

THE RADIOACTIVE MANGANIFEROUS NODULES FROM TANOKAMI, OOMI PROVINCE.

By **Satoyasu IIMORI.**

Received December 23, 1925. Published March 28, 1926.

The feeble radioactive property of the characteristic black nodules from the bed of the Kichijo River, that runs along the Tanokami Hill, Oomi Province, has not been noticed until the author visited the locality in November, 1922. On that occasion, similar ones were also found embedded in a part of the rock body which lies just on the back of the hill side where the stream takes its rise. The nodules vary in size from about a half to two centimeters across, occurring as a pebbly constituent of the gravel-bed of the river, and are irregular in shape often with rounded edges. Some of them, often consisting, in the interior, of a mass of quartz pieces and grains of pale greenish clayey matter, are merely surrounded by a thin coating of the black material. Lying embedded in the rock which chiefly consists of coarse grains of quartz and the same clayey material as that which sometimes forms the inner parts of certain pebbly specimens, the nodules are considered to be composed of the essential black concretionary matter filling cracks of the rock.

Thin sections proved at once the black portion to be opaque and amorphous in structure, cementing abundant minute inclusions consisted of frag-

ments of quartz and other siliceous minerals, and its secondary nature was well brought out. The mean density, determined upon six pieces containing the inclusions which amounted to about sixty per cent of the material, was found to be 2.72. Both of the specimens were brittle with a hardness of about 3 and brown black to steel grey in colour. The luster was resinous, sometimes dull and coke-like, the fracture was often fibrous or conchoidal and the streak brown or black. By treatment with hydrochloric acid, the black portion of the nodule was readily and completely dissolved with evolution of chlorine, leaving a considerable residue of nearly white sandy matters, and the solution mainly gave the reactions of manganese and iron.

Analysis. In selecting material for analysis it was found practically impossible to avoid siliceous inclusions. A number of specimens of both varieties, therefore, were separately pulverized, and the portions which contained least amount of inclusions were taken for analysis; nevertheless, the insoluble gangue was present to the extent of 60 to 90 per cent as indicated in the analytical results mentioned below. Since the radioactive property was not detected in the insoluble portion, the investigation was principally directed to ascertain the composition of the soluble part. To carry out the analysis, the manganese was separated from iron and alumina by using barium carbonate in a neutral solution and by a basic acetate precipitation. The state of oxidation of manganese was determined by iodometry, that is to say, in measuring the quantity of iodine, which was liberated by the chlorine evolved by the action of hydrochloric acid upon the sample. The analytical results were as follows:

Constituents	Per cent in the pebbly nodule, found on the stream bed.		Per cent in the nodule, found on the hill side.
	(a)	(b) *	
Residue insoluble in hydrochloric acid	68.57	69.26	89.66
MnO ₂	14.64	15.76	4.55
MnO	3.69	(as Mn ₃ O ₄)	(as Mn ₃ O ₄)
Fe ₂ O ₃	4.66	4.70	1.20
Al ₂ O ₃	0.78	0.83	0.82
PbO	—	—	0.40
CuO	—	—	trace
ZnO	—	—	0.31
CaO	0.74	(not looked for)	—
Ignition loss, less oxygen due to conversion of MnO ₂ to Mn ₃ O ₄	6.75	(not looked for)	2.95
Oxygen due to MnO ₂ → Mn ₃ O ₄	—	—	0.40 **
	99.83		100.29

* Determined on a separately powdered portion of the same sample.

** Assuming that the ratio of MnO₂ to MnO is the same as the pebbly nodules.

In the insoluble residue of the pebbly nodule mentioned in the above table contains 55.9 per cent of silica, while 70.0 per cent of silica was found in the nodule from the hill side. The following table contains the results of the analysis recalculated excluding the insoluble part. For the purpose of comparison, some of analysis of wads given in Dana's Mineralogy⁽¹⁾ were quoted in the same table, together with the author's results.

Constituents	The pebbly sample	The hill-side sample	Wad	
			(A)	(B)
MnO ₂	49.7	} 59.8	66.2	68.9
MnO	12.6		7.9	7.5
Fe ₂ O ₃	15.8		—	} 2.2
Al ₂ O ₃	2.6	9.9	—	
PbO	—	4.8	} 0.2	—
CuO	—	(small)		—
ZnO	—	3.7		—
CaO	2.5	—	5.0	14.4(BaO)
H ₂ O	16.8	7.2	15.3	5.1
(MgO & Na ₂ O)	—	—	3.8	—
Total	100.0	100.0	100.0	98.1

The water was calculated from the ignition loss taking in consideration of the necessary correction for the oxidation of the manganese and the evolution of oxygen. Since the material of the rock body in which the nodules were included is practically identical with the insoluble residue previously described, similar determinations on the ignition loss were made on some pieces of the mother rock. The difference of these two determinations furnishes an approximate value of the water for the soluble part of the nodules, taking the percentage of the insoluble portion into consideration.

On the examination of the arc spectra taken by means of a quartz spectrograph, it was shown that besides the lines of the elements above described those of lead, copper, cobalt and molybdenum were detected in the soluble portion of the pebbly sample. The residue from the insoluble portion which was obtained by expelling silica by repeated evaporations with hydrofluoric acid and sulphuric acid, gave the lines of copper, tin, iron, aluminium, zinc and manganese. And in the zinc fraction of the hill-side sample, the lines of aluminium and cobalt were observed.

On the whole, it may be said that the chemical compositions of these two kinds of nodules are nearly the same and they belong to the same mineral. The analytical results, as well as the physical properties of the

(1) E. S. Dana, System of Mineralogy, IV Edition, p. 258.

soluble portion pretty resemble with those of certain wads, except the facts that the former contains some iron oxide.

The Radium Content. Though none of radioactive constituents was chemically detected in both of the nodules, they clearly show a feeble radioactivity, when roughly examined by means of an alpha-ray electroscope. The following results, compared with the activity of uranium oxide, were obtained.

Materials examined.	Activity per gr.
Uranium oxide (as a arbitrary standard)	100.
Hokutolite from Shibukuro (for the comparison)	3.5
<hr/>	
The pebbly sample (siliceous inclusions: 70.4%)	1.3
The hill-side sample (siliceous inclusions: 92.0%)	2.0
The insoluble residue, obtained from the pebbly sample by once extraction with HCl	0.25
Pieces of the rock, in which the nodules were found embedded . .	0.1
A mass of minute biotite flakes, collected on the bed of the Kichijo River	0.00
Pieces of a rock, stained black with the manganese oxide, collected on the river bed	0.2

Thus it appears that the radioactivity is almost concentrated in the soluble portion of the nodules, namely, in the black manganiferous matter. The activity is, however, so feeble that it needs exposures of more than three weeks in order to give the distinct effect on a photographic plate. Accordingly, there was no proper means for determining the radioactive constituents in these specimens except the measurement of the radium content. The estimation method of radium simply consisted in boiling about one gram of the powdered sample with about 4 c.c. of concentrated sulphuric acid in a test tube made of quartz glass. The emanation liberated was transferred into an emanation electroscope of the Soddy's type⁽¹⁾, and its effect on the rate of leak was measured in the usual way. The electroscope was standardized by using an aliquot portion of a preparation of barium-radium chloride which was previously evaluated by the γ -ray method. The constant of the electroscope, thus determined, was 24.8×10^{-12} (*i.e.* one division per minute = 24.8×10^{-12} gr. radium). The results obtained are given below, the activities recorded being the means of several observations.

(1) F. Soddy, *Phil. Mag.*, [6], 18 (1909) 846.

Substances	Sample taken (gr.)	Activity (div. per min.)	Amount of Ra. (%)
The pebbly nodule	0.9139	4.24	1.15×10^{-8}
The hill-side nodule	1.3273	6.95	1.30×10^{-8}
" " "	0.9929	5.27	1.32×10^{-8}

As the whole activity is, however, attributed to the soluble part of the nodules, it follows that the amount of radium in the soluble portion of the pebbly nodule is 3.88×10^{-8} per cent, and that of the hill-side nodule 1.64×10^{-7} per cent. Thus the most remarkable character of these nodules is the fact that they contain radium in the black soluble portion, the amount of which is nearly thousand times that of the ordinary igneous rocks. The ordinary igneous rocks contain generally about 10^{-10} per cent of radium. And as might be expected, the nodules found on the river bed carries somewhat less amount of radium which is considered to have been lost probably under the action of stream water. Besides these nodules there are found in the same river bed, several rock blocks, impregnated with this radioactive secondary manganese iron oxide. This fact suggests the previous existence of primary uranium bearing minerals in this vicinity.

In conclusion, the author wishes to thank Messrs. J. Sasaki and J. Ooe for their laborious assistance in collecting the minerals, and Mr. J. Yoshimura for help in the spectroscopic examination.

The Institute of Physical and Chemical Research,
Hongo, Tokyo.