

SULPHUR DIOXIDE AS A SOURCE OF VOLCANIC SULPHUR.

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The reaction expressed by the equation $\text{H}_2\text{S} + \text{SO}_2 = \text{H}_2\text{O} + 2\text{S}$ was investigated by Cluzel¹ as far back as 1812. This reaction was accepted by geologists and chemists² as being back of the origin of volcanic sulphur: hydrogen sulphide and sulphur dioxide gases, escaping from vents and fumaroles, come in contact and bring about the formation of sulphur. Brun³ opposes this theory of the origin of sulfatara sulphur, and he, in turn, is opposed by others. The reader is referred to the literature on geochemistry for details.⁴

In case of sulphur deposition, where hydrogen sulphide is detected as a volcanic exhalation, it is supposed that the sulphur is formed as a result of the partial oxidation of the hydrogen sulphide.⁵

While investigating the flame reactions of the sulphur group of elements, I noticed that when a mixture of sulphur dioxide and illuminating gas is heated in a glass tube, an opalescence is produced due to the precipitation of sulphur. Illuminating gas is a mixture of different reducing gases, and, on the whole, the reaction resembles the one described by Berthelot,⁶ which is expressed by the equation $\text{SO}_2 + 2\text{CO} = 2\text{CO}_2 + \text{S}$. Since volcanic exhalations contain carbon monoxide, as well as methane and hydrogen, then why not suppose that volcanic sulphur is formed from sulphur dioxide through a reaction of reduction, say, with carbon monoxide? The sulphur thus formed will have to cool and condense before it comes in contact with oxygen, otherwise it will burn back to sulphur dioxide. Some means of sudden cooling is especially favorable for its formation instantly upon reduction from sulphur dioxide. Such a means is to be found in the case of the sulphur recovered from Lake Ponto, which is a crater lake in the southwestern part of Kunashiri Island, Japan.⁷ The water of this lake is strongly acid⁸ and has a temperature of 40° C. Around the margins

¹ Ann. Chim. Phys. 84, 162 (1812); Jour. Phys. Chem. 15, 1 (1911).

² Ries' "Economic Geology", 4th ed., p. 293; Roscoe and Schorlemmer's "Treatise on Chemistry" 1, 365 (1905); Erdmann's "Lehrb. anorg. Chemie", 2nd ed., p. 235 (1900).

³ Chem. Zeit. 15, 127 (1909).

⁴ Clarke's "Data on Geochemistry", 3rd ed., pp. 270 and 575.

⁵ Habermann: Zeit. f. anorg. Chem. 38, 101 (1904).

⁶ Compt. rend. 96, 298 (1883).

⁷ Y. Oinouye: Jour. of Geology 24, 806 (1916).

⁸ Professor Oinouye, in a private communication dated April 29, 1918, informs me that the water smells of sulphur dioxide

through innumerable small fissures sulphur is deposited, and the country rock is strongly impregnated with it. The amount of gas emitted is ordinarily not very great, but is increased enormously when the atmospheric pressure is low. During periods of crater activity, paroxysmal eruptions of gas and water are noticed near the center of the lake at intervals of from one to three hours, and whenever the bubbling begins, workmen row to the spot. By means of a pulley attached to a framework resting upon two boats, the men lower an iron bucket in the center of the bubbling area to the bottom of the lake. When the bucket is withdrawn it is practically filled with sulphur grains. In this manner, while the crater is active, a hundred buckets of sulphur are easily brought up in a day. This sulphur is for the most part dark grey in color and consists of oolitic grains.

The process of sulphur deposition just described is not to be taken as typical, and Oinouye himself remarks¹ that the production of sulphur in crater lakes is very unusual even in sulfatara sulphur fields. But this particular process illustrates strikingly the possibility of sulphur coming from sulphur dioxide. The fact that the water of Lake Ponto is charged with sulphur dioxide bears unmistakable evidence of the existence of this gas as a volcanic exhalation. Its reduction to elementary sulphur can be assumed to take place through its interaction with carbon monoxide, which is very commonly found in volcanic exhalations together with other reducing gases. The freshly formed sulphur cools suddenly on coming in contact with the water in the lake and condenses in the form of oolitic grains.

The theory set forth in this paper is not meant to displace other accepted theories on the origin of sulphur, but rather to supplement them. No one theory can explain the origin of the different deposits of sulphur; each deposit has to be dealt with separately, and it is hoped that some cases of sulphur deposition can be explained on the basis of this theory.

The study of the origin of sulphur was undertaken at the suggestion of Dr. W. N. Logan of Indiana University, to whom my sincerest thanks are due.

Since this note has been written an article by J. B. Ferguson appeared on "The Equilibrium Between Carbon Monoxide, Carbon Dioxide, Sulphur Dioxide and Free Sulphur."² Mr. Ferguson states that he undertook his work with the purpose to shed some light on the role of sulphur gases in volcanic activity.

¹ Loc. cit.

² Jour. Amer. Chem. Soc. 40, 1626 (1918).