Geochemical Nature of Hot Spring Waters in Hot Springs National Park of Arkansas*

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ABSTRACT

1) The author found that there are linear relationships between water temperature and the content of total solids, between the bicarbonate and total solids contents, between the calcium and bicarbonate contents, between the bicarbonate and silica contents, between the calcium and magnesium contents, between the sodium and potassium contents, and between the sodium and chloride contents in hot spring waters, the data by Haywood were used. From these results, it is clear that all the hot spring waters in Hot Springs National Park, Arkansas are created by mixing of the thermal water rich in bicarbonate, calcium, silica and total solids, and slightly rich in sodium, potassium and magnesium etc., but poor in chloride and sulphate, rising from the depths of the earth with the shallow ground water poor in the above mentioned components.

2) The gases emitted from the orifices of the hot springs were found to be composed of about 97 % N_2 and others, about 3 % CO_2 and almost 0 % O_2 in volume. Hydrogen sulphide was not detected.

I) Introduction

About 44 hot springs are found on the strip of land, about 700 m long, at the foot of Hot Springs Mountain, all of which were covered for use as therapeutic water except two display springs.

The thermal waters from these springs were collected in a large reservoir and from there sent by pump to a tank located at a higher position on the mountain. Then, the water was distributed to each bath house by using hydrostatic pressure, after it had been cooled by heat exchange to a suitable temperature for bathing.

The chemical composition of 46 samples of water obtained from Hot Springs was reported by J. K. Haywood[1], 1902 who was at that time the Chief of Miscellaneous Division of the Bureau of Chemistry.

According to the report by Haywood, the hot spring waters contained about 280 ppm of total solids. The highest temperature of springs was 63 ℃. The data of water temperature and the contents of chemical components of 46 spring waters obtained by Haywood were used in

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* This work was done by the author during his stay in the University Arkansas as a Visiting Professor from September 1961 to August 1962.

** The author retired from the Professorship of Tokyo Metropolitan University in March 1969 and was granted the title of Emeritus Professor of the same university.

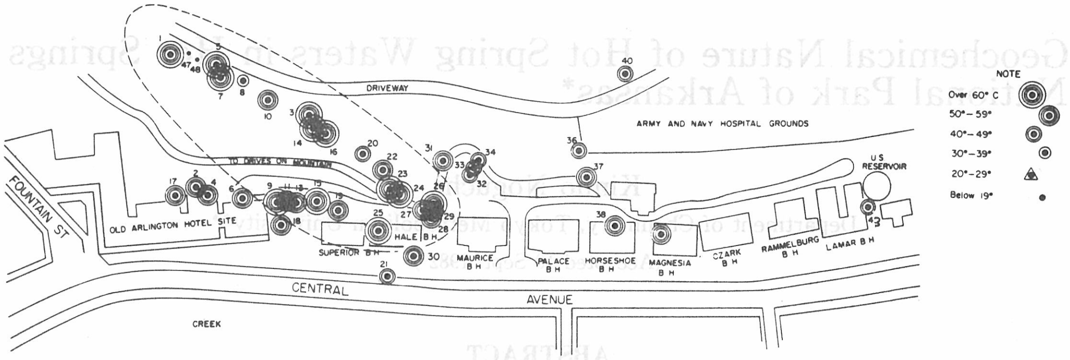

Fig. 1 Location of hot springs in Hot Springs National Park.
The numerals used in this figure are the spring numbers given by Haywood and Weed. The marks represent the temperature of springs. The highest temperature zone is surrounded with a dotted line.

the following discussion. The location of these springs is shown in **fig. 1.** This figure was originally made by W. H. Weed, geologist. The numerals in this figure are the spring numberes given by Haywood and Weed. In fig. 1 of this article the temperatures of springs are expressed with the marks in order to make clear the distribution of temperature in the hot springs area.

The temperature data and chemical data were not taken on the same day by Haywood and in many cases the time delay was considerable.

The variation of the chemical composition of water occurs almost always in accordance with the change of water temperature.

Therefore, the accurate temperature determination taken at the same time as the water samples were taken for analysis is necessary to obtain correct results. In the case of the discussion on the relation existing between water temperature and chemical components by using the data obtained by Haywood in 1901, it will be possible roughly to relate the chemical composition of one spring to the water temperature of the same spring.

II) Discussion on the chemical components of hot spring waters in Hot Springs National Park

If the position of 46 samples are plotted on a graph by taking water temperature on the vertical axis and total solids content on the abscissa, **fig. 2** is obtained. It is clear that a linear relationship exists between water temperature and the total solids content. In this case, samples Nos. 2, 8 and 43 etc. are slightly deviated to the lower temperature side from the linear relationship. It is supposed that the temperature of these samples dropped mainly on account of being not collected strictly at the orifices of the springs, or by cooling with the surrounding rocks owing to their small rate of flow.

If the bicarbonate content is taken on the vertical axis and the total solids content on the abscissa, **fig. 3** is obtained. In this case, a linear relationship clearly exists between the

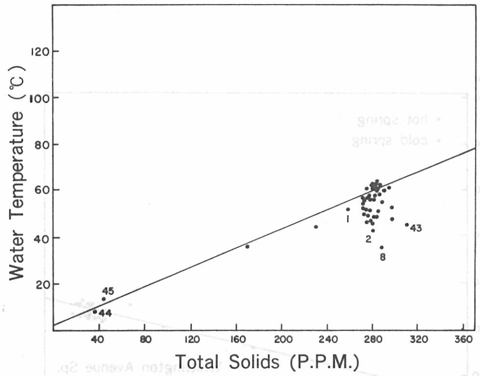

Fig. 2　Relation between water temperature and total solids content

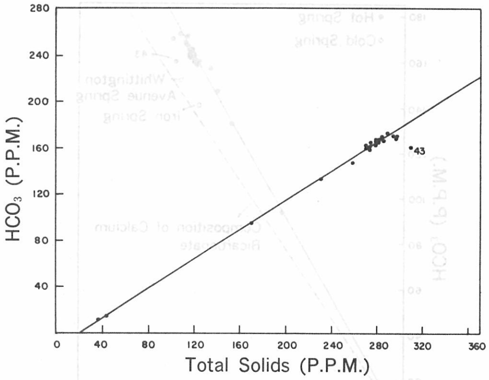

Fig. 3　Relation between bicarbonate and total solids contents

bicarbonate and total solids contents. No. 43 sample is slightly deviated from the linear relationship to the lower HCO_3 / tatal solids ratio. Between the bicarbonate and calcium contents there exists a linear relationship as shown in **fig. 4.** The fact that the HCO_3 / Ca ratio of hot spring waters is larger than that of calcium bicarbonate indicates that other bicarbonates such as bicarbonate of magnesium and iron etc. are contained in the hot spring waters.

If the silica content is taken on the vertical axis and the bicarbonate content on the abscissa, **fig. 5** is obtained. A linear relationship also exists between them. It is noteworthy that the SiO_2 / HCO_3 ratio of the cold springs such as Whittington Avenue Spring and Iron Spring are distinctly lower than that of hot spring waters.

Between the magnesium and calcium contents in the hot spring waters there exists a linear relationship as shown in **fig. 6** If the potassium content is taken on the vertical axis and the sodium content on the abscissa, **fig. 7** is abtained. A linear relationship also exists between them. The K / Na ratio of sample No. 43 is distinctly higher than those of other hot springs.

Between the chloride and sodium contents, between the chloride and total solids contents and between the sulphate and total solids contents there are linear relationships as shown in figs. 8 and 9. In **fig. 8**, it is noteworthy that the Cl / Na ratio of hot spring waters is distinctly lower than that of sodium chloride. It means that sodium dissolves in hot spring waters mainly not as chloride, but as bicarbonate. Sample No. 43 is clearly higher than other hot springs in the Cl / Na ratio. As for chloride in the hot spring waters, as shown in **fig. 9**, the content is very low. A line which passes through the points representing each spring except No. 43 is almost pararell to the abscissa. Also, in the case of sulphate, the content is very low. A line which passes through the points representing each spring except Nos. 43 and 37 is almost parallel to the abscissa.

From the above mentioned results, it can be explained as follows : In the hot springs area of Hot Springs National Park, Arkansas all the hot spring waters are created by mixing of the thermal water rich in bicarbonate, calcium, silica and total solids, and slightly rich in sodium, potassium and magnesium etc., but poor in chloride and sulphate, rising from the

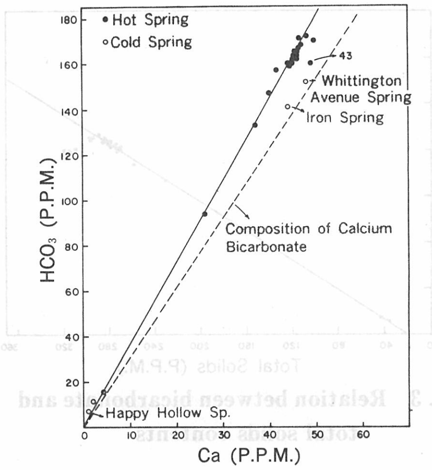

Fig. 4 Relation between bicarbonate and calcium contents

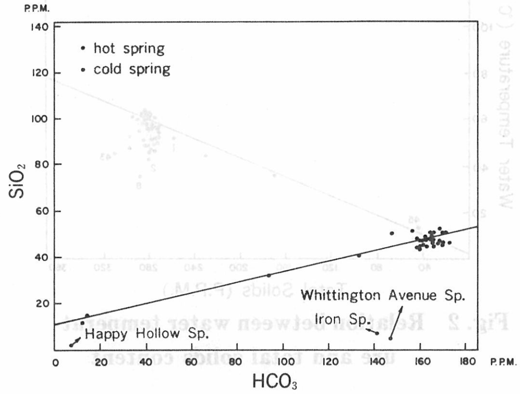

Fig. 5 Relation between silica and bicarbonate contents

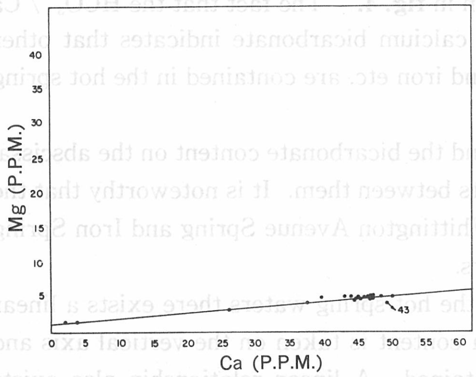

Fig. 6 Relation between magnesium and calcium contents

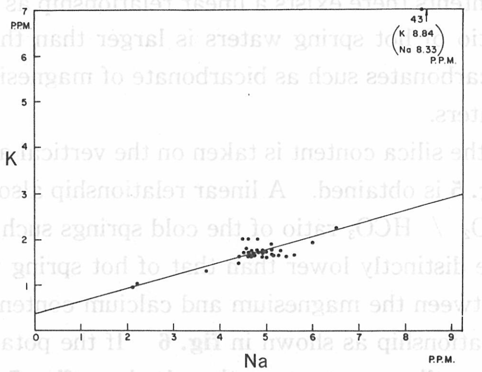

Fig. 7 Relation between potassium and sodium contents

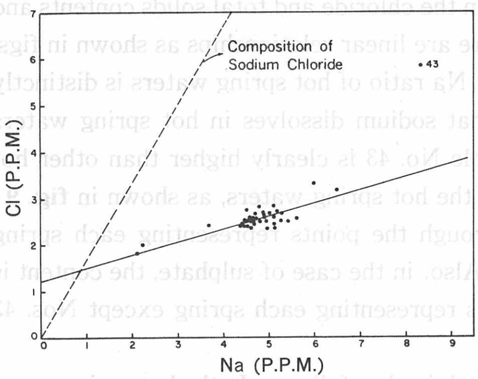

Fig. 8 Relation between chloride and sodium contents

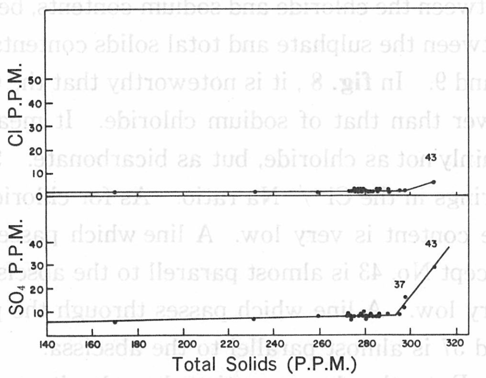

Fig. 9 Relation between chloride and total solids contents, and between sulphate and total solids contents

depths of the earth, with the shallow ground water poor in the above mentioned components.
As shown in fig. 1 ,No. 43 spring is located far from the central part of the thermal springs area. Therefore, it is supposed that the chemical composition of No. 43 spring has been slightly changed from that of the main thermal water by the reaction with its surrounding rocks during the ascent of thermal water.
If the hot spring waters are compared with the cold spring waters, the former are rich in silica, while the latter are poor in it.

III) Chemical composition of gases emitted from the orifices of hot springs in Hot Springs National Park

In 1901, Haywood examined the gas in the water samples from hot springs in Hot Springs National Park. In 1962, the author collected gases emitted from the orifices of Disply Spring No. 1 and Quapaw Bath House Spring in Hot Springs National Park and analyzed them at the orifices by using a gas apparatus of the Halden Type.
The results are as follows :

Table 1 Chemical composition of gases

Sample No.	Name of spring	Date	Water temperature	CO_2 vol.%	O_2 vol.%	N_2 and others vol.%
1)	Display Spring No. 1	Apr. 16, 1962	57.3℃	2.4	0.0	97.6
2)	Quapaw Bath House Spr.	Apr. 19, 1962	61.1	3.1	0.1	96.8

From table 1 , it was found that the gases emitted from the orifices of Display Spring No. 1 and Quapaw Bath House Spring were composed of about 97 % N_2 and others and about 3 % CO_2 in volume. The gas contained almost no oxygen. Hydrogen sulphide was not detected.

IV) Genesis of the thermal water in Hot Springs National Park

It was found that the hot spring waters in Hot Springs National Park were rich in bicarbonate and silica, while poor in chloride and sulphate and that the gases emitted from the orifices of hot springs, being accompanied with thermal water, was composed of about 97 % N_2 and others and 3 % CO_2 in volume. Almost no oxygen was contained. No hydrogen sulphide was detected.

From these facts, as for the genesis of thermal water in Hot Springs National Park, it js supposed as follows :
Volatile matters from the magma in the depths of the Hot Springs area are estimated to have been in a later stage and so the gaseous matters were composed of a large amount of water vapour and a small amount of carbon dioxide and nitrogen. No hydrogen chloride and no gaseous sulphur compounds such as sulphur dioxide and hydrogen sulphide were contained. During the ascent of the gaseous matters, they mixed with ground water in the depths. By

such a process, thermal water containing carbon dioxide was created. By the reaction of carbonic acid in the thermal water with its surrounding rocks, the solution rich in bicarbonate and in silica was created and at the same time the amount of carbon dioxide in gaseous matters decreased.

Consequently, nitrogen content in the gas phase increased.

It is presumed that all the hot spring waters in Hot Springs National Park were created by mixing of the thermal water, rich in bicarbonate and silica, which was made by the above mentioned process, with the shallow ground water poor in them.

Acknowledgments

Acknowledgment is made of the valuable advice and encouragement of Dr. K. Kuroda, Professor of the Universitiy of Arkansas.

References

1) Haywood, J. K., 1902
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2) Weed, W. H., 1902, Geological Sketch of Hot Springs, Arkansas ;
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