ACTIVATION METHOD FOR DETERMINING THE CARBON CONTENT OF NATURAL CRYSTALS

V. M. MINAEV,* S. N. SHILOBREEVA,***+ A. A. KADIK**

*Moscow Engineering Physics Institute, Kashirskoye shosse, 31, Moscow (Russia)
**Vernadsky Institute of Geochemistry and Analytical Chemistry
of the Russian Academy of Sciences, Kosygin st. 19, Moscow 117975, (Russia)

A method for determination of carbon content in natural silicate crystals has been elaborated using the $^{12}C(d,n)^{13}N$ reaction. Etching of crystal surfaces by acid solutions is proposed to remove the pollutant surface layers. Carbon contents varying from 8 to 100 ppm were measured for olivine, orthopyroxene and garnet crystals.

The accurate determination of carbon in geological materials (crystals, silicate glasses) has long been a problem because of complicated chemical and phase composition of these materials as well as the small size of phases. Until recently standard carbon analysis techniques such as gas chromatography,[1] mass spectrometry,[2,3] gas manometry,[4] infrared spectroscopy,[5,6] Raman spectroscopy,[7,8] Auger spectroscopy,[9] and electron microprobe[10–12] have been applied to natural and synthetic C-bearing samples. Some of these analytical techniques are destructive and require relatively large geological samples. In addition, the low atomic number of carbon and its ubiquity as a surface contaminant make it a difficult element to analyze at trace concentrations (< 1 wt.% C) by some of these techniques. Besides, not all C-bearing species are detectable by these methods, for example, graphite is not detectable by infrared spectroscopy.

In the last ten years the $^{12}C(d,p)^{13}C$ nuclear reaction has been applied to the measurement of carbon contents of natural and synthetic silicate glasses and crystals.[13,14] This beam technique is nondestructive and allows to avoid some of the problems connected with analysis of low-level carbon contents by the techniques mentioned above. The beam surface ranges from 5 to 50 μm^2 and the analyzed depth is up to 10 μm, depending on sample composition.[15] However, the problem of carbon surface contaminant determination remains during the analysis of such sample depths.

In this paper we describe the employment of activation analysis using the $^{12}C(d,n)^{13}N$ nuclear reaction for determining the carbon content in natural crystals of

+To whom all correspondence should be sent.

deep origin. This technique has been used previously for the analysis of carbon in metals[17] and olivine crystals.[18] Detection limits and accuracy of activation analysis depend on surface effects arising during preparation and irradiation of the sample. A surface contamination level and thickness of pollutant layer depend on the way the sample is prepared as well as the physico-chemical characteristics of the samples. When irradiating samples by charged particles, the vapor of vacuum oil can condense on the activated surface and result in an increased carbon content on the sample surface. The radiation and thermal influence of a deuteron beam results in the diffusion of ^{13}N nuclei and carbon into the sample volume. Moreover, during the nuclear interaction the deuteron passes a part of its kinetic energy to the ^{13}N nuclei and that also causes a displacement of a few μm inside the sample.

In the processes of activation of different metals, alloys and monocrystals of semiconductors, the displacement of atoms according to the mechanism of radiation-induced diffusion does not usually exceed the maximum range of recoil nuclei, therefore, it does not influence the choice of the thickness of the removed layer.[17,19,20] However, when analyzing the carbon in minerals of deep origin, the structural defects both existing in natural monocrystals and forming in the thin surface layer during the preparation of the sample for irradiation can affect the thickness of the layer contaminated by carbon.

Two ways in which surface contamination influences the quantitative results of carbon measurements in olivines using the ^{12}C(d,n)^{13}N nuclear reaction were considered in Reference 18. One way was polishing with a finely dispersed powder of chromic oxide to remove the surface layers. In another case the ^{12}C(d,p)^{13}C nuclear reaction was used in order to take into account the surface pollutant. The thickness of the layer removed by polishing of samples[18] was 1–2 mg/cm^2 and this method let us reach a detection limit of the order of 10^{-3}%. However, the defects of sample surface are not completely removed after the polishing and may be a source of errors when determining the carbon content of natural crystals of deep origin.

Here we demonstrate a new way of removing the surface layer by etching with a solution of mineral acids as well as the use of activation analysis for the measurement of carbon in natural crystals of olivines, pyroxenes and garnets.

Experimental

Materials: The samples studied in the present work were very pure olivine, pyroxene and garnet crystals from spinel and spinel-garnet xenolites of alkaline basalts, eruptive center of Shavaryn Tsaram, Mongolia. Most of the olivine and pyroxene crystals were as large as 3 mm in maximum dimension, while the garnet crystals were as large as 1 mm in maxinun dimension. The composition of crystals studied are given in Table 1.

Table 1
Mineral phase compositions, %

Component	Olivines				Orthopyroxenes			Garnet
	3–1	314–56	4334–11	8505/2	3–2	79/1	79/4	8531/10
SiO_2	41.01	41.61	41.03	41.96	55.20	55.79	56.13	39.26
Al_2O_3	–	–	–		3.97	4.93	5.20	22.48
TiO_2	–	–	–	–	0.13	0.16	0.14	–
FeO	10.93	10.63	10.72	9.73	6.54	7.22	6.89	16.13
CaO	–	0.08	–	0.05	0.46	0.73	0.84	5.34
MgO	48.79	49.10	48.11	49.01	32.57	31.62	30.88	16.61
Na_2O	–	–	–	–	0.05	0.14	0.16	–
MnO	0.13	0.13	0.13	0.12	0.15	0.13	0.13	0.44
Cr_2O_3	–	–	–	–	0.25	0.29	0.33	0.01
NiO	0.31	0.39	0.51	0.36	0.14	0.07	0.05	–
	101.17	101.94	100.5	101.23	99.46	101.08	100.75	100.27

Table 2
Characteristics of nuclear reactions and radionuclides occurring
upon irradiation of silicates[22]

Element	Nuclear reaction	Half-life of radionuclide	Gamma-energy, keV
Carbon	$^{12}C(d, n)^{13}N$	9.97 m	511
Boron	$^{10}B(d, n)^{11}C$	20.4 m	511
Oxygen	$^{16}O(d, n)^{18}F$	109.8 m	511
Sodium	$^{23}Na(d, p)^{24}Na$	15.0 h	1368
			2754
Magnesium	$^{26}Mg(d, p)^{27}Mg$	9.46 m	170
			843
			1013
Aluminium	$^{27}Al(d, p)^{28}Al$	2.24 m	1779
Nitrogen	$^{14}N(d, n)^{15}O$	2.05 m	511
Silicon	$^{30}Si(d, p)^{31}Si$	2.62 h	–

Sample preparation and irradiation: First all the crystals were mounted in Wood's alloy and ground. The prepared surfaces of the crystals were irradiated by a 1.7 MeV deuteron beam for 10 minutes in a cyclotron. The current density was no more than 5 $\mu A/cm^2$ to prevent radiation and thermal effects of the deuteron beam on surface layers of the samples. After the irradiation, polishing for 20 seconds with a finely

dispersed powder of chromium oxide was used to remove the surface layer and then the crystal was melted from the metallic alloy. Etching with mineral acids (25 ml H_2O + + 25 ml H_2SO_4 + 25 ml HNO_3 + 5 ml HF) at 50–90 °C for 6–15 minutes was used to remove the surface layers. When irradiating silicate in the matrix there are numerous nuclear reactions which result in the formation of eight main radionuclides (Table 2). Short-lived radionuclides of ^{15}O and ^{28}Al decay quickly and their interference is negligible in determining the carbon content of natural crystals. The long-lived radionuclides of ^{24}Na and ^{31}Si are discriminated from ^{13}N by both the decay type and half-life so they do not interfere in the determination of carbon. Radionuclide ^{27}Mg formed from magnesium by the reaction $^{26}Mg(d,p)^{27}Mg$ has a half-life close that to of ^{13}N but the energy of β-particles and γ-rays of ^{27}Mg is higher than the energy of particles and γ-rays of ^{13}N. The activity of ^{27}Mg is a thousand times higher than the activity of ^{13}N radionuclide. However, the irradiation of ^{27}Mg radionuclide was not recorded as the scheme of γ–γ coincidence with the threshold of 0.3 MeV, which is higher than the energy of one of the coincidence γ-rays, of ^{27}Mg (170 keV) but it is lower than the energy of ^{13}N was used.

The thickness of the removed layer was controlled on decreasing the activity of ^{27}Mg. Radionuclide ^{27}Mg has sufficient activity, therefore it was used as internal monitor for the irradiation dose. The activity of ^{27}Mg was recorded by γ-scintillation spectrometery using a NaI(Tl) detector and was used to pinpoint the thickness of the removed layer. As the cross section of the nuclear reaction $^{27}Mg(d,p)^{26}Mg$ is unknown, the curve of relative output of ^{27}Mg radionuclide with subsequent removal of layers was measured during the activation of pure metallic magnesium. The layers of activated magnesium were removed by etching with nitric acid in ethanol (4%). Thickness of the removed layer was measured by the weight method with an accuracy of 0.01 mg/cm². The average curve of relative output of ^{27}Mg radionuclide (Fig. 1, curve 2) was a result of 3 activation processes.

The carbon concentration was measured by a relative method comparing the activities of ^{13}N radionuclide in the crystals and a steel sample with known carbon content (0.24%), from the surface of which (with regard to the difference in decelerating capacities of these materials) the layer similar in deuteron energy losses had been removed. Positron activity on the ^{13}N radionuclide was recorded by counting coincidences of annihilation of γ-rays in two crystals of 70 mm × 70 mm NaI(Tl). The spectrum of γ–γ coincidence contains only one peak of 511 keV, the intensity of which depends on the activity of four positron emitters (^{15}O, ^{13}N, ^{11}C and ^{18}F). The curve of annihilation peak intensity versus waiting time for an olivine sample with a carbon content of 20 ppm is presented in Fig. 2. The determination of initial activities of four radionuclides was carried out by the weighted least-squares method. It can be seen from the data that the activity of ^{15}O radionuclide becomes negligibly small after a waiting
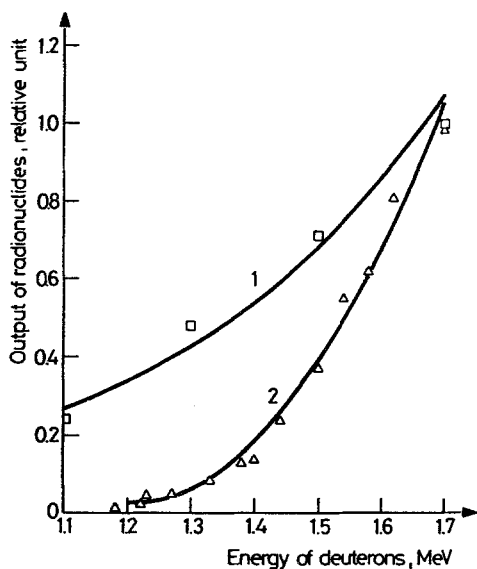
Fig. 1. Dependence of ^{13}N (curve 1) and ^{27}Mg (curve 2) output on the deutron energy during the reactions $^{12}C(d,n)^{13}N$ and $^{26}Mg(d,p)^{27}Mg$, respectively

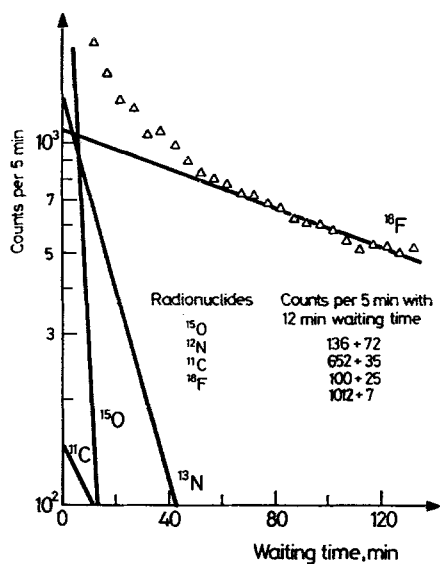| Radionuclides	Counts per 5 min with 12 min waiting time
^{15}O	
^{13}N	136 + 72
^{11}C	652 + 35
^{18}F	100 + 25
	1012 + 7

Fig. 2. Dependence of count rate of annihilation γ-rays on the waiting time. Points indicate the β^+-decay curve of Olivine 3–1

151

time of 20 minutes. Long-lived ^{18}F interferes with the determination of carbon but its activity could be measured with high accuracy. The accuracy of determination of ^{13}N and ^{11}C radionuclides is lower due to a similarity of half-life periods. Therefore the presence of boron in the sample exerts an appreciable influence on the possibility of carbon determination.

The carbon concentration C_x in the samples studied can be calculated from:

$$C_x = C_s \cdot A_x/A_s \cdot A_m/A_{mx} \cdot R_s/R_m \cdot W_m/K$$

where C_s is the carbon concentration in steel sample, A_x and A_s are the activities of ^{13}N radionuclide of the crystal and steel, respectively, A_m and A_{mx} are ^{27}Mg activities of pure magnesium and sample, respectively, R_s and R_m represent the deuteron ranges in steel and pure magnesium, W_m is the content of magnesium in the crystal, K is a coefficient taking into account the decrease of ^{13}N activity in the sample at the removed layer. This coefficient was determined from Fig. 1 (curve 1), illustrating the calculated dependence of output of ^{13}N radionuclide on the thickness of removed layer in a homogeneous sample. This curve was obtained with the use of data.[21]

If the carbon surface contaminant was removed entirely, the limit of carbon detection was 2 ppm for large crystals with an irradiated surface of 5 mm^2. However, the detection limit depends on sample size and thickness of the removed layer as well as on the boron content in the sample. If the sample size does not exceed 0.5 mm^2, the detection limit will be of the order of 10^{-3}% in the best case. For reliability, the thickness of removed layer should be 2–3 times higher than the thickness of carbon contaminant layer. However, in this case the activity of the measured radionuclide decreases abruptly both on account of the decline of nuclear reaction output and radionuclide decay during the etching of the sample. The rate of etching depends strongly both on the crystal compositions and the structure of surface layer. The influence of boron on the limit of carbon detection becomes important, provided the boron content is compared with the carbon content.

Results and discussion

Results of the analysis for carbon in mass units are given in Table 3. The error is 15–20 rel.%. It is clear that natural crystals of deep origin contain low concentrations of carbon and the activation analysis method described allows determination of these concentrations.

Influence of the thickness of removed layer on the results of analysis is presented in Table 3. The thickness of carbon contaminant layer for olivines is usually not larger than 2 μm because the carbon determinations do not change with increased thickness of

Table 3
Carbon contents in natural samples

Samples	Time of etching, min	Temperature of solution, °C	Thickness of re-moved layer, μm	Carbon content, %
Olivines				
3-1	3	60	5.4	0.002
	3	50	3.2	0.0008
314-56	3	90	5.8	0.007
	3	90	1.6	0.006
	3	90	2.3	0.008
4334-11	3	90	2.3	0.004
	3	90	2.9	0.009
8505/2	3	65	5.8	0.014
	3	90	3.0	0.003
	3	90	3.8	0.002
Orthopyroxenes				
3-2	9	90	1.5	0.015
	9	90	1.2	0.033
	9	90	1.9	0.011
	9	90	1.7	0.016
	14	90	1.5	0.017
79/1	9	90	1.2	0.009
	15	90	1.5	0.006
	14	90	1.4	0.006
79/4	9	60	1.0	0.046
	8	70	1.0	0.100
	9	90	1.9	0.087
	14	90	0.9	0.039
Carnets				
8531/10	9	90	1.6	0.010
	9	90	1.2	0.020
	9	90	1.4	0.005
	9	90	1.2	0.004

the removed layer for most olivine samples. As olivine crystals were etched very quickly, it became possible to remove a layer of more than 2 μm and to increase the reliability of analysis. The thickness of removed layers for orthopyroxenes and one garnet are significantly lower and are not greater than 2 μm. The rate of etching for orthopyroxenes is very low and sometimes it is difficult to remove the carbon contaminant layer during this time. Therefore, we are not sure that all contaminant layers of orthopyroxenes are removed during the analysis. There is no direct correlation between the thickness of removed layer and the carbon content in the crystals studied. For some samples the carbon content in the crystal is higher for thicker removed layers.

Moreover, inhomogeneous etching was observed. The upper layers are etched 2–3 times more rapidly due to the large amount of defects in these layers.

The results (Table 3) show the inhomogeneous distribution of carbon in olivine, pyroxene and garnet crystals. This may be attributed to the presence of small inclusions containing carbon. On the average, the carbon content in orthopyroxenes is higher than in olivines and garnets. But the contents of carbon in olivine crystals are 3–5 times lower than the content in olivines reported previously.[18] Apparently, the difference is connected with the more reliable removal of a contaminant layer with chemical etching in comparison with mechanical polishing. It is clear that during the etching of silicates with a mixture of acids, the accelerated disetching of defect zones as well as boundaries of grains and cracks occurs. Carbon penetrates these places during radiation-induced diffusion, and chemical etching helps to remove it more completely. It should be worthwhile to point out that the detection limit of carbon according to the present method is 5 times lower than according to Reference 18.

Application of activation analysis does not permit, with sufficient definiteness, the determination of the species of carbon in crystals of deep origin. To address this question, it is necessary to carry out additional research.

*

References

1. O. F. MIRONOVA, Zh. Analyt. Khim., 28 (1973) 1561.
2. F. PINEAU, M. JAVOY, Earth Planet Sci. Lett., 62 (1983) 239.
3. J. R. DELANEY, D. W. MUENOW, D. G. GRAHAM, Geochim. Cosmochim. Acta, 42 (1978) 581.
4. D. M. HARRIS, Geochim. Cosmochim. Acta, 45 (1981).
5. T. N. TINGLE, R. D. AINES, Contrib. Mineral. Petrol. 100 (1988) 222.
6. R. A. FOGEL, M. J. RUTHERFORD, Amer. Mineral., 75 (1990) 1311.
7. C. S. RAI, S. K. SHARMA, D. W. MUENOW, D. W. MATSON, C. D. BYERS, Geochim. Cosmochim. Acta, 47 (1983) 953.
8. B. O. MYSEN, D. VIRGO, Americ. Mineral., 65 (1980) 885.
9. I. S. T. TSONG, U. KNIPPING, C. M. LOXTON, Phys. Chem. Minerals, 12 (1985) 261.
10. E. A. MATHEZ, J. R. DELANEY, Earth Planet Sci. Lett., 56 (1984) 217.
11. G. E. BLANFORD, K. L. THOMAS, D. S. McKAY, Meteoritics, 23 (1988) 113.
12. MAKJANIC, J. L. R. TOURET, R. D. VIS, H. VERHEUL, Meteoritics, 24 (1989) 49.
13. G. J. FINE, E. M. STOLPER, Earth Planet Sci. Lett., 76 (1985/86) 105.
14. E. WILMART, M. MOSBAH, C. R. Acad. Sci. Paris, 308 Serie II (1989) 1243.
15. G. OBERHEUSER, H. KATHREIN, G. DeMORTIER, H. GOUSKA, F. FREUND, Geochim. Cosmochim. Acta, 47 (1983) 1117.

16. E. A. MATHEZ, J. D. BLACIC, J. BEERY, C. MAGGIORE, M. HOLLANDER, Geophys, Res. Lett., 11 (1984) 947.

17. Ju. F. BABIKOVA, A. N. IVANOV, V. M. MINAEV, G. G. RJABOVA, At. Energiya, 65 (1988) 202.

18. S. N. SHILOBREEVA, A. A. KADIK, V. M. MINAEV, S. KAZAKOV, L. Y. KUZ'MIN, Dokl. Akad. Nauk SSSR, 297 (1987) 457.

19. G. BLONDIAUX, A. GIOVAGNOLI, K. ISHII, C. KOEMMEREZ, M. VALLENDON, J. L. DEBRUN, J. Radional. Chem., 55 (1980) 407.

20. G. BLONDIAUX, C. S. SASTRY, M. VALLANDON, J. L. DEBRUN, J. Radional. Chem., 56 (1980) 163.

21. Ya. BARIT, L. E. KUZMIN, A. M. KAZANTSEV, J. Radioanal. Nuclear Chem., 97 (1986) 97.

22. P. P. DIMITRIEV, Output of Radionuclides in Reactions with Protons, Deuterons, Alpha Particles and Helium-3, Energoatomizdat, Moscow, 1986 (in Russian).