

# Effect of Oxygen Fugacity on the Etching Rate of Diamond Crystals in Silicate Melt

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**Abstract**—Experimental data on the etching of diamond crystals in basaltic melt at 1130°C with variable oxygen fugacity in the environment are considered. The oxygen fugacity was set with the HM and NNO buffers. The study was carried out on a 0.6–0.8 mm fraction (powder) of natural diamond crystals. It has been established that, at the same temperature, the rate of diamond etching (oxidation) in silicate melt depends on the oxygen fugacity in the environment. The etching rate decreases with decline in the oxygen fugacity from the case where the melt comes into contact with atmospheric air to the conditions controlled by the HM and NNO buffers. Under the conditions of the HM and NNO buffers, oxidation was accompanied by surface graphitization of diamond crystals.

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## INTRODUCTION

The rate of mineral dissolution varies depending on the solvent concentration. This is also valid with respect to diamond. For instance, the oxidation rate of diamond crystals depends on oxygen fugacity, as has been demonstrated by etching of diamonds in the gas phase (Sonin et al., 2000a). Oxygen is the strongest diamond oxidizer among those available under natural conditions. The rate of diamond oxidation with oxygen is much higher than the rate of its oxidation with water vapor or carbon dioxide (Rudenko et al., 1979).

This paper presents the results of continuing study in this field, with silicate melt being involved.

## EXPERIMENTAL

The experiments were carried out with a device created on the basis of a SUOL electric pipe furnace equipped with a gas feeder. The research methods were described by Sonin et al. (2000a). Since the etching of diamonds was performed under reducing conditions, molybdenum beakers were used (Sonin et al., 1997).

The oxygen fugacity was controlled by buffers (Gramenitsky and Kotel'nikov, 1984; Huebner, 1971). For this purpose, a molybdenum beaker filled with silicate powder and diamonds was covered with a loose lid, placed into an alundum crucible, and filled up from above with a buffer mixture: hematite–magnetite (HM) or nickel–bunsenite (NNO). The alundum crucible was covered with a close-fitting alundum lid. This assembly

did not allow the powdered buffer mixture to mix with the sample under analysis but enabled gas exchange with the mixture. During a run, the device was blown through with an inert gas. The initial volumetric proportions of components in the buffer mixtures were hematite : magnetite = 4 : 1 in the HM buffer and nickel : bunsenite = 1 : 1 in the NNO buffer.

It is commonly assumed that the buffer technique works and the oxygen fugacity is maintained at a certain level as long as the components of a buffer mixture are retained. The retention of components in buffer mixtures after runs was controlled by XRD analysis on a DRON-3.0 diffractometer (Tables 1, 2).

In this study, we used a 0.6–0.8 mm powder fraction of natural diamonds  $7 \pm 0.1$  mg in weight ( $35 \pm 1$  grains). A glass of natural alkaline basalt with a rather low melting temperature was used as the silicate component of samples. The basalt composition was as follows (wt %): 47.0 SiO<sub>2</sub>, 2.20 TiO<sub>2</sub>, 16.30 Al<sub>2</sub>O<sub>3</sub>, 3.89 Fe<sub>2</sub>O<sub>3</sub>, 8.12 FeO, 0.15 MnO, 6.40 CaO, 4.55 MgO, 5.69 Na<sub>2</sub>O, 5.0 K<sub>2</sub>O, 0.54 LOI, and 99.82 in total. The charge of basalt was  $200 \pm 10$  mg in weight.

The runs were performed at a temperature of 1130°C. The temperature was measured with a Pt/(Pt–Rh<sub>10</sub>) thermocouple with an accuracy of  $\pm 3^\circ\text{C}$ . The analyzed samples were placed into the working zone of the device as soon as the latter had reached a given mode of operation. The samples were cooled by quenching.

After the runs, the silicate glass was successively dissolved in the acids HF and HCl. Further, diamond grains were washed in distilled water, dried, and weighed with an accuracy of  $\pm 0.01$  mg. In the series of

**Table 1.** Variations of the HM buffer ( $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ ) composition depending on run duration at 1130°C, as indicated by X-ray diffraction data

Phase	HM (30 min)		HM (60 min)	
	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>
H	24	3.69	12	3.67
M	31	2.96	36	2.96
H	64	2.69	29	2.69
M (H)	100	2.53	100	2.53
M	9	2.42	5	2.42
H	15	2.21	6	2.20
M	18	2.10	18	2.09
H	20	1.84	9	1.84
M	9	1.71	9	1.71
H	26	1.69	12	1.69
M	32	1.62	26	1.61
H	48	1.50	35	1.48
M (H)	13	1.45	7	1.45
H	10	1.31	–	–

**Table 2.** Variations of the NNO buffer composition depending on run duration at 1130°C, as indicated by X-ray diffraction data

Phase	NNO (30 min)		NNO (60 min)	
	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>
NO	45	2.41	31	2.41
NO	77	2.10	56	2.09
N	100	2.03	100	2.03
N	38	1.76	37	1.76
NO	29	1.48	18	1.48
NO	–	–	8	1.26
N	–	–	15	1.25
NO	8	1.21	5	1.21

runs, previously etched diamond grains were used in subsequent experiments. The change in morphology of diamonds was estimated under MBS-10 and MBI-15 binocular microscopes.

## RESULTS AND DISCUSSION

The changes in the weight of diamond crystals placed into basaltic melt at 1130°C and an oxygen fugacity controlled by the HM and NNO buffers are summarized in Tables 3 and 4 and shown in the figure. It was established that the etching rate increased at a higher oxygen fugacity (the HM buffer). The difference in the etching rate relative to the NNO buffer was about 1.5 times.

For comparative purposes, the figure shows lines indicating the loss of weight in a 0.6–0.8 mm diamond fraction in basaltic melt in contact with atmospheric air (Sonin et al., 2000b) and lines showing the loss in weight of octahedral diamond monocrystals (with an initial weight of about 10 mg) when they were etched in basaltic melt under the conditions of the HM and NNO buffers at 1130°C (Sonin et al., 1997). It should be noted that, when the oxygen fugacity corresponds to the levels of the HM and NNO buffers, the rates of etching of diamond powder and monocrystals are very close to each other. The relatively greater weight loss of diamond powder as compared with monocrystals under equal oxygen fugacity may be explained by the fact that 0.6–0.8 mm diamond grains mostly have nonsingular surfaces and represent crystal fragments. There is no doubt that, in all the above-mentioned cases, the etching of diamonds in basaltic melt was a result of oxidation with oxygen that diffused into the melt from outside. The etching of 0.6–0.8 mm diamond grains under the conditions of the HM and NNO buffers, just like in the case of the etching of diamond monocrystals (Sonin et al., 1997), is accompanied by surface graphitization, which was manifested in blackening of the surface of diamond crystals due to the appearance of graphite films.

Thus, it has been experimentally proved that, at equal temperatures, the etching (oxidation) rate of diamonds in silicate melt depends on the oxygen fugacity

**Table 3.** Etching of diamond crystals in basaltic melt at a temperature of 1130°C under the HM buffer conditions

Run duration, min	Duration of a run series, min	Weight of crystals		Change in the weight of crystals	
		before the run, mg	after the run, mg	during the run, mg	in a run series, mg
30	–	7.02	6.65	0.37	–
60	–	7.03	6.50	0.53	–
120	120	7.10	5.40	1.70	1.70
120	240	5.40	3.85	1.55	3.25
180	180	6.98	4.45	2.53	2.53
120	300	4.45	3.51	0.94	3.47
60	360	3.51	2.17	1.34	4.81

**Table 4.** Etching of diamond crystals in basaltic melt at a temperature of 1130°C under the NNO buffer conditions

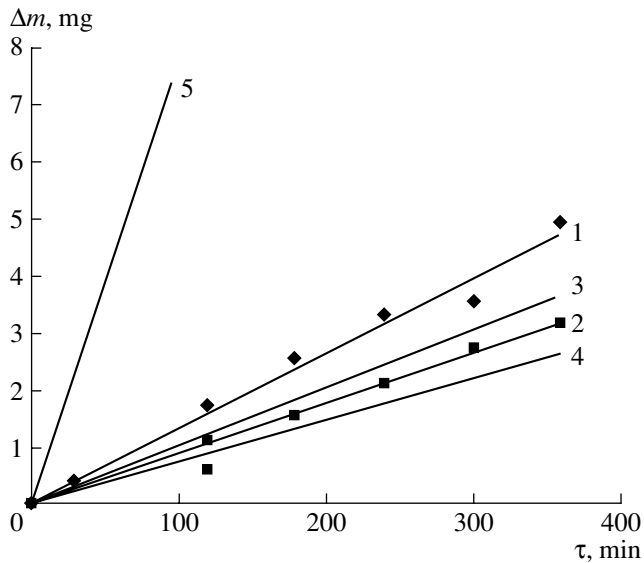
Run duration, min	Duration of a run series, min	Weight of crystals		Change in the weight of crystals	
		before the run, mg	after the run, mg	during the run, mg	in a run series, mg
120	–	7.09	6.00	1.09	–
120	–	7.10	6.00	1.10	–
120	120	7.05	6.45	0.60	0.60
60	180	6.45	5.51	0.94	1.54
60	240	5.51	5.00	0.51	2.05
60	300	5.00	4.41	0.59	2.64
60	360	4.41	3.95	0.46	3.10

in the environment. The etching rate progressively declines as the oxygen fugacity decreases from that in the case of contact with atmospheric air to the conditions of the HM and NNO buffers.

The data obtained might be helpful for interpreting the epigenetic evolution of impact diamonds at a regressive stage of astrobleme formation. Oxygen fugacity is a main parameter affecting the stability of solid carbon, diamond included, and the fluid composition in the C–O–H system at a high total pressure in the Earth's interior.

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Time-dependent ( $\tau$ ) variations in diamond weight ( $\Delta m$ ) as a result of etching in basaltic melt at 1130°C at different oxygen fugacities. (1) 0.6–0.8 mm diamond fraction under conditions of the HM buffer; (2) 0.6–0.8 mm diamond fraction under conditions of the NNO buffer; (3) diamond crystals of octahedral habit under conditions of the HM buffer; (4) diamond crystals of octahedral habit under conditions of the NNO buffer; (5) 0.6–0.8 mm diamond fraction in the case of contact of basaltic melt with air.