conditions of the inclusions formation and their chemical composition. The isotopic characteristics of the gases from the inclusions are studied in much less degree. However it is the isotopic research that could provide detailed information about fluid sources and fluid-rock interaction processes, the important factors of formation and alteration of geological objects.

In continuation of the work on the investigation of isotopic characteristics of the mantle rocks fluid phase using stepwise crushing initiated by us [Buikin et al., 2009], we studied carbon, argon and nitrogen isotope variations and their elemental ratios in fluid inclusions from chilled basalt glasses, sampled during 31st cruise of the scientific research ship "Professor Logachev" in the MAR rift valley at 20°–$22^{o}30$' North, representing typical N-MORB ($K_2O/TiO_2 = 0.08$–0.10). The sample preparation technique including gas extraction and separation can be found in [*Buikin et al.,* 2010].

Isotope compositions of carbon and oxygen from CO_2 were analyzed on Thermo Finnigan Delta Plus mass-spectrometer (GEOKHI RAS) using «microvolume» system with cold finger, which allows to make reliable measurements of small gas amounts (0.01–0.02 cc). Argon and nitrogen isotope compositions were analyzed on a high-sensitivity complex Finesse consisting of three mass-spectrometers at the Open University (Milton Keynes, UK). Concentrations of helium and carbon (in the form of CO_2) in the studied samples have been obtained on the same machine. It should be noted that the analyses of He, C, N and Ar have been performed simultaneously from the same sample. The obtained data are shown in figures 1–9 and table 1.

Results and discussion

The $\delta^{13}C$ values in the sample fractions vary from -2.8 to -9.5 ‰ vs. PDB, $\delta^{18}O$ – from +7.2 to +18.8 ‰ vs. SMOW. These results are within the range obtained earlier for fluid inclusions from MORB chilled glasses using one-step-extraction crushing [*Pineau et al.,* 2004, *Cartigny et al.,* 2001 etc]. As it has already been mentioned in [*Buikin et al.,* 2009], in general, the $\delta^{13}C$ values increase with increasing number of strokes (fig. 1) from values close to atmospheric CO_2 (-7.5 ‰) to those characteristic of mantle (about -3 ‰). Such a trend can reflect mixing between mantle and some contaminating carbon components similar to that known for mantle and atmospheric components for noble gases in these rocks [i.e., *Trieloff et al.*, 2000; *Buikin et al.*, 2005]. The contamination can occur both in the source of the basaltic melts and during their outflow and cooling in contact with sea water. If oceanic water is the contaminating source of the basalts, one must take into account all carbon forms present in the water: dissolved atmospheric CO_2, carbonates, organic matter. All those forms could be reduced to CO_2 at the temperatures of the basaltic magma. It is just addition of organic CO_2 that can be responsible for the light carbon component with $\delta^{13}C$ lower than -7.5‰. It's worth to note that the $\delta^{13}C$ values increase systematically with increasing number of strokes not for all the samples. In some cases carbon shows approximately the same low, non mantle $\delta^{13}C$ values for all steps, for example, as for the sample 323-1 II (Fig. 1). This sample was analyzed twice and showed a poor reproducibility of the results, that can be related to the inhomogeneous distribution of inclusions within the sample. The other sample (133-4), which was also studied repeatedly, has shown good reproducibility and has a clear trend from "organogenic" to mantle $\delta^{13}C$ values depending on the number of strokes.

There is also a trend between $\delta^{13}C$ values and amounts of gas in the fraction: the higher the amount the lighter the carbon (Fig. 2a). This trend is clearer visible in Fig. 2b, where the data for the total gas release are present. Indirectly, this can be regarded as a confirmation of the above assumption about the contamination of the samples by the component with a light carbon isotopic composition. We cannot also exclude that this trend can be a result of carbon isotope fractionation in the melt-fluid system.
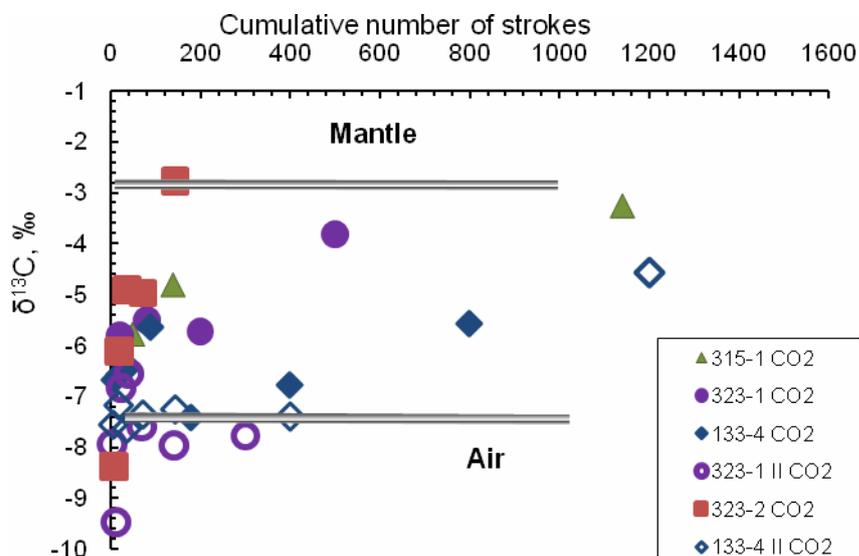
Fig. 1. Variations of carbon isotope composition depending on number of strokes.
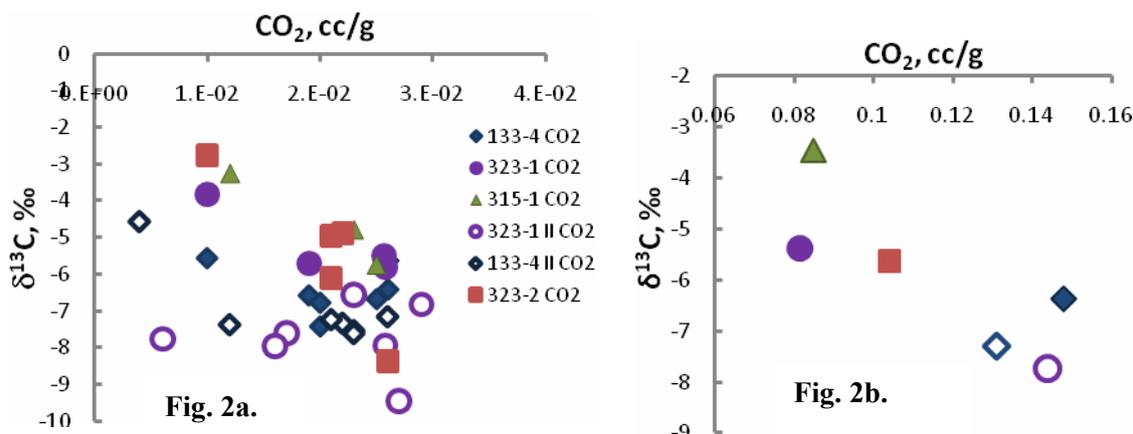
Fig. 2. Variations of carbon isotope composition depending on the amount of CO_2 in the sample fractions (a) and for the total gas release (b).

The data for argon and nitrogen isotopic compositions and concentrations of carbon, nitrogen, argon and helium in fluid inclusions from the samples described above are shown in table 1. The concentrations of all gases, except for nitrogen, in the samples vary by a factor of 2; for nitrogen it is by a factor of 5. The gas concentrations released in the crushing steps are correlated with each other (Figs 3, 4), which suggests they are located in the same inclusions and have a common source.

The argon isotopic composition indicates a significant amount of the atmospheric component in some samples to be present (the largest in the sample 31L-133-4, where $(^{40}Ar/^{36}Ar)_{total} = 1000$, and $\delta^{13}C$ is also close to the atmospheric value for $CO_2 \sim -7.5‰$). Also, the $\delta^{13}C$ value in the samples increases with increasing the $^{40}Ar/^{36}Ar$ ratio (i.e. with increasing the fraction of the mantle component). The only exception is the sample 31L-323-1, in which at $\delta^{13}C = -5.4$ ‰ the $^{40}Ar/^{36}Ar$ ratio reaches 24600 – a typical mantle value for the MORB chilled glasses. Probably, a carbon and nitrogen isotope fractionation in the magmatic process and during fluid-melt interaction has had a contribution to the isotope variations of the elements. As can be seen from fig. 5, having a typical mantle value for the $^{40}Ar/^{36}Ar$ ratio this sample has $\delta^{15}N$ slightly shifted to a light nitrogen value (-7.5 ‰, instead of -4÷-5‰ accepted for the

upper mantle) that can be regarded as an independent indication of the isotope fractionation. However it cannot be excluded that an ancient organic rich matter could have been introduced into the mantle source of the basalts, where it was homogeneously mixed with the melt, that resulted in such a low $\delta^{15}N$ value. Notably, that in this sample (323-1) the nitrogen isotopic composition in the crushing steps is rather homogenous regardless of the argon isotope composition variations (excluding the very last step, in which a proper blank correction was difficult to make).

Table 1. Elemental and isotope compositions of gases in fluid inclusions from N-MORB chilled glasses (Mid Atlantic Ridge, 20°-22°30'N).

Sample/cumul. number of strokes	^{4}He, 10^{-8} ccm/g	C, ng	N_2, ng	^{40}Ar, 10^{-8} ccm/g	δ^{15}N, ‰ Air	^{40}Ar/^{36}Ar	^{4}He/^{40}Ar*
31L 133-4 (1.02534 g)							
6	585	48504	50	35	-4.6	606	32
24	285	41993	25	18	-4.2	1798	19
70	215	23253	18	11	-4.2	1951	24
150	69	3246	4	31	1.6	1151	3
1150	68	137	13	32	5.9	533	5
Total	**1222**	**117133**	**111**	**127**	**-3.0**	**1000**	**14**
31L 323-2 (0.82764 g)							
12	834	45564	362	178	-6.3	641	9
40	260	15199	90	40	-7.5	6494	7
160	146	-	17	9	-2.7	1243	22
1160	196	2	9	4	-0.8	337	372
Total	**1435**	**60765**	**478**	**231**	**-6.3**	**1672**	**8**
31L 315-1 (1.00379 g)							
4	279	38213	98	55	-5.7	10696	5
14	229	25944	63	35	-5.2	9579	7
50	189	15184	32	24	-4.0	3213	9
200	144	111	10	6	-5.3	2640	25
1200	174	-	7	38	0.1	384	20
Total	**1016**	**79452**	**210**	**159**	**-5.1**	**6510**	**7**
31L 323-1 (1.05235 g)							
2	316	28406	149.4	53	-7.2	15567	6
8	267	24791	129.5	46	-7.2	24471	6
24	266	22766	122.9	43	-7.1	27961	6
120	226	8419	50.9	29	-6.8	25611	8
1120	215	9	73.0	35	-9.7	313	110
Total	**1290**	**84391**	**526**	**206**	**-7.5**	**24593**	**6**
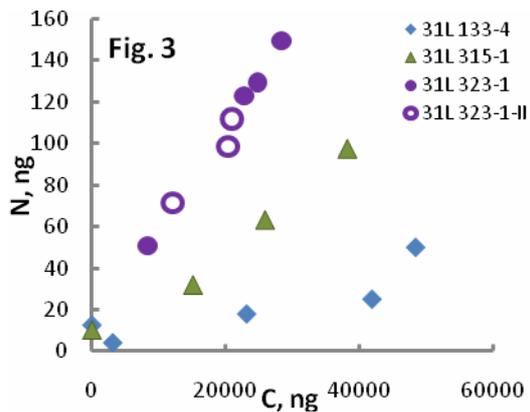
Fig. 3. Carbon and nitrogen amount co-variations in the sample fractions
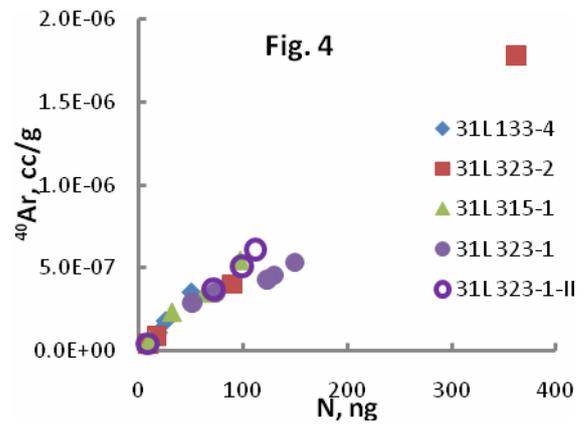
Fig. 4. Argon and nitrogen amount co-variations in the sample fractions
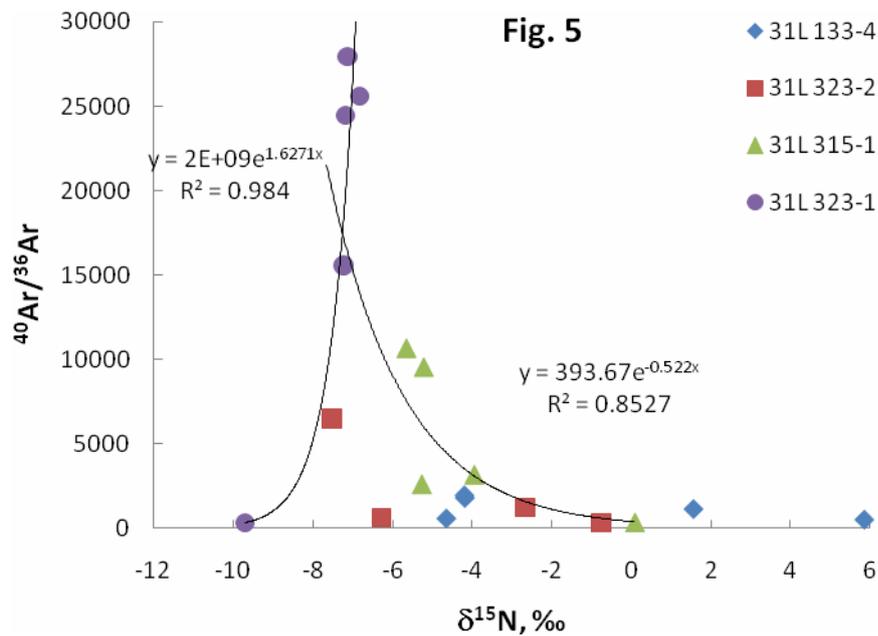
Fig. 5. Variations of $^{40}Ar/^{36}Ar$ ratio in the sample fractions depending on the nitrogen isotopic composition
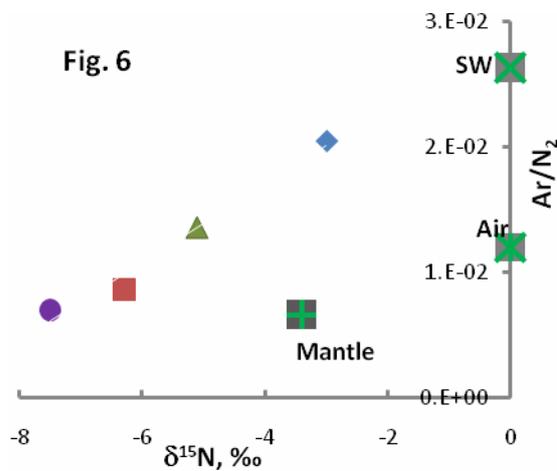
Fig. 6. Correlation of Ar/N_2 ratios and $\delta^{15}N$ values in the total gas extractions
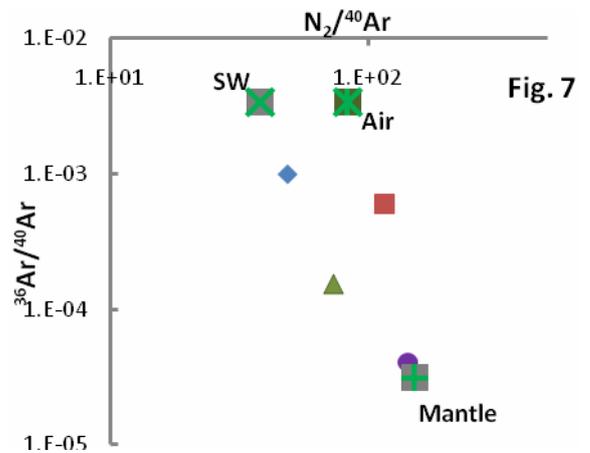
Fig. 7. $^{40}Ar/^{36}Ar$ vs. N2/Ar diagram for the total gas extractions showing mixing between sea water (or air) and mantle end members

Nitrogen isotopic compositions in the crushing steps vary significantly – from -10‰ to +6‰, but for the total extraction the values are between -3 and -7.5 ‰. The heavy nitrogen is released in the last extraction steps where the amounts of N are very low. We cannot definitely identify whether these positive values are artifacts (related to a contamination of the samples' surface with organics), or they do associated with real sources and/or processes that have existed/taken place during inclusion entrapment. Such a heavy nitrogen (positive $\delta^{15}N$) in MORB chilled glasses has been reported before [e.g. *Marty and Zimmermann*, 1999], for which the oceanic sediments are considered as a possible source.

In the figures 6 and 7 the total extraction data are shown in coordinates Ar/N_2 vs. $\delta^{15}N$ and $^{36}Ar/^{40}Ar$ vs. $N_2/^{40}Ar$; for reference the mantle, atmosphere and sea water compositions are also shown. The correlation between the $\delta^{15}N$ and Ar/N_2 ratios in the samples (fig. 6) reflects a mixing process. For the sample 133-4, the most severely contaminated by the atmospheric component, sea water input is the most likely to be considered. The other end-member of the mixture has the Ar/N_2 ratio corresponding to that estimated for the N-MORB [*Marty and Zimmermann,* 1999], but has essentially lighter nitrogen isotopic composition ($\delta^{15}N$ is about -7.5‰) than that accepted for the upper mantle. The data in fig. 7 also point to the mixing between sea water and N-MORB mantle for three of 4 samples. For the fourth sample (323-2) the mixing between mantle and pure atmospheric component can be assumed.

Fig. 8. Correlations between He/N_2 and C/N_2 ratios in the total gas extractions	**Fig. 9.** Variations of $C/^{40}Ar$ ratios in the total gas extractions depending on C/N_2 ratios in the samples
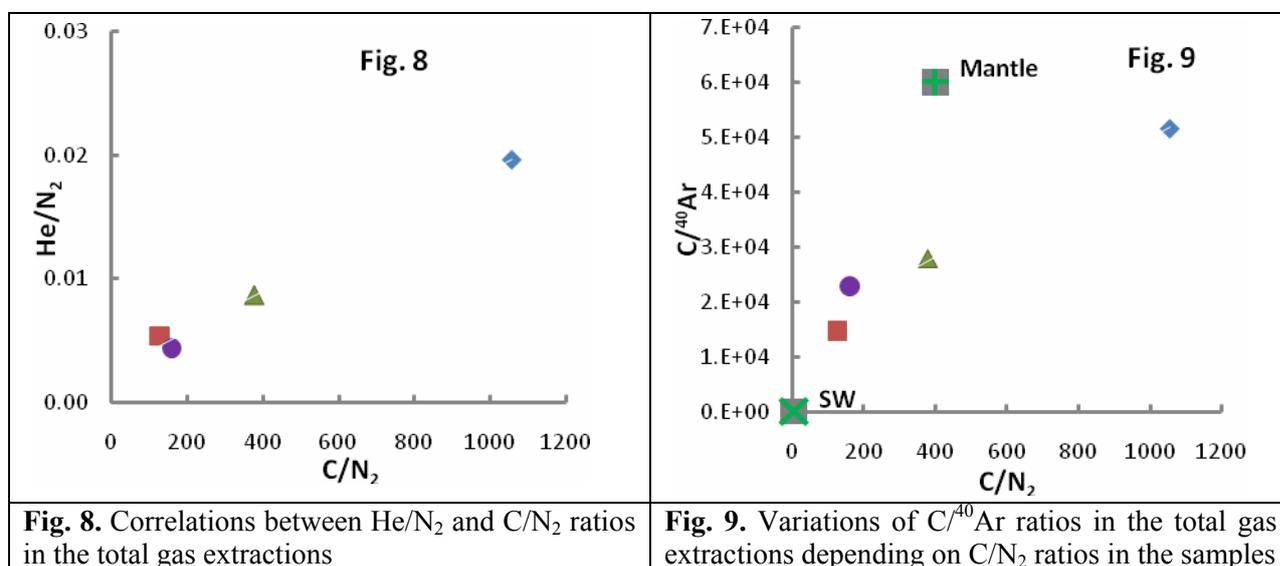
The total extraction values for $^4He/^{40}Ar^*$ ratios (where $^{40}Ar^*$ is the excess or trapped radiogenic argon, calculated assuming that all ^{36}Ar is atmospheric) are 6-14 (table 1), which is several times higher than the mantle production ratio (~1.5). It points to a relatively small elemental fractionation during vesicles formation (due to the different solubility of He and Ar in basaltic melt), in contrast to the most published data for MORB glasses, which show a significantly higher fractionation (the $^4He/^{40}Ar^*$ ratios are from several tens to hundreds). The data on the plot He/N_2 vs. C/N_2 (fig. 8), where the helium and carbon to nitrogen ratios for the total extraction are positively correlated, also point to the elemental fractionation associated with the solubility effect, since He and CO_2 have essentially the same solubility in basaltic melts but significantly higher than that for nitrogen. The data in fig. 9 can be explained the same way, however some authors consider this as an indication of existence of a carbon rich reservoir in the mantle with high (>1000) C/N_2 ratios.

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