Studies on Nickel and Cobalt in Mineral Springs. III. Nickel Content of Some Mineral Springs and Their Deposits.

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The author's previous studies[1][2] on the nickel content of mineral springs were confined to that of acid vitriol springs rich in iron. Those poor in iron and high in pH value, for example, the carbonate spring and the common salt spring, are considered to contain smaller quantities of nickel. Their atomic ratio of nickel to iron is also not yet known to us.

After the publication of the last of this series, the author has planned the determination of nickel in mineral waters of all kinds. The study, which had to be given up half-way because of the investigation along the other line, has been published in this report.

Experimental.

Mineral Waters.

Methods for nickel determination. Nickel was determined colorimetrically by measuring the colour of nickelic dimethylglyoxime compound, which develops by the addition of the dimethylglyoxime reagent to nickel compound in the nickelic state. The details of the method were described in the previous paper[1], the outline of which is as follows. Nickel in mineral waters was converted into nickel dimethylglyoxime by the addition of the dimethylglyoxime reagent in the presence of tartaric or citric acid. Nickel dimethylglyoxime was extracted with chloroform, and, in the chloroform layer, was decomposed with dilute hydrochloric acid. After the acid layer was treated with bromine, the dimethylglyoxime reagent was added again, then the colour of nickelic dimethylglyoxime thus developed was measured by the Pulfrich photometer using the filter S45 (450 mμ).

Acid Hydrogen Sulphide Springs.

In the prveious papers the nickel content of acid vitriol springs was represented. The acid hydrogen sulphide springs, however, are considered to belong to another group. The examples taken up here are:

(1) Sirahata no yu, Kusatu.
(2) Netu no yu, Kusatu.
(3) Yubata no yu, Kusatu.

Nickel and iron contents, determined by the colorimetric and the volumetric methods respectively, are:

(1) N. Tanaka, this Bulletin, **18** (1943), 201.
(2) N. Tanaka, this Bulletin, **18** (1943), 365.

		Nickel content (γ/l.)	Iron content (g./l.)
(1)	Sirahata no yu	less than 2	0.0376
(2)	Netu no yu	less than 2	0.0144
(3)	Yubata no yu	less than 2	0.0603

Therefore, the atomic ratio of nickel to iron is calculated as follows.

(1)	Sirahata no yu	less than 0.51×10^{-4}
(2)	Netu no yu	less than $1.3_2 \times 10^{-4}$
(3)	Yubata no yu	less than 0.32×10^{-4}

Carbonate Springs.

The samples taken up here are:

(4) Nanasigure, Iwate Prefecture.
(5) Zyōhōji, Iwate Prefecture.

Both are noted for containing the large quantity of boric acid. They were determined by Dr. K. Kuroda and his co-worker(3) in August, 1941 and reported as follows.

		Temp. (°C)	pH	Content of boric acid (g. B_2O_3/l.)
(4)	Nanasigure	16.0	6.4	2.594
(5)	Zyōhōji	12	6.5	2.5788

Taking a large amount of the sample waters, the determination of nickel was made. The results obtained:

		Sample taken	Nickel content		Total residue
		(l.)	(γ)	(γ/l.)	(g./l.)
(4)	Nanasigure	11.00	8.55	0.78	11.691
(5)	Zyōhōji	9.50	16.9	1.78	18.792

The iron content of Nanasigure, determined colorimetrically, is 131.2 γ/l. The nickel percentage in total residue and the atomic ratio of nickel to iron obtained are as shown in the following.

		Nickel in total residue (%)	Ni/Fe -atomic ratio
(4)	Nanasigure	0.67×10^{-5}	0.57×10^{-2}
(5)	Zyōhōji	0.95×10^{-5}	——

Simple Cold Springs.

Mamegara-hudō-yu, which is located near Sirakawa, Hukusima Prefecture, was taken up as an example. In this spring the occurrence of nickel had been found with spectrograph.(4) The spring belongs to the simple cold spring, with 12.5°C in temperature and 6.7 in pH value (determined on the 1st of June, 1941). The nickel content, the total and the ignition residues are:

(3) K. Kuroda and T. Tagaya, *Bull. Inst. Phys. Chem. Research* (Tokyo), **21** (1942), 181.

(4) By Prof. Kenjiro Kimura.

Nickel content	6.7_5 γ/l.
Total residue	0.0803 g./l.
Ignition residue	0.0633 g./l.

Therefore, 0.0084% was obtained as the nickel percentage in total residue.

Determined by the colorimetric method, on the other hand, the iron content of this spring was 246 γ/l. and, therefore, the atomic ratio of nickel to iron is 2.6×10^{-2}.

Ikaho, Gunma Prefecture.

At Ikaho, there are many mineral springs of several types. All of these are drawn into a pipe, from which the sample water was taken. Nickel and iron in both of "the filtrate" and "the precipitate" were determined separately, because some precipitates had appeared in the sample waters from being kept on standing for a long time. One litre of the filtrate contains 1.9 γ of nickel and 53 γ of iron, while the precipitate derived from one litre of the water contains 1.8 γ of nickel and 4.44 mg. of iron. From the results, it was known that one litre of the original water contains 3.7γ of nickel and 4.49 mg. of iron. The atomic ratio of nickel to iron, therefore, was calculated as follows.

Ni/Fe-atomic ratio	7.8×10^{-4}

The atomic ratio of nickel to iron in the filtrate is so much larger than that in the precipitate that it is concluded that the nickel remains mostly in the filtrate even after almost all of iron has precipitated from the solution.

Service Water of Tokyo.

The nickel content of the service water of Tokyo was determined for the purpose of estimating the nickel content of river waters. The sample was taken every day from November 14, 1942 to December 2. The nickel, iron and total residue contents shown in the following, therefore, mean the averages of those for some twenty days.

Nickel	1.18 γ/l.
Iron	82.5 γ/l.
Total residue	0.04430 g./l.

From the result, the nickel percentage in total residue and the atomic ratio of nickel to iron are calculated at 0.0026_6% and 1.36×10^{-2} respectively.

Deposits.

The deposits taken for the present investigation are of three types, which are formed from the mineral spring Ikaho. The first (Sample No. 1) is the so-called "ocherous deposit", the second (Sample No. 2) calcareous deposit, and the third (Sample No. 3) also calcareous but with somewhat different appearance.

No. 1 mainly consists of ferric oxide, and is apparently non-crystalline. No. 2 and No. 3 consist mainly of calcium carbonate with a little of ferric compound, the former of which shows crystalline appearance, while the latter is non-crystalline. X-ray powder photograph of No. 2 agrees with that of calcite type, while that of No. 3, that of aragonite type. It, therefore, becomes clear that the difference of the appearance between No. 2 and No. 3 is due to the difference of their crystalline state, and is attributed to the difference of the condition of formation. The determination of nickel was made in the same way as in the case of the mineral waters, using the filtrates obtained by decomposing the samples with hydrochloric acid. The nickel content of these deposits is shown in Table 1, together with the contents of iron and of insoluble residue (mainly SiO_2).

Table 1.

	No. 1	No. 2	No. 3
Nickel (%)	0.79×10^{-4}	$<2.0\times10^{-4}$	$<2.0\times10^{-4}$
Iron (%)	38.0	2.2	3.2
Insoluble residue (%)	22.08	1.29	0.90
Ni/Fe-atomic ratio	2.0×10^{-6}	$<8.7\times10^{-5}$	$<6.0\times10^{-5}$

The analyses of No. 2 and No. 3 were carried out to find out the difference between the nickel content of No. 2 (calcite type) and that of No. 3 (aragonite type). However, the purpose was not attained owing to the lack of the samples.

Atomic Ratio of Nickel to Iron.

The determination of nickel in mineral waters of several types has been carried out polarographically by K. Heller, G. Kuhla and F. Machek[(5)]. The nickel content of the common salt spring ("Marienbader Quelle"), according to their report, falls between 8.3 γ/l. and 0.28 γ/l., that of the bitter spring ("Karlsbader Quelle"), less than 0.43 γ/l. and that of the radioactive spring ("Curiequelle"), less than 0.14 γ/l. In the present study, the maximum content of nickel is 6.7_5 γ/l. of the simple cold spring, Mamegara-hudō-yu, while the minimum is 0.78 γ/l. of the carbonate spring, Nanasigure, with the exception of the hydrogen sulphide springs, Kusatu giving less than 2 γ/l. As shown in Table 2 the nickel content of most of these springs is much smaller than that of acid vitriol springs represented in the previous papers.

Table 2.

Type of mineral spring	Number of samples	Nickel content (γ/l.) Maximum	Minimum	Median
Acid hydrogen sulphide spring	3	<2	<2	<2
Acid vitriol spring	17	9.38×10^{3}	4.1_5	133
Carbonate spring	2	1.78	0.78	1.28
Simple cold spring	1	—	—	6.7_5
Ikaho (Iron carbonate spring+Bitter spring)	1	—	—	3.7

(5) K. Heller, G. Kuhla and F. Machek, *Mikrochemie*, **23** (1937), 78.

On the other hand, it seems that there is a relation between the atomic ratio of nickel to iron and the type of mineral spring. The atomic ratio of nickel to iron of each type is summarized in Table 3, together with that of the acid vitriol springs.

Table 3.

Type of mineral spring	pH	Ni/Fe -atomic ratio		
		Maximum	Minimum	Median
Acid hydrogen sulphide spring	1.5	$<1.32\times10^{-4}$	$<0.32\times10^{-4}$	$<0.51\times10^{-4}$
Acid vitriol spring	2.4*	16.21×10^{-4}	0.67×10^{-4}	1.35×10^{-4}
Carbonate spring	6.4	—	—	0.57×10^{-2}
Simple cold spring	6.7	—	—	2.6×10^{-2}
Ikaho (Iron carbonate spring +Bitter spring)	—	—	—	7.8×10^{-4}

* Median.

The data of nickel content of mineral springs other than acid vitriol springs are too deficient to discuss the relation of the atomic ratio of nickel to iron and the type of mineral spring. The difference between each type, however, is so marked that we can find a relation thereof. The atomic ratio of acid vitriol springs shows to be smaller than that of mineral springs of other types, and than either that of the abundance ratio in the earth crust or that of the igneous rocks. On the contrary, the atomic ratio of nickel to iron of the carbonate spring nearly corresponds to that of the igneous rocks. Even it, however, is remarkably small in comparison with the atomic ratio of nickel to iron in the sea water (about 1/20) obtained by V. M. Goldschmidt[6]. The simple cold spring, Mamegara-hudō-yu, shows the remarkably great atomic ratio of nickel to iron, but

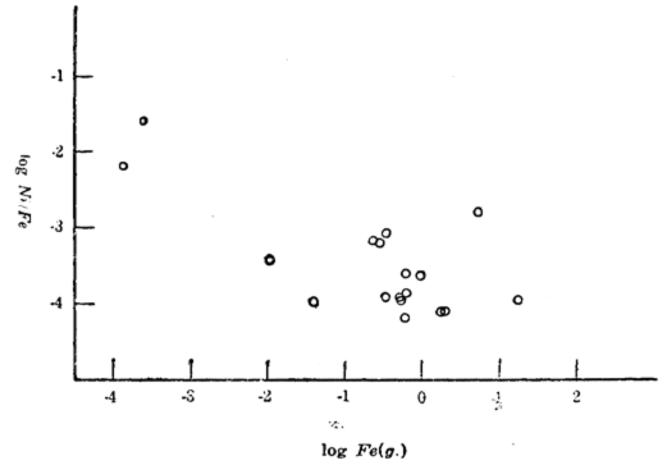

Fig. 1.

(6) V. M. Goldschmidt, *Fortschr. Mineral. Krist. Petrog.*, **17** (1933), 112.

it is considered to be exceptional, because it contains a larger quantity of nickel than others of the same type. The idea would be verified by the fact that nickel is detected spectroscopically in this spring contrary to most of the simple cold springs in which no nickel is detected by the same method. Since the spring, on the other hand, contains iron in the ordinary quantity to most of the simple cold springs, the atomic ratio of nickel to iron of the former shows greater than that of the latter. Consequently, most of the simple cold springs seem to be of smaller atomic ratio of nickel to iron than the spring, Mamegara-hudō-yu.

Service water of Tokyo, gives the intermediate value of the igneous rocks and the sea water.

In Fig. 1, the relation between the iron content and the atomic ratio of nickel to iron is shown. The smaller the iron content, the greater is the atomic ratio of nickel to iron.

Fig. 2 shows the relation between the pH value and the atomic ratio of nickel to iron. In general, the greater the pH value, the greater is the atomic ratio of nickel to iron.

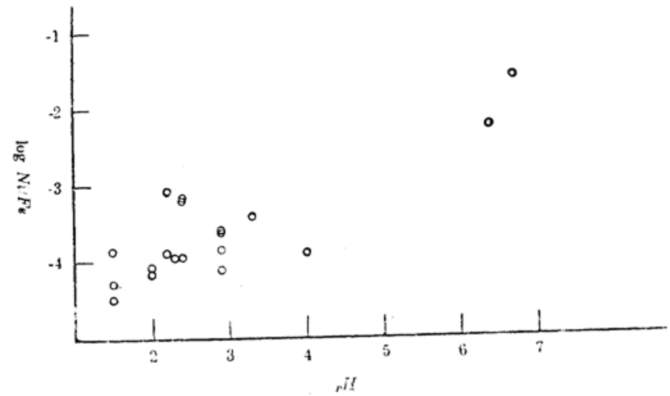

Fig. 2.

The fact that the sea water shows the greatest atomic ratio of nickel to iron is explained by the investigation on the distribution of nickel between the solution and the deposit. It has been confirmed in the experiment on the mineral springs, Kinkei and Tentoku, that the ferric oxide produced from the mineral waters by being kept on standing is generally accompanied by little nickel. In the present study the same fact is found in the mineral waters of Ikaho. The atomic ratio of nickel to iron, both of the filtrate and precipitate, is summarized as shown in Table 4.

Table 4.

	Ni/Fe -atomic ratio	
	Filtrate	Precipitate
Kinkei	7.7×10^{-4}	0.082×10^{-4}
Tentoku	17.9×10^{-4}	1.7×10^{-4}
Ikaho	3.4×10^{-2}	3.9×10^{-4}

Moreover, the fact that the ocherous deposit of Ikaho contains a very minute quantity of nickel, and that its atomic ratio of nickel to iron is extremely smaller than the atomic ratio of the waters, shows the same phenomenon occurs in nature as in the laboratory.

In the weathering zone, iron of the hydrosphere deposits accompanied by little nickel, and therefore, it produces ocherous deposits poor in nickel, while nickel is transported with the surface waters, increasing the atomic ratio of nickel to iron with the deposition of ferric hydroxide. It finally enters into the sea, where since most of the rest of iron deposits, the atomic ratio of nickel to iron becomes the greatest.

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