On the Geochemical Study of Carbon 14. I. The Ozegahara Peat

By Makoto Shima

Introduction

It is well known that ^{14}C is continuously produced in the atomsphere by the action of neutrons produced by cosmic-rays, involving the reaction $^{14}N(n, p) \rightarrow {}^{14}C$. Libby[1], with a number of associates, for the first time recognized that atmospheric carbon dioxide, including those present in hydrosphere and biosphere, showed radio-activity of the order of 15.3 dpm. per g, (about $1.5 \times 10^{-10}\%$). He also found that the age of substances containing carbon can be calculated from the half-life of ^{14}C (5568±30 years). Since these pioneering experiments[2,3], Libby and Arnold measured and published the ages of more than 100 specimens, including neary every conceivable kind of relic of the past. In Japan, T. Hamada and F. Yamazaki set up a counter of Libby's type and mainly measured the amount of ^{14}C in the biological and archaeological substances[4].

The present author took up this method to determine the age of peat in Ozegahara in his study of geochemistry with special reference to the sedimentation of coal. It was found that the layer of 2 m. beneath the surface is about 1000 years old and that of 3 to 4 m. is about 5000 years old. The rate of sedimentation is about 1.6 mm. per year at present and appears to have been 1 mm. and 0.25 mm. per year when the layers 2 m. and 3–4 m. beneath the surfaces were formed, respectively. This fact suggests that the apparent volume of the peat has been changed to such an extent in the course of the years concerned.

Sample Occurrence

Ozegahara exists on the boundary of Tochigi, Fukushima, Niigata and Gumma prefectures. It is a famous subtundra. The peat of Ozegahara had been formed upon the lake sediments of the old Ozegahara lake.

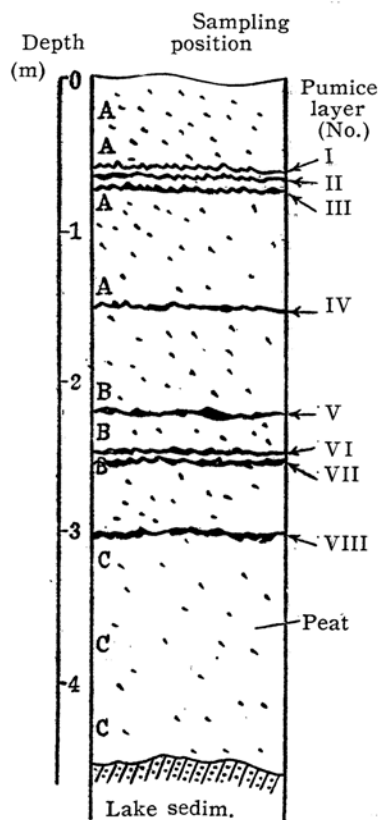The samples at Nakatashiro (P11) are illustrated in the column section (Fig. 1). At

Fig. 1. The column section of peat occurence.

480 cm. depth there are sand and clay layers of the old Ozegahara lake sediments. During the peat sedimentation, volcanic action occurred several times and then layers of volcanic ash and pumice were formed as shown in Fig. 1. The peat is found in two different types of texture in the layers, and the two types are mixed with each other. One is fibrous and maintains the original plant organ; the other is so-called sedimentary peat and the texture has been destroyed by volcanic sediments. The volcanic sediments has 8 layers; among them, No. 2, No. 3 (both Ikaho pumice), No. 6 and No. 7 (Nantai pumice) predominate. The sampling position is shown in Fig. 1. "A" represents the

1) W.F. Libby et al., *Science*, 109, 227 (1949); ibid, 110, 678 (1949); *Phys. Rev.*, 81, 64 (1951); *R. S. I.*, 22, 225 (1951).
2) W. F. Libby, "Radiocarbon Dating", Univ. of Chicago Press (1952).
3) T.P. Kohman and N. Saito, *Ann. Review of Nuclear Sci.*, 4, 401 (1954).
4) T. Hamada, *Nuclear Study*, 1, No. 3, 187 (1954) (in Japanese).

samples of the first unit, "B" those of the second and "C" those of the third.

Chemical Procedure

Chemical processing was almost the same as Libby's[2], except several points as shown below.

a) Chemical Procedure.—The apparatus, in which the main part of the chemical procedure was conducted, is shown in Fig. 2. The combustion of the sample (40-50 g. dry peat) is carried
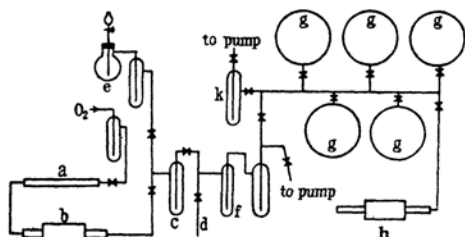

Fig. 2. Chemical preparation apparatus.

out in the quartz tube (a). Oxygen is slowly passed over the sample, which is ignited at its one end. The combustion gas is passed through the copper oxide wire, heated at about 600°C (quartz tube b) to complete the oxidation, is dried in the dry-ice trap (c) and introduced into ammonium hydroxide solution.

In this method, the final product consists only of carbon dioxide, contaminated by oxides of nitrogen and sulfur, resulting from combustion of minor constituents of the peat. It is necessary to carry out a chemical purification before carbon dioxide is submitted to reduction. Therefore the combustion gas is taken out through (d).

A 1 l. flask containing 500 ml. of 6 N ammonium hydroxide is attached to the end of (d). In this vessel, carbon dioxide is absorbed by ammonia and is converted into $(NH_4)_2CO_3$. A rapid absorption of the gas is effected. During this reaction the flask is shaken to insure the absorption until the sample is burnt off. A second solution, containing 180 g. of calcium chloride in 180 ml. of water, is heated nearly to boiling. The flask is removed from the line, and the hot calcium chloride solution is added slowly with stirring. A rapid precipitation of calcium carbonate takes place. The precipitate is filtered and washed with water on a Buechner funnel. At this point, all of the oxides of nitrogen and sulfur have been left behind in the form of soluble salts. After washing, the precipitate is dried in an air bath. This calcium carbonate (about 130 g.) precipitate is transferred to flask (e). Carbon dioxide is now recovered from the precipitate, using the same system employed in the combustion by adding concentrated hydrochloric acid. The stopcock leading to the flask is opened, and acid is added from a separatory funnel (about 200 ml.).

The chemical purification procedure is thus completed. The recovered gas is passed through the dry-ice trap (c) into two successive liquid air traps (f) in which the carbon dioxide is condensed. The Dewars are removed and the solid carbon

dioxide is evolved. The gas is passed into the system of reserver (g) (total volume, 25 l.) which has been already evacuated, and then the gas is ready for the reduction step. Reduction is carried out in a seamless stainless steel tube (h) which is filled with 80 g. of magnesium turning together with a little of cadmium turning as a catalyst. An electric furnace, capable of reaching about 800°C, is placed around the tube. One end of the tube is sealed with a rubber stopper and wax, and the reduction system is evacuated and tested for freedom from leaks. Carbon dioxide is now admitted to the tube up to a pressure approaching one atmosphere, and external heat is applied to the magnesium filling. When it gets the melting point of magnesium (660°C), the reaction begins violently and produces sufficient heat to maintain itself, provided that the gas is admitted at a moderate rate from the bulbs. Since the reaction "$2Mg+CO_2=2MgO+C$" yields no gaseous products, no circulation is required. It is the practice to run the gas from the bulb until the pressure is reduced to about 200 mmHg, when the next bulb is cut in. In this way the gas can be reacted smoothly before the other end of the magnesium filling is reached. To complete the reduction, it is necessary to apply external heat using the furnace. The remaining gas is condensed in the trap (k) and may either be expanded into a single bulb or allowed to react directly. After this method, has been used the remaining gas is no more than 50 mmHg. The reduction tube is allowed to cool, and the carbon, magnesium oxide and unreacted magnesium are removed from the tube using an iron rod. These products are transferred to a 5 l. beaker. Concentrated hydrochloric acid is cautiously added (total, of about 800 ml.); violent evolution of gas takes place. The mixture is allowed to stand overnight. It is then brought to boiling point on a large hot plate. One litre of water is added and it is again boiled for about fifteen minutes. The supernatant is then removed by filtration, using a sintered glass filter stick operating directly into a water aspirator; 300 ml. of nitric acid is added to the residue. The nitric acid solution is again nearly boiled for fifteen minutes and filtered. It is recognized that this method eliminates the carbon ash at least down to a fraction of a percent. One and a half litres of water are added; the solution is once again boiled for fifteen minutes and filtered. This cycle is repeated three times more. After the carbon is washed into a small beaker, the water is removed using the filter stick. This beaker is transferred into an air-bath and the carbon is thoroughly dried. The carbon thus obtained weighs about 12–15 g. It is now ready for mounting and measurement. The overall yield of the chemical processing sequence, described above, is in the neighborhood of 80% of the carbon content of the peat. One of the problems in producing a final product free from intrusive radioactivity is, of course, the purity of the reagent used. After burning, the peat ash was analysed by the common plant analytical method. Water content of peat was measured in

a water stop trap. The carbon ash was analysed by the combustion method and the total impurity (mainly Fe, Mg, Ca, etc.) was measured.

b) Mounting Procedure.—At the carbon corrected by the above methods is coarse, it is fully ground by an agate motor. About 8 g. of carbon are weighed into a 150 ml. beaker. Water (total volume, about 50 ml.) is added little by little continuously with stirring, until the well-stirred slurry maintains just the proper consistency. This can be judged by the rate of flow on tipping the beaker. The slimy mass is transferred to the one of the pair of a split cylinder which can be connected together, (for details of counter construction see below), using a long glass rod.

The cylinder is continuously rolled with a moter driven rotator throughout the mounting. A small portion of the slime is placed on the one end of the cylinder and spread with the aid of a long glass rod so that a uniform layer is formed on the inner surface of the cylinder. Care must be taken to make the slurry just slimy enough to keep itself on the surface. Then a hot stream of air is blown over the inside of the rotating cylinder with a hair dryer. After about five minutes, sufficient water will be thus removed and the carbon layer is fixed on the surface so firmly that no appreciable amount falls down during the further procedure. The pair of the cylinders are connected together and inserted into the screen-wall counter through the free end. When the layer is too dry, it may be torn off forming a crack on the surface. Therefore the drying must be given up before it gets too dry. The end cap is put on and attached to a vacuum system and the remaining water is generally pumped off through a dry ice trap. This operations must be carried out rapidly and with special attention not to touch the cylinder or the

sample by hand. After two days when no leakage is observed, ethylene (6 mmHg) and argon (100 mmHg) are introduced into the cylinder. After one night the whole is transferred into a shielding box and submitted to measurement.

After each run, the sample is removed from the cylinder with a spatula. The final cleaning of the cylinder (before mounting a new sample) is achieved by carefully wiping it with a powder-paper.

Instrument

The author has used the counter that was made by Yamazaki's group. The instrument is illustrated by Mr. T. Hamada in detail[4].

a) Screen-wall Counter. — The screen-wall counter has the grid wire between the anode and the cathode of an ordinary cylindrical Geiger-Müller tube. The counter, presently in use, is illustrated in Fig. 3. The main part is almost the same as the Libby's counter, but is not so in some material used. The counts of the sample and background can be directly compared by sliding the cylinder from one end to the other.

b) Anticoindence Counter.—It is a common cosmic-ray counter shown in Fig. 4. The necessary reduction in background can be achieved by connecting the screen-wall counter and the eleven shielding counters placed around it in anticoin-tences. These counters are filled with ethyl-formate (7 mmHg) and argon (100 mmHg).

c) Shiled.—A shiled is constructed of steel plates (1 inch thick; contributed by the Yahata Iron Company); the arrangement is shown in Fig. 5. The total thickness is 7 inches and the total weight amouts to 4.3 tons. The door is made of the same steel plates, and can be moved forward on the rail by hand.
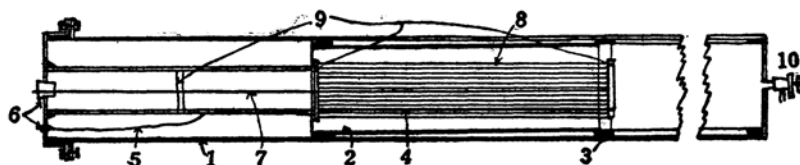

Fig. 3.   The screen-wall counter.

1. Screen-wall counter body, brass-made.   Inside diameter 75 mm., length 614 mm., thickness 1 mm.
2. Sample tube, copper-made. Inside diameter 67 mm., length 200 mm., two unit.
3. Joinband of above two copper tubes.   4. Grid support 5 drillrod.
5. Lead wire of grid.   6. Stupakoff seal.
7. Center wire. #28 Dumet wire.   8. Grid wire #30 Dumet wire 33 wires.
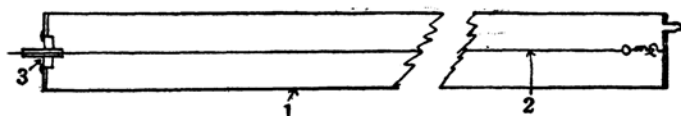9. Methacryl-resin.   10. Bellows value.

Fig. 4.   The anticoindence counter.

1. 2″ Copper tube. thickness 2 mm., length 784 mm.
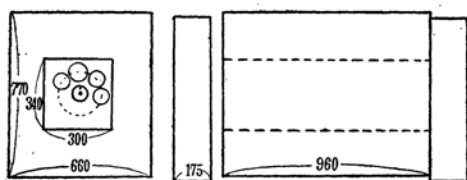2. Center wire 0.1 mm. W wire.
3. Stupakoff seal.

Fig. 5. The shielding.

High voltage and plate supply voltage are stabilized in the usual way.

Result

Sample A represents the upper part, sample B the mean part and sample C the lower part of the peat sediments. Chemical components of these ashes are analysed and shown in Table I.

TABLE I

CHEMICAL COMPONENT

Sample No.	Total Ash (%)	H_2O (%)	HCl (%) Insoluble	Si (%)	Al (%)	Fe (%)	Ca (%)	Mg (%)	Na (%)	K (%)
A	10	40	11.4	—	0.62	0.25	0.75	0.51	0.03	0.07
B	11	36	9.8	tr.	1.09	0.18	0.66	0.28	0.02	0.05
C	10	40	10.4	—	0.36	0.35	1.28	0.47	0.01	0.06

d) Electronic Circuit.—The circuit is shown in Fig. 6 in block diagram. High voltage regulator is shown it Fig. 7; this circuit is an automatic control of high voltage. Univibrator has
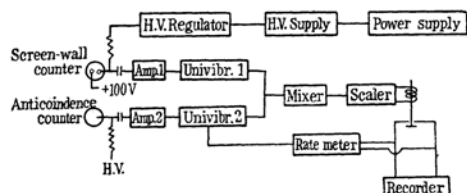

Fig. 6. Blockdiagram of circuits.

The variation of chemical components indicates that sample B has more clay part than the others. It can be explained in two ways: the pumice layer was dispersed into the peat layer or the chemical component migrated into the peat layer.

A chemical study has also been carefully made by Dr Yamagata[5]. Age determination of peat, carried out by the above method, requires about forty hours, for the background measurment twenty hours, and for the sample twenty hours. The two measurement can be carried out by changing the
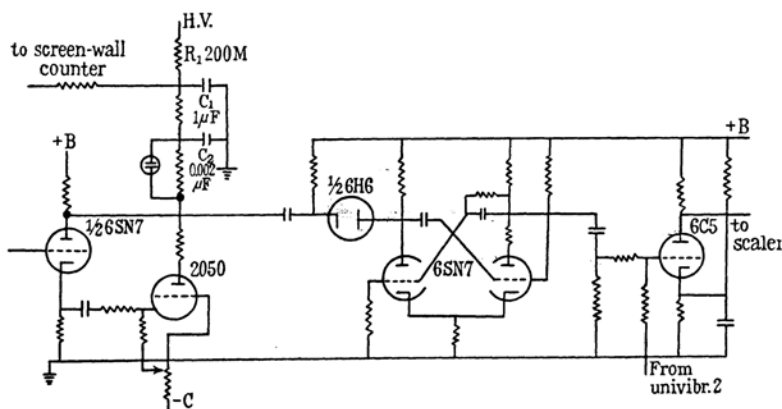

Fig. 7. High voltage regulater.

a dead time of 15 mμ seconds to prevent multiple pulses of the screen-wall counter. The mixer consists of the resistance network. The scaler is a scale of 16 using for 12AU7'S. The output of the scaler is fed to a thyratron. Each 16 counts of the screen-wall counter mark a knick on the recording paper, writing the background counting rate of the anticoindence counters, which is about 1400 cpm. During very long unattended runs which have to be made, there is the possibility of accidents. For this reason the automatic recording device was used.

position of the cylinder. These results are shown in Table II. Background of the instrument used, was about 4.5–5.5 cpm.

Conclusion

Several examples of the counts of the biological substances were shown by Yamazaki's[4] group and found to come between 5.5–6.3 cpm. Then the author considers that

5) N. Yamagata, Read before 1954's Geochemical Meeting of Chem. Soc. of Japan.

sample A can be regarded in the same way as the recent ones.

If so, sample B must be about 1000 years old and sample C 5000 years. The data are shown in Table II.

Dating by means of natural radio-carbon has some problems: constancy of ^{14}C specific activity, contamination by ^{14}C from different sources, constancy of cosmic ray flux, accuracy of measurement etc..

TABLE II

THE COUNTS OF NATURAL RADIO CARBON

Sample No.	Background			Sample counts			C^{14} c. pm.	Dating (y)	Carbon Ash (%)
	Time (min.)	Counts	c. p. m.	Time (min.)	Counts	c. p. m.			
A	1145.5	5856	5.11±0.067	1429.5	15296	10.7 ±0.086	5.59±0.10	0	4.79
B	1350.5	5856	4.34±0.056	1469.0	14584	9.25±0.084	4.91±0.10	1000±250	2.42
C	1161.5	5344	4.61±0.063	1095.5	8320	7.59±0.083	2.98±0.10	5000±400	2.40

The rate of sedimentation of peat is considered to be 1.6 mm. per year for sample A, 1.0 mm. per year for sample B, and 0.25 mm. per year for sample C.

If the rate of sedimentation has been the same as at present, sample C might have decreased its volume to about 1/6. During the 5000 years, sample C could have been pressed on the upper part or have lost some of its components by dissolution to descrease the volume to such an extend.

The volume of sample B has been also slightly decreased during the 1000 years. During the 5000 years, sedimentation of the total depth of this column region as thick as 480 cm. has been accumulated.

In other words the apparent mean rate of sedimentation is 0.7–0.9 mm. per year.

The author is of the opinion, however, that the present study is not interfered with by such factors, so far as the samples obtained from different depths at one position are studied. Further development is expected by fundamental experiments and by geochemical studies.