FORMATION OF THE RADIOACTIVE MANGANIFEROUS DEPOSITS FROM TANOKAMI, AND THE SOURCE OF MANGANESE IN THE DEEP-SEE MANGANESE NODULES.[1]

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In the previous paper[2] it has been shown that the feebly radioactive manganiferous deposit from the Tanokami district, Oomi Province, occurs in two modes, one in irregular masses charging narrow cracks of the hill-side rock, and the other in small nodular forms as one of the pebbly constituents of the gravel-beds of a stream. Both of them leave, on treatment with hydrochloric acid, a considerable residue of quartz grains with a large amount of faint yellowish green clayey matter. It so happens on close examination that this residue is practically identical with the fragments of rock body on the hill side, through which the deposit is disseminated. The rock, with which this manganiferous deposit is so intimately associated, seems to be consisted essentially of a kind of altered granitic rock, a marked feature being the presence of the above stated greenish clayey matter.

Similar manganese nodules, hitherto reported, have chiefly been found on the bottom of the deep sea and sometimes of particular creeks or rivers. The following will probably be the conspicuous cases so far as known, namely, those from the beds of Pacific Ocean[3] and of Loch Fyne in Scotland[4], from Onybygambach, New South Wales[5], and those found in Mesozoic deep-sea deposit from Borneo, Timor and Rotti[6], and on the bed of the River Vistula[7]. All of these nodules are in accord with one another in respect of being largely composed of insoluble siliceous gangue and constantly containing a tolerable amount of iron besides manganese in the black portion soluble in hydrochloric acid. The proportion of the gangue varies of course considerably, but the composition of the soluble part is

(1) Read before the Annual Meeting of the Chemical Society of Japan, April 5, 1927.

(2) This journal, **1** (1926), 43.

(3) J. Gibson, "Challenger Rept. Deep-Sea Deposits," (1891), 417–423; F. W. Clarke, "The Data of Geochemistry," (1924), 135. (Challenger Collection).
A. Agassiz, *Am. J. Sci.*, [4] **9** (1900), 33. (Albatross Collection).

(4) J. Y. Buchanan, *Chem. News*, **44** (1881), 253; *Proc. Roy. Soc. Edinburgh*, **18** (1890), 19.

(5) W. M. Doherty, *Australassian Assoc. Adv. Sci.*, **6** (1898), 339; *Am. J. Sci.*, [4], **9** (1900), 72.

(6) G. A. F. Molengreaff, *Proc. Roy. Acad. Amsterdam*, **18** (1915), 415; cf. "Neues Jahrb. Min. Geol"., (1916), II 233.

(7) E. Dittler, Tsch. Min. Mitt., **36** (1924), 164: cf. *J. Chem. Soc.*, **128** (1925), Abs. (ii), 322.

generally in close analogy in different sorts. The radium content of the nodules, however, has not been determined by the former investigators, except the ones from the bed of Pacific Ocean.[1] For the comparison of the chemical constituents, therefore, the original analyses by J. Gibson[2] and by J. Joly[3] made on the oceanic nodules from the Pacific Ocean, as well as that of the Tanokami nodules previously made by the author[4] are reproduced in the following tables.

Analyses of the soluble portion of the nodules.

Constituents / Nodules from	MnO_2 & MnO	Fe_2O_3	Al_2O_3	PbO	CuO	ZnO NiO CoO	CaO	MgO	H_2O	Tl_2O	Acidic oxides	Total
The Tanokami Hill, Japan. (4)	59.8	14.6	9.9	4.8	(small)	3.7	—	—	7.2	—	—	(100)
The Pacific Ocean. (2)	52.4	27.0	6.3	0.1	0.7	2.7	4.0	4.6	—	0.06	2.0*	99.0

* MoO_3, V_2O_5, P_2O_5, SO_3, CO_2.

Amount of radium in the nodules

Manganese nodules from	Variety.	Amount of the insol. gangue. %	Radium content	
			Ra per gr. of the material. gr.	Ra per gr. of the soluble portion. gr.
Tanokami[4]	The hill-side deposit.	89.7	131×10^{-12}	1640×10^{-12}
	The river nodule.	68.9	115	388
Pacific Ocean[3]	Nodule, collected at a depth of 2750 fathoms.	16.0	24	29
	" " " " " 2370 fathoms. (off W. Coast of S. America.)	17.9	21	26

Although the two differ in certain particulars, as in lime, magnesia, thallia and acidic oxides, yet the general correspondence is remarkably close, and the presence of minor constituents, such as lead, copper, zinc, nickel, cobalt and radium, is strikingly harmonious. As regards the

(1) J. Joly, *Phil. Mag.*, **16** (1908), 190.
(2) Loc. cit.
(3) Loc. cit.
(4) Iimori, loc. cit.

content of radium in the Tanokami nodules, attention has already been directed to the fact that the irregular masses of the manganiferous deposit occurring on the hill-side carry more radium than that in the nodules existing on the river bed, viz. the amount of radium in the former being about four times as much as that in the latter. This fact is possibly to be ascribed to the leaching action of stream water. The far less content of radium in the oceanic nodules will, therefore, be so explained that they have lost the greater part of the radium or uranium while lying on the bottom of the deep sea through a long period of geological time, and yet, as will be seen in the above figures, the richness in radium of the oceanic manganese nodules is obviously greater than that which we are aware of the rocks on the land, the average values being 1.7×10^{-12} and 1.1×10^{-12} grams radium per gram for igneous and sedimentary rocks respectively.(1)

Regarding the source of manganese which constitutes the deep sea nodules, no opinion seems yet to be substantially decisive. G. W. Gümbel supposes that the manganese is derived from submarine springs.(2) J. Murray attributes it to the product of the subaqueous decomposition of volcanic débris.(3) J. Y. Buchanan(4) and others(5) solely regard as due to the manganese dissolved in the sea water. Being formed, however, of the manganese universally dissolved, usually contained but in trace, in the sea water, the nodules would be found in everywhere of the bottom of the sea. But, in fact, such a mode of distribution has never been observed, and its sporadic occurrence in the bottom of the deep sea or special creeks shows, I suppose, that the manganese may probably be derived from certain manganese minerals, possibly peculiar ferromanganese minerals containing uranium, locally cropped out on the ocean floor.

Hence it will be so explicable that the manganese deposits from the Tanokami district should be formed by the same process as the cases of the sea nodules. While the region of the Tanokami hill and the neighbourhood had, once in early ages, been lying beneath the water, the veins and dykes of granitic pegmatite including the original manganese and iron bearing radioactive minerals, for instance, such as wolframite which is now sometimes found in this district in small quantity, were subjected to the aqueous alteration. Some of the constituents such as manganese, iron etc.

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(1) A. Z. Eve and D. Mc Intosh, *Phil. Mag.*, [6], **14** (1907), 231.
(2) *Jahr. Min.*, (1876), 869; cf. *J. Chem. Soc.*, **38** (1880), Abs., 16.
(3) *Proc. Roy. Soc. Edinburgh*, **9** (1876), 255; cf. *Bull. U. S. Geol. Survey*, **770** (1924), 135.
(4) *Proc. Roy. Soc. Edinburgh*, **18** (1890), 17; cf. *J. Chem. Soc.*, **60** (1891), Abs., 994.
(5) J. B. Boussingault, *Ann. Chim. Phys.*, (5) **27** (1882), 289; L. Dieulafait, *Compt. rend.*, **96** (1883), 718; R. Irvine and J. Gibson, *Proc. Roy. Soc. Edinburgh*, **18** (1890), 54; cf. *J. Chem. Soc.*, **60** (1891), Abs., 995; E. Dittler, loc. cit.

of the minerals imbedded in the rock went into solution and was precipitated with radium or uranium near its points of derivation between the cracks of the rock or around any nuclei which happened to be at hand, accordingly around the fragments of the altered rock yielding the radioactive manganiferous nodules. It will therefore be thought that the formation of the Tanokami nodules would never take place unter the stream water, seen at the present time, but in the quiet depths of the sea or lake throughout the geological ages. It would be expected, accordingly, that the rock body on the hill side of the Tanokami district have come up from the deep water, and the black impregnation on the rock blocks lying on the river bed, now frequently seen, will be due to the manganese and iron derived as the result of recent weathering and erosion from the above mentioned manganiferous deposits and nodules.

Finally, one thing which is much suggestive in this connection, is the origin of the radium contained in the oceanic water and the deep-sea deposits. It has been so considered by J. Joly[1] that the oceanic radium has entirely been supplied by the rocks and minerals on the land, having been leached by the rain water and poured by rivers into the sea. It may, however, be concluded from the foregoing considerations that some parts of the oceanic radium come from certain radioactive minerals cropped out sporadically on the bottom of the sea. In this way it will also easily be accounted for the less content of radium in the river water than that in the sea water. The critical revision of radium content in all the manganese nodules known is highly desirable.

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(1) J. Joly, "Radioactivity and Geology," (1909), p. 54.