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요 약. 연구용 질량분석기의 검체계안에서 분쇄검출된 자연 다이아몬드내에 모인 기체에서 미루워 보아 다이아몬드의 생성에 대한 그 외계의 기체조성을 검토 제의한다. 200 °C, 10^{-9} torr 의 진공내에서 분쇄된 다이아몬드로부터 생성된 물질들을, 검출된 양의 순으로 나타낸다면, 물, 수소, 질소, 이산화탄소, 메탄, 일산화탄소, 아르곤 및 에탄올등이다.

Abstract. Using gases trapped within natural diamonds as detected by crushing in the sample system of a research mass spectrometer, a proposed gaseous environment for the formation of diamonds is presented. Diamonds crushed under a vacuum of 10^{-9} torr at a temperature of 200 °C yielded, in order of abundance, water, hydrogen, nitrogen, carbon dioxide, methane, carbon monoxide, argon, and ethanol.

INTRODUCTION

In dealing with the origin of natural diamonds, several experimental approaches have been tried. One involves an analysis of the solid inclusions found in many diamonds. It now appears that scores of different minerals may be found in diamonds[1~4]. Results based upon solid inclusions, as of the present time, have not yielded consistant data for the temperature and pressure required for natural diamond growth. Another approach is an examination of the gases trapped within diamonds. This method has been studied by this laboratory[5~10]. The present work continues an investigation into the gaseous inclusions in natural diamonds as a clue to the conditions of formation. Nineteen different diamonds from the same mine have been crushed and their gases studied. All of the diamonds were obtained from the Prairie Creek diamond mine near Murfreesboro, Arkansas U. S. A., the only location in North America where diamonds are found in their natural matrix, a rock called kimberlite.

The origin of diamonds is of interest beyond the simple experimental study since diamonds are one of the very few minerals apparently from the upper mantle of the earth that have

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made their way to the surface. With the present interest in plate tectonics and the fluid nature of the upper mantle in earthquake studies, a knowledge of the gaseous environment within the earth from 25 to 100 kilometers in depth is quite important. Diamonds represent a unique container of very great strength containing samples of the gases found within the earth.

EXPERIMENTAL

The apparatus used in this work is essentially the same as that used in earlier work[5,11]. The mass spectrometer is a single-focussing 90° instrument of 15.25 cm radius of curvature. The detector system consists of a 14-stage electron multiplier placed immediately after the final exit slit and attached to a vibrating-capacitor electrometer. The diamonds are crushed in the gas sample inlet system by means of a unique high-vacuum crusher shown in *Fig.* 1. The crushing pistons are composed of a vacuum-sintered alloy of 95% tungsten, 3.5% nickel, 1.5% iron. A base pressure of at least 10^{-9} torr is obtained by use of oil diffusion pumps. One modification of the instrument from the earlier work is the substitution of an all-metal sample system of stainless steel rather than a borosilicate glass system in order to allow better baking of the system to reduce the base pressure from that using the earlier system. Liquid nitrogen trapping is used throughout. To correct for any gases released by the pistons in the crushing process, an investigation of the gases released under typical shock conditions by the pistons was conducted. The volume of gas released by the pistons upon being struck was at least two orders of magnitude less than the volume of gases released from the diamonds and was composed of 75% hydrogen and 25% carbon dioxide. Determination of selective adsorption of the released gases was made and corrected for in the results. All diamonds, as well as the pistons, were treated in acid baths followed by cleaning with ethanol and drying for at least 24 hours at 150 °C followed by water washing and drying at 150 °C for another 24 hours prior

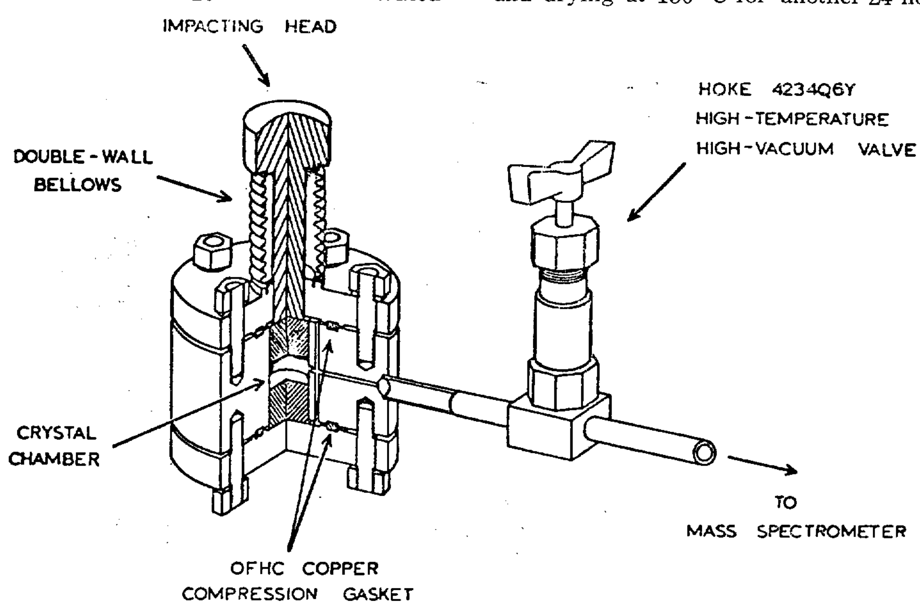

Fig. 1. Diamond crusher.
ALL components made of 316SS except copper vacuum gaskets and vacuum-sintered carbide pistons above and below crystal chamber.

to being placed in the crusher. After being assembled, the crusher and contents were heated to 200 °C for 24 hours in order to remove any adsorbed gases under a vacuum of 10^{-7} torr.

All diamonds were Type I in the classification of Robertson, Fox, and Martin[12].

After crushing, the fragments were then burned in a closed system to study the products of combustion. The results of this work have been published elsewhere[13].

RESULTS

The composition of gas released by crushing the diamonds varied markedly from diamond to diamond and has been interpreted on the basis of variation in environment during formation; however, the general order of abundance is fairly consistant. As shown in *Table* 1, the most abundant gas released was water, followed by hydrogen, nitrogen, carbon dioxide, methane, carbon monoxide, and argon. A trace of ethanol was found in several of the diamonds, probably formed by chemical reactions within the crystal. *Table* 2 describes the diamonds and volume of gas released.

The abundance of water within the gas phase of these diamonds is much less than that for diamonds of the cubic form[6]. It appears that the upper mantle of the earth may contain more water than had been earlier thought. Since a very small amount of water will lower the melting temperature of rocks, the presence of water in the upper mantle in such abundance may indicate more melting of rocks at shallower depths than had been thought. This would increase the fluid nature of the upper mantle

Table 1. Percentage composition of gas phase released from crushing diamonds.

Specimen	H_2O	H_2	N_2	CO_2	CH_4	CO	Ar	EtOH
1	26.39	21.22	21.44	20.66	8.86	0.34	1.09	trace
2	62.81	32.35	14.17	20.64	3.21	2.63	0.19	trace
3	20.96	9.86	27.67	19.88	18.42	2.80	0.41	
4	19.72	20.18	22.14	20.64	14.07	2.59	0.66	trace
5	22.81	17.25	23.95	24.82	10.77	0.35	0.05	trace
6	19.02	33.78	18.54	20.01	7.18	1.18	0.29	
7	24.35	17.53	22.97	23.09	10.52	1.05	0.49	
8	18.49	26.98	21.27	21.88	8.15	3.10	0.13	
9	36.65	13.47	19.16	19.99	5.14	5.57	0.02	
10	25.12	21.32	21.53	21.63	6.78	3.26	0.36	trace
11	36.73	20.42	15.52	16.65	5.28	5.35	0.05	
12	28.15	20.89	15.48	18.04	8.86	7.74	0.84	trace
13	22.73	20.27	25.68	21.41	8.48	1.35	0.08	
14	11.85	26.90	26.06	26.39	7.56	1.19	0.05	
15	15.90	31.21	19.76	20.32	6.86	5.58	0.37	trace
16	26.77	19.70	18.85	19.09	7.27	8.26	0.06	
17	32.19	17.86	23.06	18.70	4.10	4.02	0.07	
18	20.81	20.61	20.64	20.81	14.67	2.12	0.34	
19	37.22	29.51	12.66	14.62	3.75	1.99	0.25	
Average	24.88	22.17	20.55	20.49	8.42	3.18	0.31	
Standard devation	7.06	6.38	4.08	2.64	3.93	2.34	0.30	

Table 2. Description of diamond specimens and volume of gas released.

Specimen	Weight (carat)	Volume of gas ($\times 10^{-5}$cc) at STP	Color
1*	0.1540	4.5	none
2*	0.0764	3.3	none
3	0.0911	0.5	straw
4	0.1295	0.8	none
5*	0.1222	6.5	none
6	0.0811	0.3	none
7	0.0612	6.4	brown
8	0.5017	4.2	milky
9	0.5330	2.6	tan
10	0.1849	5.2	none
11*	0.1998	4.5	yellow
12*	0.1280	0.9	none
13	0.1948	3.2	none
14*	0.0964	2.8	none
15*	0.0700	2.9	none
16*	0.1690	6.4	none
17	0.2888	5.6	yellow
18	0.1555	3.1	tan
19	0.1495	1.9	tan

*Contained solid inclusions.

and better account for the movement of crustal plates in plate tectonics. The release of gases from rocks has also bee proposed as a clue to earthquake prediction[14].

DISCUSSION

The gaseous environment in diamond formation appears to be a water-hydrogen-carbon dioxide-rich environment with lesser amounts of nitrogen, methane, carbon monoxide, and argon. Using the experimental results for the gaseous inclusions in diamonds, a later paper will examine the theoretical thermondynamic conditions and reactions within the mantle that would lead to such a gas phase. On the basis of atomic percentages, hydrogen and oxygen are the most abundant atoms present followed by carbon (in the gas phase), nitrogen, and argon.

The gases from the diamonds may be used to estimate depths for diamond formation from the temperature-pressure relationships. This will be considered in the later paper.

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