Radium, Vanadium, Chromium and Molybdenum Contents of the Hot Springs of Yunohanazawa, and their Seasonal Variations.

By Kazuo KURODA.

(Received January 18, 1940.)

It has recently been discovered spectroscopically by K. Kimura that the minute traces of vanadium, chromium and molybdenum are widely distributed in the mineral waters of Japan.[1] The author published on the vanadium, chromium and molybdenum contents of a number of hot springs of Japan, in the previous paper.[2]

In the present work, the author attempted the quantitative estimation of the amounts of these elements in the hot springs of Yunohanazawa, Hakone and the observation of their seasonal variations depending upon external conditions, such as abundant rain or drought. The radium content and its seasonal variation was also studied.

Methods of analysis. The analytical procedures are quite the same as those which were described already.[2] For the determinations of vanadium, chromium and molybdenum, Sandell's colorimetric method[3] was adopted. For the determination of radium, a 6000 c.c. portion of the mineral water was taken each time.

Results. A. *Temperature, pH and Total Residue.* The result of observation of the seasonal variations of temperature, *p*H and total residue is given in Table 1.

(1) Not yet published.
(2) This Bulletin, **14** (1939), 307.
(3) E. B. Sandell, *Ind. Eng. Chem.*, Anal. Ed., **8** (1936), 336.

Table 1. Temperature, *p*H and Total Residue of the "Gongen-yu" Spring.

No.	Date	Temperature (°C.)	*p*H	Total Residue (g./l.)
1	Aug. 20, 1938	42.0	2.6	0.85
2	Dec. 11, 1938	35.3	2.9	0.72
3	Mar. 16, 1939	48.0	2.8	0.82
4	Aug. 2, 1939	48.6	2.75	1.24
5	Aug. 22, 1939	50.3	2.6	1.41
6	Sept. 1, 1939	51.6	2.6	1.23
7	Sept. 9, 1939	51.6	2.6	1.22

B. *Vanadium, Chromium and Molybdenum Contents of the Hot Springs of Yunohanazawa and their Seasonal Variations.*

The variations of the amounts of vanadium, chromium and molybdenum in the "Gongen-yu" spring are shown in Table 2 and Fig. 1. The seasonal variations were found to be unexpectedly marked. The amount of vanadium fluctuated in the period of experiments between 28×10^{-6} and 98×10^{-6} g. per litre. The maximum amount (98×10^{-6} g.) occurred in the summer of 1939 after a heavy rain, and the minimum (28×10^{-6} g.) in the autumn of 1938 after a long drought. The amount of chromium fluctuated in the same period between 16×10^{-7} and 39×10^{-7} g. per litre, and the amount of molybdenum between 7×10^{-7} and 16×10^{-7} g. per litre. The relations between water temperature, *p*H and vanadium content are shown in Fig. 2 and Fig. 3.

Table 2.

A. Seasonal Variations of the Vanadium, Chromium and Molybdenum Contents of the Hot Springs of Yunohanazawa.

No.	Date	Temperature (°C.)	*p*H	V (g./l.)	Cr (g./l.)	Mo (g./l.)
1	Aug. 20, 1938	42.0	2.6	*98×10^{-6}	*25×10^{-7}	*7×10^{-7}
2	Dec. 11, 1938	35.3	2.9	28 ,,	23 ,,	8 ,,
3	Mar. 16, 1939	48.0	2.8	51 ,,	39 ,,	14 ,,
4	Aug. 2, 1939	48.6	2.75	72 ,,	16 ,,	10 ,,
5	Aug. 22, 1939	50.3	2.6	82 ,,	20 ,,	10 ,,
6	Sept. 1, 1939	51.6	2.6	84 ,,	23 ,,	16 ,,
7	Sept. 9, 1939	51.6	2.6	94 ,,	16 ,,	10 ,,

B. Seasonal Variations of the Vanadium, Chromium and Molybdenum Contents Expressed in Percentages to the Total Residue.

No.	Date	V	Cr	Mo
1	Aug. 20, 1938	0.0116	0.00029	0.00008
2	Dec. 11, 1938	0.0039	0.00032	0.00011
3	Mar. 16, 1939	0.0062	0.00048	0.00018
4	Aug. 2, 1939	0.0051	0.00012	0.00007
5	Aug. 22, 1939	0.0058	0.00014	0.00007
6	Sept. 1, 1939	0.0068	0.00019	0.00013
7	Sept. 9, 1939	0.0077	0.00013	0.00007

*) Quantitatively estimated by S. Oana.

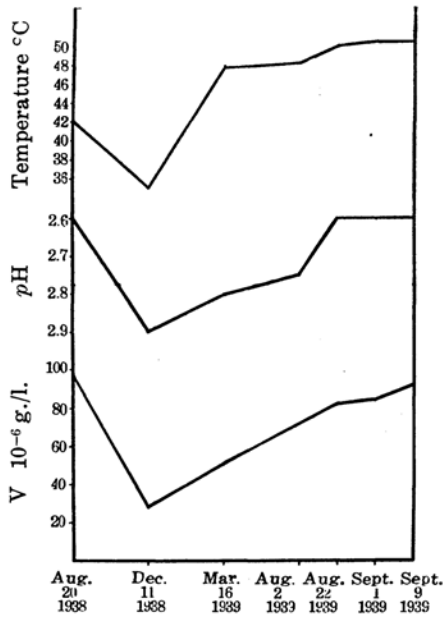


Fig. 1. Seasonal Variation of Temperature, *p*H and Vanadium Content.

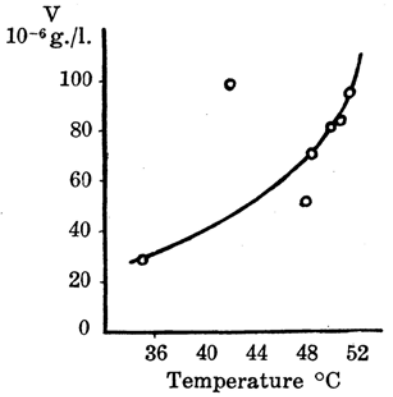


Fig. 2. Temperature and Vanadium Content.

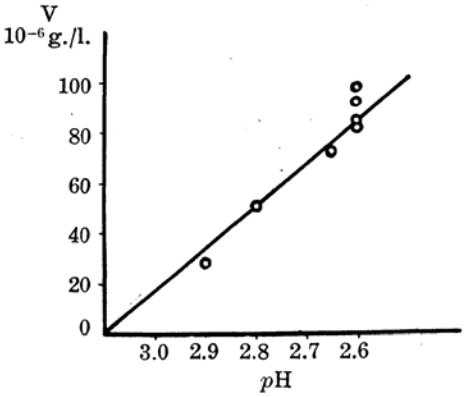


Fig. 3. *p*H and Vanadium Content.

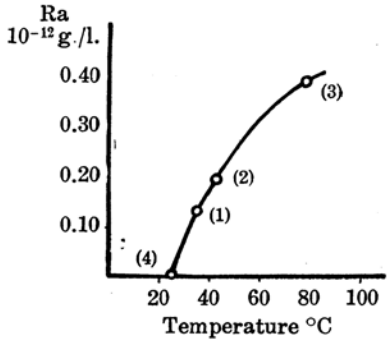
C. *Radium Content and its seasonal variation.* The results from the quantitative estimation of the amount of radium and the observation of its seasonal variation are shown in Table 3 and Table 4. The seasonal variation was also found. The relations between *p*H, temperature and radium content are shown in Fig. 4 and Fig. 5. The seasonal variation of the amount of radium seems to be quite the same as that of vanadium, as is shown in Fig. 6.

Table 3. Radium Content of the Hot Springs of Yunohanazawa. (Dec. 11, 1938).

No.	Springs	Temperature (°C)	*p*H	Ra (g./l.)	Ra (g. per g. of dry residue)
1	Gongen-yu	35.3	2.9	0.13×10^{-12}	0.18×10^{-12}
2	Kōbō-yu	41.0	2.8	0.19 ,,	0.19 ,,
3	Yoemon-yu	78.0	2.3	0.39 ,,	0.22 ,,
4	Fuezuka-yu	25.0	3.5	0.00 ,,	0.00 ,,

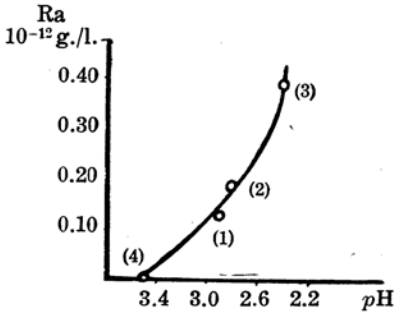
Table 4. Seasonal Variation of the Radium Content of the "Gongen-yu" Spring.

No.	Date	Temperature (°C.)	*p*H	Ra (g./l.)	Ra (g. per g. of dry residue)
1	Aug. 20, 1938	42.0	2.6	0.60×10^{-12}	0.71×10^{-12}
2	Dec. 11, 1938	35.3	2.9	0.13 ,,	0.18 ,,
3	Mar. 16, 1939	43.0	2.8	0.31 ,,	0.38 ,,



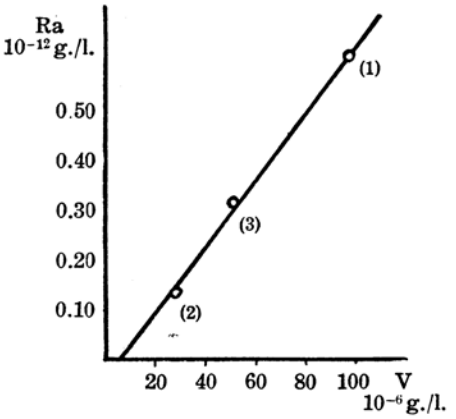
(1) Gongen-yu (2) Kōbō-yu
(3) Yoemon-yu (4) Huezuka-yu

Fig. 4. Temperature and Radium Content of the Hot Springs of Yunohanazawa.



(1) Gongen-yu (2) Kōbō-yu
(3) Yoemon-yu (4) Huezuka-yu

Fig. 5. *p*H and Radium Content of the Hot Springs of Yunohanazawa.



(1) Aug. 20, 1938 (2) Dec. 11, 1938
(3) Mar. 16, 1939

Fig. 6. Vanadium and Radium in the "Gongen-yu" Spring.

D. *Seasonal Variation of Iron Content and its Relation to that of Vanadium, Chromium and Molybdenum Content.*

The seasonal variation of iron in the same period is shown in Table 5. The amount of iron fluctuated between 21.7 and 0.2 mg. per litre. The maximum amount (21.7 mg.) occurred in the summer of 1938 after a heavy rain, and the minimum (0.2 mg) in the autumn of 1938 after a long drought. In Table 6, the seasonal change of the ratio of the amount of vanadium, chromium and molybdenum to that of iron is given.

Table 5. Seasonal Variation of the Iron Content of the Hot Springs of Yunohanazawa.

No.	Date	Fe (g./l.)	Fe (g. per g. of dry residue)
1	Aug. 20, 1938	0.0217	0.0258
2	Dec. 11, 1938	0.0002	0.0003
3	Mar. 16, 1939	0.0053	0.0065
4	Aug. 2, 1939	0.0011	0.0008
5	Aug. 22, 1939	0.0097	0.0068
6	Sept. 1, 1939	0.0034	0.0028
7	Sept. 9, 1939	0.0023	0.0019

Table 6. Seasonal Variation of the Ratios of Vanadium, Chromium and Molybdenum to Iron.

No.	Date	V/Fe	Cr/Fe	Mo/Fe
1	Aug. 20, 1938	45×10^{-4}	11×10^{-5}	3×10^{-5}
2	Dec. 11, 1938	1400×10^{-4}	1150×10^{-5}	400×10^{-5}
3	Mar. 16, 1939	962×10^{-4}	74×10^{-5}	26×10^{-5}
4	Aug. 2, 1939	655×10^{-4}	150×10^{-5}	91×10^{-5}
5	Aug. 22, 1939	85×10^{-4}	21×10^{-5}	10×10^{-5}
6	Sept. 1, 1939	247×10^{-4}	68×10^{-5}	47×10^{-5}
7	Sept. 9, 1939	408×10^{-4}	70×10^{-5}	44×10^{-5}

The ratios increased in the winter after a long drought, and decreased in the summer as a result of abundant rain.

The abundance of iron in the earth's crust is 4.7%. Vanadium constitutes 0.016% of the ten-mile crust, while chromium constitutes 0.033% and molybdenum 0.00075%. From these values, we can calculate the ratio of vanadium, chromium and molybdenum to the amount of iron in the earth's crust as shown in Table 7.

Table 7. Vanadium, Chromium, Molybdeum and Iron in the Earth's Crust.

V/Fe	Cr/Fe	Mo/Fe
34×10^{-4}	70×10^{-4}	16×10^{-5}

The ratio of vanadium to iron in the hot springs of Yunohanazawa is considerably greater than that of the earth's crust. The ratio of chromium to iron is (with one exception) always smaller than that of the earth's crust, while the ratio of molybdenum to iron is (with one

exception) greater than that of the earth's crust. Heavy metals, such as vanadium, chromium and molybdenum are supposed to be present abundantly in deep within the earth and, according to A. Gautier,[4] they are the essential constituents of juvenile waters. The author is of the opinion that the changes of the relative abundance of these metals are dependent upon the variations of the proportion of juvenile water in the mineral water, and it is expected that we can estimate the proportion from the results of the quantitative determination of these heavy metals in the mineral waters.

Summary.

(1) The radium, vanadium, chromium and molybdenum contents of the hot springs of Yunohanazawa, Hakone were determined.

(2) The seasonal variations of the amount of these elements were studied.

In conclusion, the author wishes to express his hearty thanks to Prof. Kenjiro Kimura for his kind guidance. It is also the author's pleasant duty to acknowledge the valuable advice offered by Dr. S. Oana. The expence for the experiments has been defrayed from a grant given to Prof. Kimura by the Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

---

(4) *Compt. Rend.*, **150** (1910), 436.