ON THE PRESENCE OF INERT GASES IN SOME MINERAL SPRING GASES IN JAPAN.

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Introduction. One of the authors, I. Suganuma, who has long been studying mineral springs and their products in Japan[1] from chemical points of view expected the presence of helium in the natural gases from Masutomi Springs in Yamanashi Prefecture, from the fact that the springs contain radon in a very high quantity, the highest among the springs in Japan.

Gases of Masutomi Springs, gushing out with water, generally contain carbonic acid gas to the extent of 98–99%, oxygen to 0.2–0.8%, and the rest is almost entirely nitrogen. We collected the spring gases from two sources, one of which is Kumitoriyu Spring of Tuganerô Hotel and the other is the left side spring of Fujimotorô Hotel in order to determine helium contents. The water of the former contains radon to 266 mache per liter at 22°C., and the latter to 965 mache at 19°C.[2].

The Procedure and the Apparatus. According to F. Paneth and his collaborators[3] the methods of isolating inert gases can be divided into

(1) I. Suganuma, this Bulletin, **3** (1928), 69, 73, 87.

(2) The figures of radon contents in "The Mineral Springs of Japan", by R. Ishizu (1915), are somewhat different from ours.

(3) F. Paneth, H. Gehlen, and K. Peters, *Z. anorg. allgem. Chem.*, **75** (1928), 383.

two classes, one may be called a chemical method, fixing nitrogen by calcium or magnesium metal or by electric discharge with oxygen, and the other is to be called an adsorption method, fixing nitrogen by active charcoal cooled in liquid air. The treatment carried out by the present authors is as follows.

The gases collected at Masutomi Springs or later at other places were first freed from their active constituents, i.e. carbonic acid gas by means of concentrated caustic alkali, oxygen by alkaline pyrogallol solu-

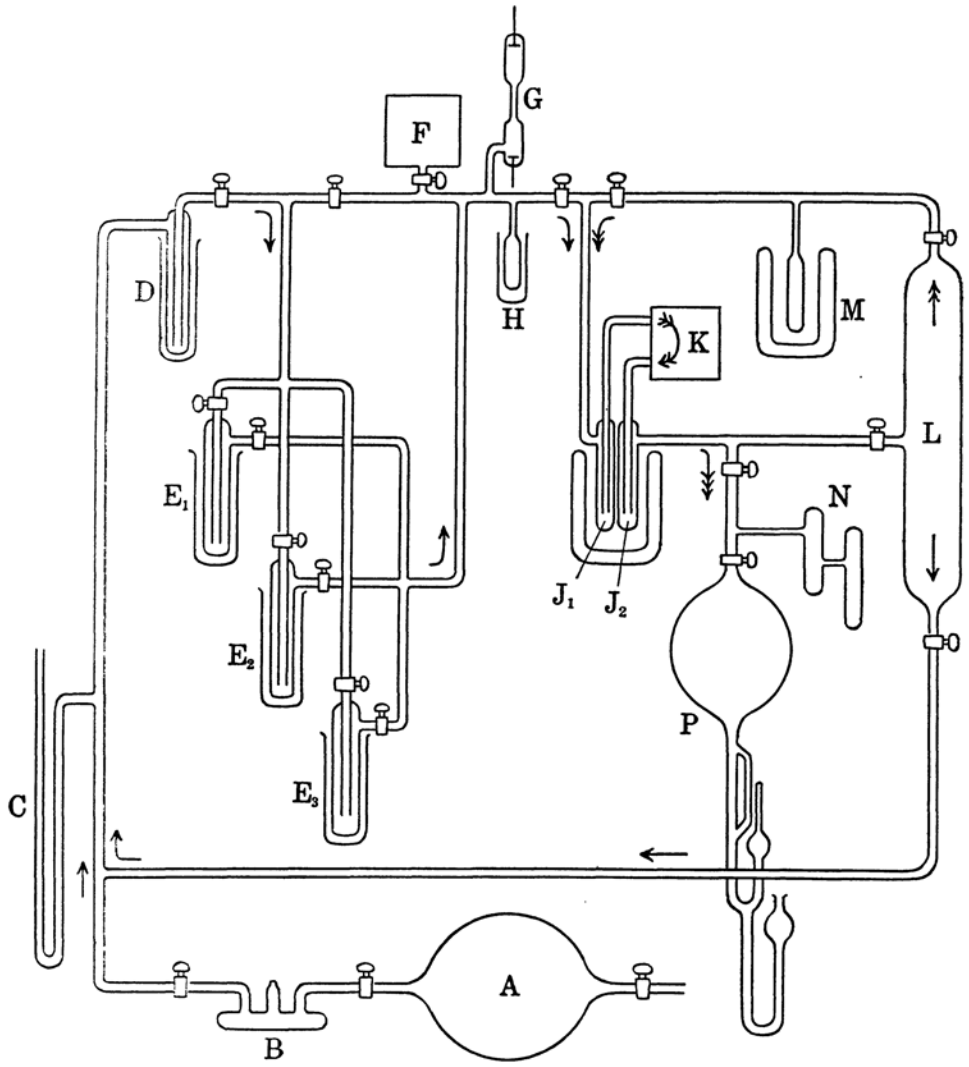

Fig. 1.

tion, heavy hydrocarbons by fuming sulphuric acid, and methane by explosion with oxygen, and the crude nitrogen, which contains probably the inert gases were studied.

The apparatus devised to detect helium in the crude nitrogen is shown in Fig. 1. A is a glass bulb of about one liter capacity, B a tube containing phosphorus pentoxide, C a mercury manometer, D a Pyrex-glass tube containing some copper filings with an electric furnace attached, E_1, E_2, and E_3 three Pyrex-glass tubes, each provided with an electric furnace and containing a mixture of metallic calcium and magnesium oxide prepared from quick lime and metallic magnesium powder, in the proportion of five parts of the former and three parts of the latter, by heating at about 550°C. in vacuum, one of the three tubes being used at a time while the others serving as reliefs, F a Langmuir mercury condensation pump, accompanied by an oil pump serving as a fore-pump, G a Geisler tube for measuring the pressure of nitrogen in the tubes above described, H a Pyrex-glass tube containing palladium powder, previously heated at red heat in vacuum, J_1 and J_2 two traps placed in a Dewar vessel for condensing mercury vapour from another Langmuir condensation pump K working in three steps and carrying the gases in one direction only, i.e. from J_1 to J_2, L a glass bulb of one liter capacity, all the gases under experiment being able to be confined in this bulb if desired, M a glass side tube placed in a Dewar vessel and containing about one c.c. of cocoanut charcoal, previously heated at about 250°C. in vacuum, N a Geisler tube for detecting helium and other inert gases, and P a McLeod manometer provided with a large glass bulb, its capacity, together with that of N, being 1100 c.c.

The whole apparatus is first evacuated with pump F, while D,E's,H, and M are heated until no more gas evolves there. About 750 c.c. of crude nitrogen under experiment, already freed from the active constituents as mentioned above, are introduced and confined into bulb A from the reservoir by the method of water substitution. Dried on passing through B, the gas proceeds to D,E,G,H,J_1,J_2,K, and L, returning to D as shown by the arrows in the figure.

During the circulation, the gas is first freed from all traces of oxygen by copper filings in D heated at about 400°C. Then nitrogen is removed by metallic calcium in one of E's heated at about 500°C., and hydrogen is removed with metallic palladium in H heated at about 250°C.

When the pressure is gradually lowered and no trace of nitrogen cocks, the gas is circulated in the order of J_1,K,J_2,L,M, and J_1 as shown can be seen any longer at G, by an appropriate management of the stop-

by double arrows in the figure, during which time the condensable inert gases are adsorbed by the charcoal in M cooled in liquid air, and almost all of helium is left behind.

Finally the gas is collected in N as shown by the triple arrow in the figure, where the spectra of the gas are photographed and the pressure of the gas in P is also measured by the manometer attached.

In the earlier stages of the investigation, the magnesium arc method was applied instead of calcium powder method for fixing nitrogen, but in the former method the time required for the purpose was much longer than in the latter.[4]

The Comparison of Inert Gases Obtained from the Springs Masutomi, Nozawa, etc., with those of the Ordinary Atmospheric Nitrogen. It has been found by the spectral observation, that the crude nitrogen from Masutomi Springs contains a little helium and the spectra of the sample from Kumitoriyu Spring of Tuganerô Hotel are shown on plate Ia, Fig. 2, where the spectral lines of not only helium but also neon can be seen. If the spectra of the gas are examined without the complete treatment of charcoal adsorption, some spectral lines of argon, say 6677 and 7067 Å, can also be seen. It may therefore be suspected that the gas has been contaminated with the atmospheric nitrogen either on the earth or underground. It was therefore necessary to compare these inert gases from the springs with those in the air.

Then, 750 c.c. of the atmospheric nitrogen prepared from air, the volume of which is almost the same as that taken in the preceding experiment, was subjected to the spectral examination as before with the same apparatus. The spectra of the remaining inert gases are shown on plate Ib, Fig. 2. By comparing the two plates Ia and Ib, it can be easily seen that the characteristic lines of helium, especially the line 5015 Å, on the former plate are more intense than those on the latter. It can be supposed that the gas from Masutomi Springs originally contained helium and other inert gases.

Now arises a question whether the presence of helium in the gas from Masutomi Springs is due to the radioactivity product or the primordial atmosphere underground. It has long been questioned why certain natural gases are rich in helium,[5] but the question has not yet been satisfactorily answered.

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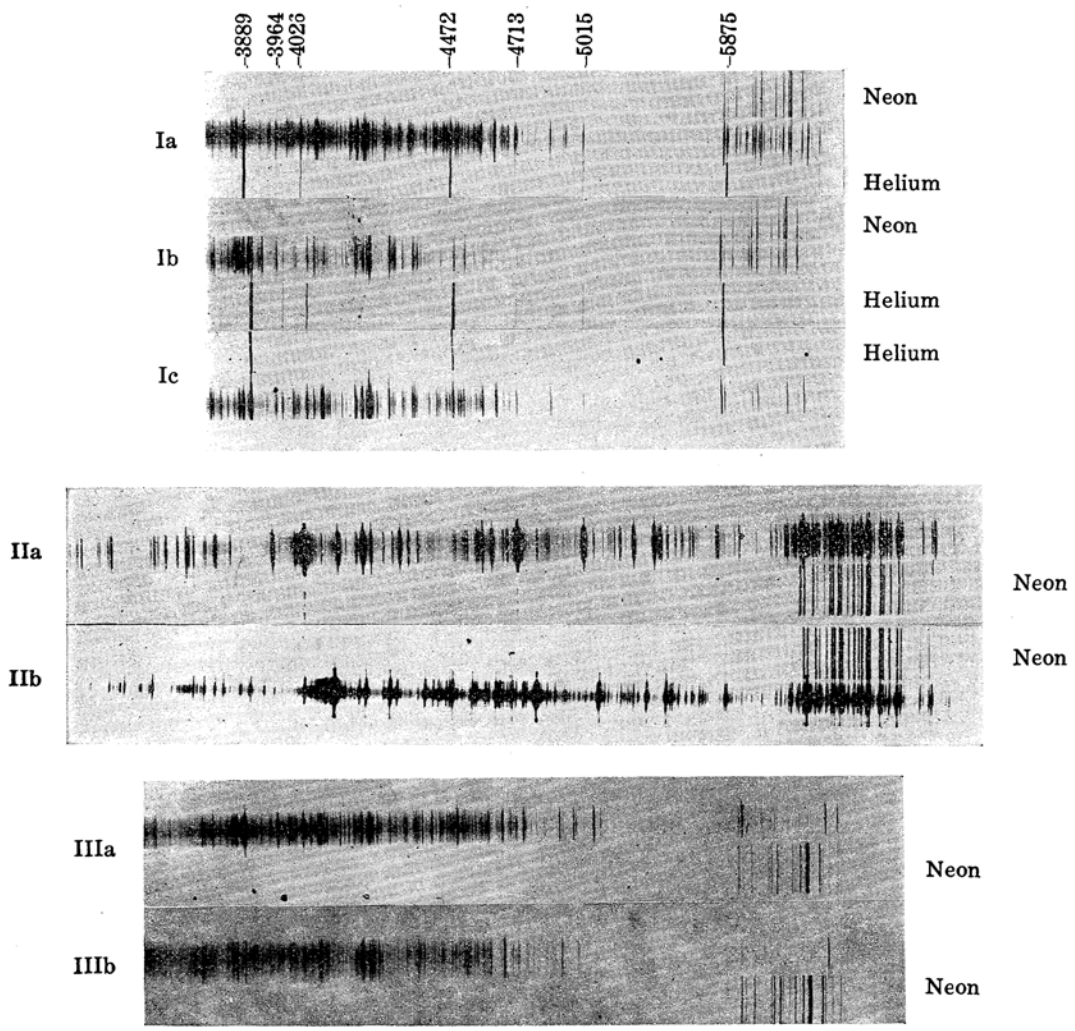
(4) Paneth and his collaborators (*loc. cit.*) preferred metallic calcium for fixing hydrocarbons as well when crude nitrogen contains them.

(5) A. Holms, "The Age of the Earth", 1931, 396, where the literature concerning this point of the question is abundantly cited.



Time of exposure 5 minutes.

Fig. 2.

It has been repeatedly ascertained that as experimental facts the origin of helium in natural gases is not directly related to the radioactivity.(6) We feel, on the other hand, a temptation to consider the richness of helium be somehow connected with the radioactivity, for an

(6) Jeffreys, "The Earth", 1929, 310. Kano and Yamaguchi, *Rep. Aeronaut. Res. Inst. Imp. Univ. Tokyo*, Vol. **13** (1926). Paneth and others, *loc. cit.*

easy liberation of helium may be caused by the cracking[7] and the diffusion of helium through rocks or glasses has been observed.[8]

However the fact that we have found the presence of neon and argon, accompanied with helium, does not favour that temptation. The authors compared the experimental results of the gas from Masutomi Springs with those of the other spring gases which are not or almost not radioactive. For this comparison the gas from Nozawa Springs in Nagano Prefecture was first taken.

The water of the springs is slightly alkaline, containing some quantity of calcium sulphate and calcium bicarbonate. The gas from the springs is combustible, chiefly consisting of methane but mixed with only a little nitrogen. On treating the gas in the same way as mentioned above, the spectral lines of helium and neon were observed, as shown on plate Ic, to be nearly as intense as those in the case of Masutomi Spring gases.

The authors now put importance on the fact that the helium in both cases is accompanied by neon and probably also by the other inert gases of argon, etc. Yamaguchi and Kano, in their studies on natural gases in our country, proved in their plates the presence of helium but none of other inert gases. They adopted exclusively charcoal adsorption method by which neon and argon were probably adsorbed. So it was thought worth while by us to repeat some researches of the inert gases in the same natural gases as studied by them.

The results of our experiments on the inert gases from the springs of Katayamazu and Wakura in Ishikawa Prefecture are shown on plates IIa and IIb, Fig. 2, respectively, where the distinctness of spectral lines has fully convinced us of the presence of the larger contents of helium and neon.

The two other spring gases of Futai near Yusawa Station and of Hirota near Kashiwazaki City, both of which are situated in Niigata Prefecture, were collected and studied by us. The gas of Futai Spring resembles that of Masutomi mentioned above in being rich in carbonic acid gas, but it is different in having almost no radioactivity. The gas of Hirota Spring is combustible owing to its petroleum nature and is slightly radioactive.[9] About 120 c.c. of crude nitrogen obtained from those spring gases was put under the spectral examination as before, and

(7) R. J. Strutt, *Proc. Roy. Soc.*, A, **82** (1909), 166. J. A. Gray, *ibid.*, 391. D. O. Wood, *ibid.*, **84** (1911), 70.

(8) Williams and Ferguson, *J. Am. Chem. Soc.*, **44** (1922), 2160.

(9) N. Yamada, *J. Chem. Soc. Japan*, **44** (1923), 1018.

the spectra of both helium and neon were photographed, plates IIIa and IIIb, Fig. 2.

As for the quantitative estimation it was found that 0.02 for Futai Spring, and 0.2 for Katayamazu Spring, is roughly the volume percentage of helium mixed with a portion of neon to the crude nitrogen.

An Interpretation of the Presence of the Inert Gases in Spring Gases. As to the origin of helium underground Paneth and his collaborators supposed the socalled "fossil helium", which, during a long course of time, had come out of some radioactive minerals in deep places and been accumulated underground under some geological conditions.

The present authors consider that the origin of helium underground has almost no relation to the radioactivity but it is primordial, i.e., helium was contained in the ancient air which was enclosed in the internal parts of the earth, and its richness in the spring gases is due to its inertness and diffusibility causing natural accumulation underground. Oxygen and nitrogen in the ancient air were gradually lost owing to their chemical activity, leaving the inert gases behind.

These arguments are supported by the following facts: (1) So far as the present experiments have been carried out, the spring gases from different districts in Japan, contain helium accompanied by neon and most probably by argon besides. The coexistence of these inert gases has been found by Paneth and his collaborators as well as by Moureu and Lepage.[10] (2) Inert gases are always found with nitrogen in spring gases. (3) So far as the authors have observed, more or less nitrogen has always been found in spring gases, some of which consist of carbonic acid gas and some of the natural gas of petroleum nature. (4) The percentages of helium and neon in the crude nitrogen from spring gases are larger than that in ordinary atmospheric nitrogen. (5) The spring gases of Katayamazu and Wakura are comparatively rich in neon as well as in helium (cf. plates IIa and IIb).

Summary.

Researches of inert gases in some mineral spring gases in Japan have been carried out with the conclusion that the primordial inert gases were contained in the ancient air which was enclosed in the internal parts of the earth, and in the long course of time the oxygen and nitrogen were gradually lost owing to their chemical activity leaving behind inert

(10) *J. chim. phys.*, **11** (1913), 63.

gases such as helium, neon, and argon. When the spring gases are produced largely underground and gush out of the earth they are accompanied generally by the primordial gases, that is to say, they come out upwards together with the inert gases.

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