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REPLY TO "DISCUSSION OF 'COULSONITE'"

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I will comment very briefly on Mr. J. Kent Perry's article concerning my paper "Coulsonite, FeV_2O_4 . A Spinel Type Mineral from Lovelock, Nevada"; *The American Mineralogist*, **47**. The material used in the study was in part collected by myself and in part provided by a mining company for the expressed purpose of determining the source of vanadium. The samples from the company were obtained from Mr. Perry's group by the company for my study and represent material originally used and studied by the Colorado School of Mines Research Foundation. This is now a part of the ore deposits collection at Stanford University.

The photomicrographs were used in the publication with no reference to the closed-file reports by Mr. Perry by prior agreement with the mining company for whom he studied the ores. This agreement specifically stated no reference should be made to previous material within their files. The fact that Mr. Perry was not given credit for his photography is recognized and his name was omitted from the bibliography for the above reason.

The study of coulsonite was concluded with the publication in *The American Mineralogist* and was carried out independently of previous work. Certainly no slight to Mr. Perry or his earlier works was intended.

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NOTE ON ISHIGANEITE AND YOKOSUKAITE

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Ishiganeite and yokosukaite were first named by K. Kani and T. Tanaka (*Bull. Electrotechnical Lab. Japan*, **1**, 459-497, 553-555, 1937; **2**, 19-24, 291-295, 1938; *Electrochem. Japan*, **6**, 366-370, 1938; **7**, 7-16, 1939); and their mineralogical and electrochemical characters were described.

Ishiganeite, from Ishigane mine, Aichi Prefecture, Japan, is found in the weathered zones of rhodochrosite and rhodonite deposits in the Paleozoic formation in this mine. This mineral occurs as opaque and compact to loose aggregates, submetallic luster and varies from grayish-black to black in color: it shows a brownish black streak. $H=5-6$. Chemical analysis of the ishiganeite shows: MnO 60.11, O 11.82, SiO₂ 7.50, BaO 0.81, MgO 0.43, CaO tr., Al₂O₃ 8.20, Fe₂O₃ 0.55, H₂O(+) 1.44, H₂O(-) 4.02, total 94.88%, leading to a formula $4 \text{ MnO} \cdot \text{RO} \cdot \text{H}_2\text{O}$ ($R = \text{Mn}^{2+}$, Ba, Mg). The x -ray powder pattern shows strongest lines 2.4(10), 3.1(7), 4.9(6), 2.1(5), and 7.3 Å(4).

Kani and Tanaka prepared artificial ishiganeite by three methods and found it had a x -ray powder pattern different from that of an artificial yokosukaite. Artificial ishiganeite could be produced by: (a) reaction of HNO₃ (conc.) on MnSO₄ with adding KClO₃; (b) oxidation of the same solution by mixture of KMnO₄ and KClO₃. The loss of weight of artificial materials when heated up to 550° C. results from deoxidation alone, and x -ray powder pattern of heated materials show low intensity pattern. X -ray powder pattern of these materials upon heating from 800° C. to 1000° C. show patterns of Mn₃O₄. Natural ishiganeite gives an x -ray powder pattern similar to that of artificial one produced by the above mentioned method. This modification was named ishiganeite by Kani and Tanaka after the name of the mine. They concluded that both ishiganeite and todorokite consist chiefly of a psilomelane phase.

Yokosukaite from Yokosuka, Aichi prefecture, Japan, is found in the weathered zones of rhodonite and spessartite rocks in the Paleozoic formation in this locality. This mineral occurs as opaque and compact aggregates; it shows a brownish black streak. $H=4 \pm$. Analysis gave MnO 62.50, O 13.78, H₂O(+) 6.44, H₂O(-) 2.63, total 85.35%, leading to a formula $2 \text{ MnO}_2 \cdot 0.84 \text{ H}_2\text{O}$. The x -ray powder pattern has strongest lines 2.4(10), 4.3(9), 1.62(9), 2.1(5), and 6.5 Å(3). Kani and Tanaka examined five samples of oxides prepared by: (a) oxidation of MnSO₄ solution by ammonia with adding bromate water; (b) oxidation of the same solution by KMnO₄; (c) electric decomposition of MnSO₄ at room temperature; (d) spontaneous decomposition of Mn(NO₃)₂ by heating in vacuum; (e) reaction of dilute HNO₃ on MnSO₄ with adding a small amount of KHSO₅. All artificial materials thus prepared give similar x -ray powder patterns. The thermobalance curve of artificial material when heated up to 100° C. is affected by dehydration alone, and the loss in weight amounts to approximately 13.54%. It is suddenly increased at 500° C. and the secondary loss of about 22.90% in weight observed at 550° C. may be due to deoxidation. X -ray powder pattern of artificial materials heated at about 400° C. for 30 minutes shows the presence of

polianite (pyrolusite). The pattern of this material almost disappears at about 500–550° C., and it goes completely to a Mn_2O_3 phase. The electromotive force of these artificial materials and yokosukaite were better than natural manganese dioxides such as pyrolusite, etc. Yokosukaite gives an x -ray powder pattern similar to that of these artificial materials produced by the five methods mentioned above. The name was given by Kani and Tanaka for the locality, Yokosuka, Japan.

Recent knowledge of manganese dioxides has made it desirable to re-examine the terms of ishiganeite and yokosukaite. M. Nambu and K. Okada (*Jour. Soc. Earth Sci. Amat. Japan*, **12**, 249–258, 1961; *Jour. Jap. Assoc. Min. Petr. Econ. Geol.*, **48**, 76, 1962) have investigated the relationship between ishiganeite, yokosukaite, psilomelane, cryptomelane and some other phases of manganese dioxides, using the mineralogical data given by Kani and Tanaka and also by themselves. Nambu and Okada have found that ishiganeite, both artificial and natural, is in good agreement with α - MnO_2 produced by artificial methods or natural cryptomelane. The mineralogical and the electrochemical characters of Kani's yokosukaite are in agreement with those of the artificial γ - MnO_2 prepared by Cole *et al.* (*Trans. Electrochem. Soc.*, **92**, 133–154, 1947). The x -ray powder pattern of yokosukaite consists chiefly of γ - MnO_2 , with a small amount of other phases of MnO_2 . They have concluded that yokosukaite is really a new mineral, and the name should be reserved.

The writer has investigated x -ray powder pattern and differential thermal analysis of ishiganeite and yokosukaite, collected by Dr. Z. Harada. X -ray powder pattern of ishiganeite shows that it is a mixture of cryptomelane and birnessite, and the x -ray powder pattern of yokosukaite gives generally low intensity patterns similar to those of γ - MnO_2 .

Recently Zwicker and his co-workers have proposed a new mineral nsutite and have discussed its relation with other phases of manganese oxide minerals (*Am. Mineral.* **47**, 246–266, 1962). Further study is expected to throw light on the relation between yokosukaite, nsutite and other manganese oxide minerals.

Editor's Note: Sometime ago a Japanese paper referred to papers published in 1937–39 in which the names ishiganeite and yokosukaite had been proposed for manganese oxide minerals. These names had never been noted in *Am. Mineral.*, and yokosukaite does not appear in any of the reference books, including Hey. This summary report has kindly been prepared by Dr. Hariya at the suggestion of Michael Fleischer.