

석류석의 불순물인 물, 이산화탄소, 수소, 질소, 산소, 일산화탄소 및 메탄의 고찰*

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The Observations of Water, Carbon Dioxide, Hydrogen, Nitrogen, Oxygen, Carbon Monoxide and Methane as Impurities in Natural Garnets*

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요 약. 광물안의 기체불순물에 관한 연구는 특이한 파괴분석법(질량분석계를 사용)에 의하여 발전되어 왔다. 시료의 분석은 영구용 질량분석계의 고진공내에서 텅크스텐 카아바이드(tungsten carbide)로된 분석기로 행하여 졌다. 사용한 질량분석계의 측정감도는 표준상태에서 약 10^{-10} cc였다. 이 보문은 미국 조지아주 라보니아 부근에서 채집된 석류석에 대한 위의 분석법에 의한 기체조성의 확인 및 결정을 보고하는 것이며 그 조성들은 N_2 , H_2 , O_2 , H_2O , CO_2 , CO , CH_4 등이 었다.

Abstract. A unique method of destructive analysis has been developed for the study of gaseous impurities in minerals. Samples are crushed in a high vacuum sample system of a research mass spectrometer. This is done by means of a suitably designed crusher which is incorporated in the inlet system of the instrument. Crusher elements are constructed of tungsten carbide. The mass spectrometer used for this preliminary study has a detection sensitivity of about 10^{-10} cc at STP. In a study of rhodolite garnets obtained from near Lavonia, Georgia, U. S. A., the gases N_2 , H_2 , O_2 , H_2O , CO_2 , CO , and CH_4 have been identified and their composition determined.

Introduction

In order to understand the origin and chemical processes of natural minerals, it is desirable to know both the conventional chemical properties

of the minerals and also the environment under which the minerals were formed.

Garnet, a term referring to several nesosilicate minerals, is of interest as it is a fairly common high-temperature, high-pressure mineral formed under metamorphic conditions. It is often difficult to tell the various types of garnets apart by megascopic means and usually laboratory appa-

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ratus is required. The garnets used were classified as rhodolite, and were all from the same source area, and, indeed, had similar appearance.

It appears that it might be possible to determine the conditions under which the garnets were formed by studying the gaseous inclusions. Further, it is believed that this would be a sample of the original atmosphere in the earth where the garnets were formed since any gases which would have diffused into cracks and fissures in the crystal would probably follow a reversible path and be driven out upon heating under high vacuum.

There are few reported studies of gaseous inclusions in minerals in the literature. Bauer and Spencer¹, and Eppler² describe fluid inclusions in minerals that they interpreted as liquid CO₂. Roedder has identified CO₂ inclusions in olivines and garnets³. Miyashiro reports up to 0.12 % by weight of CO₂ in a garnet gneiss⁴. As for other gases, Chamberlin studies several gases in rocks by classical wet-chemical means in 1908, but was unable to investigate the gases which could not be studied by such methods. He did report CO₂ in several garnet samples⁵. Melton, Giardini, and Salotti have investigated gases in diamonds⁶, and have found different results for gases from diamonds containing differing inclusions. Since garnets are often found with, and even as inclusions in, diamonds, gases trapped within garnets are of broad interest.

We report here the positive identification of gaseous nitrogen, carbon dioxide, carbon monoxide, methane, water, oxygen, and hydrogen in garnets from northeast Georgia, U. S. A., near Lavonia, Georgia.

Experimental

Mass spectrometry is one of the most powerful

tools for gas analysis. It offers the possibility in most cases of identifying the composition of the gas phase quantitatively and of detecting gaseous components at very low relative concentrations. The research mass spectrometer is about 10⁵ times more sensitive than any other spectroscopic method⁷. Because of these considerations, the mass spectrometer is the best possible tool for the investigation of included gases in minerals.

The instrument used in this study is a 15.24-cm radius 90° sector type magnetic scanning instrument designed and built at the University of Georgia. The analyzer tube is constructed of inconel and all other parts are of stainless steel. Oil diffusion pumps are used to evacuate the system. Base pressure is better than 2×10^{-8} torr with liquid nitrogen trapping. The instrument, experimental procedures, and calibration have been described elsewhere⁶⁻⁸.

Perhaps the most important part of the instrument is the ion source. It is in this region that the neutral gas molecules are converted into an ion beam. To ensure high transmission, the exit slits for the present source are unusually large, measuring 0.635×1.27 cm. With this ion source, we measured an efficiency (ions produced versus ions collected) of 88.3 %. The large exit slits significantly decrease the resolution of the instrument, but analysis of the occluded gases in this investigation did not require high resolution. Our resolution is about 150, which is sufficient for the study of all the gases found, except for N₂ and CO, which are discussed later.

The second critical component of a research mass spectrometer is the ion detection circuit. In our case, ions are detected by means of a 14-stage electron multiplier attached to a vibrating capacitor amplifier. The output of the amplifier is fed into a strip chart recorder. This

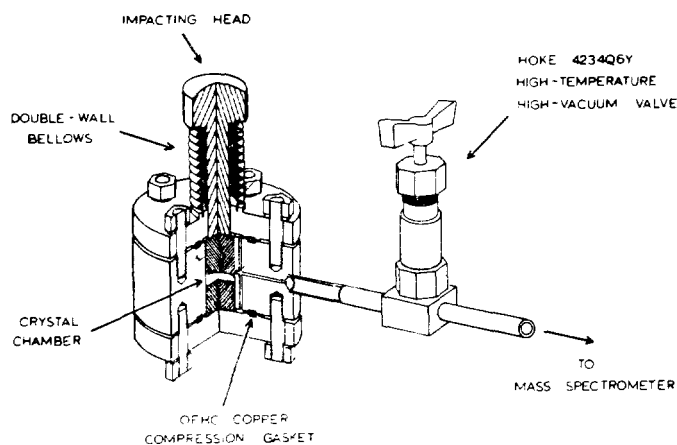


Fig. 1. Crusher

circuit is calibrated for linearity by measuring the isotopic abundance of neon on three different scales and comparing the experimental results with the known value. Our linearity is better than 0.25 % over all ranges.

A schematic diagram of the crusher is shown in Figure 1. Before crushing a garnet, the crusher was baked out under high vacuum (at least 10^{-7} torr) for at least 12 hours at 200 °C. This removed adsorbed species from the internal parts of the crusher. The crusher was then quickly taken apart and the garnet was placed in the crystal chamber between the two tungsten carbide pistons. The crusher was then resealed and evacuated for another 12 hours or more while heating at 200 °C under high vacuum. The garnets were crushed by striking the impacting head with a hammer.

A possible source of error in the investigation is the contamination by gases released from the crusher elements. To evaluate this, several experiments were run. This was done by striking a well-crystallized type Ia diamond which

thus far has resisted all efforts of crushing under the conditions of the testing, to see the composition of the gases released with respect to damage to the crushing pistons. These results are shown in Table 1. Under the conditions required to crush the garnets, there was no damage to the pistons and no measurable gas was released.

Results

In spite of the difficulties arising from the fact the garnets released only very small quantities of gases, we have succeeded

in obtaining results for the gases contained within the garnets from the northeast corner of the state of Georgia, U. S. A., near Lavonia, Georgia. The weight of samples that were analyzed ranged from 0.0148 to 0.5404 grams. The results are shown in Table 2.

Due to the low resolution of the instrument, it was not possible to determine the amounts of N₂ and CO directly, since both appear at mass 28. However, from a calibration of the

Table 1. Gases* released from tungsten carbide pistons

Gas	Percentage
CO ₂	4.5
H ₂ O	0.0
O ₂	0.0
CO	1.7
N ₂	0.0
CH ₄	6.8
H ₂	86.7
Ar	0.3

Volume of gas evolved 8.6×10^{-7} cc.

*From a similar striking force used to crush the garnet samples

Table 2. Gases released from crushing garnets

Gas	Sample G-1	G-2	G-3	G-4
CO ₂	22.47	29.57	47.02	8.13
H ₂ O	44.56	12.17	9.52	54.21
O ₂	2.01	0.87	0.00	0.00
CO	0.00	0.00	41.67	1.90
N ₂	13.56	19.13	0.00	0.00
CH ₄	1.34	1.74	0.00	0.00
H ₂	16.05	36.52	1.79	34.86
Volume(cc) Sample Weight(gm)	1.7×10^{-6} 0.0826	2.0×10^{-6} 0.0148	2.4×10^{-6} 0.0182	2.5×10^{-6} 0.5404

instrument, it was possible to calculate the amount of N₂ from the known N⁺/N₂⁺ ratio and the amount of mass 28 arising from CO⁺ from CO₂ from CO⁺/CO₂⁺. The amount of CO was determined as the amount of mass 28 remaining after N₂⁺ (calculated from N⁺) and CO⁺ (from CO₂) were subtracted from the original amount at mass 28. The results for N₂ and CO may be in error by a factor of 5 to 10 percent.

Discussion

Roedder has revealed the presence of CO₂ in garnets³. We confirm the presence of CO₂, but also indicate additional gases from the samples. It is believed that the analysis of the gases from the garnet samples provide a more complete picture of the gaseous atmosphere present during their formation. These data are pertinent to the chemical and physical conditions of genesis for garnet and other related minerals. It is

hoped that with a continuation of this study, a more complete picture of the geochemical processes of mineral formation may be obtained.

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