METAMICT PITCHBLENDE FROM GOLDFIELDS, SASKATCHEWAN AND OBSERVATIONS ON SOME IGNITED PITCHBLENDES

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Abstract

Seven metamict pitchblendes, apparently the first to be reported, are described from three localities in the Goldfields area of Saskatchewan. The changes in *x*-ray powder pattern and color of the powder after ignition are tabulated for these and two other pitchblendes; the principal changes are the restoration of the structure of metamict specimens and the occasional development of U_3O_8 with, or in place of UO_2. On the basis of these changes the nine pitchblendes examined are classified into five distinct types.

During the summers of 1947 and 1948, while employed by the Crown Company, Eldorado Mining and Refining (1944) Ltd., the first author collected a suite of pitcheblende specimens from the Ace and Christie Lake localities in the Goldfields area of northern Saskatchewan, mapped by Christie & Kesten (1949). With a view to determining roughly the U:Th ratio, the writers took *x*-ray powder photographs of two representative specimens of this suite, and were surprised to find that the patterns were very weak, suggesting that the uraninite is to a considerable degree metamict. As metamict uraninite has not, as far as the writers know, been previously described, it was decided to investigate these and other specimens further.

Laboratory Procedure

Small chips were broken from those portions of the pitchblende samples which showed the least amount of impurities, and the purest pieces selected under a binocular microscope. In some cases it was impossible to separate pieces entirely free from the associated carbonate, hematite, pyrite, and pyrrhotite. The selected pieces were then crushed and powdered in a mullite mortar, and the powder was divided into two portions. One portion was heated for five minutes in a covered crucible over a Bunsen flame (roughly 800° C.), and parts of each portion were then mounted on separate glass rods and photographed using Cu radiation and a Ni filter (Cu $K\alpha_1 = 1.5405$ A). Pitchblendes treated in this way included not only those from Ace and Christie Lakes, but also one from adjacent Beaverlodge Lake (all in the Goldfields area), one from Black Lake (Saskatchewan) situated approximately 100 miles east of Goldfields, and one from Great Bear Lake, Northwest Territories. Dr.

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G. M. Brownell Chairman of the Department of Geology, University of Manitoba, kindly provided the specimens from Beaverlodge and Black Lakes.

OBSERVATIONS AND CONCLUSIONS

The results of this investigation appear in the accompanying table. The most striking observations are first, that certain specimens give a weak UO_2 pattern before ignition and a strong UO_2 pattern after, and second, that other specimens give a weak or a strong UO_2 pattern before ignition but a combination of a UO_2 and a U_3O_8 pattern after, these two patterns varying in relative strength with different specimens. From chemical analyses it is well known that pitchblende consists of a mixture of variable amounts of UO_2, U_3O_8, and UO_3, and Goldschmidt & Thomassen (1923) have related the degree of oxidation with the *x*-ray powder pattern. Their conclusions, which offer an explanation for the present results, are summarized in Palache, Berman & Frondel (1944, p. 619):

> "Natural uraninite containing much UO_3 through oxidation is apparently structurally identical with UO_2, . . . but on ignition out of contact with oxygen it may recrystallize in part or entirely to U_3O_8, while pure UO_2 remains unchanged. The excess O in the oxidized uraninites may be in solid solution in the structure. Since UO_3 is apparently amorphous the x-ray evidence for excess O in the structure is not conclusive. Pitchblende is structurally identical with uraninite, but has a very small particle size (10^{-4} to 10^{-7} cm.) and somewhat smaller cell dimensions ($a_0 = 5.42 - 5.45$[kX])."

On the basis of Goldschmidt & Thomassen's work, and taking into account the observed metamict character of most of our specimens, it is convenient to classify them according to the *x*-ray patterns of the unheated and of the ignited powders. An extension of such a classification might well prove useful in describing the character of uraninites and pitchblendes in general. Following is our classification with the sample numbers which exemplify each type:

1. Crystalline UO_2, not oxidized; strong UO_2 pattern before and after ignition; sample 9 (Figs. 1a, 1b).

2A. Metamict UO_2, not oxidized; faint UO_2 pattern before ignition, strong UO_2 pattern after; samples 1 (Figs. 2a, 2b), 3, and 6.

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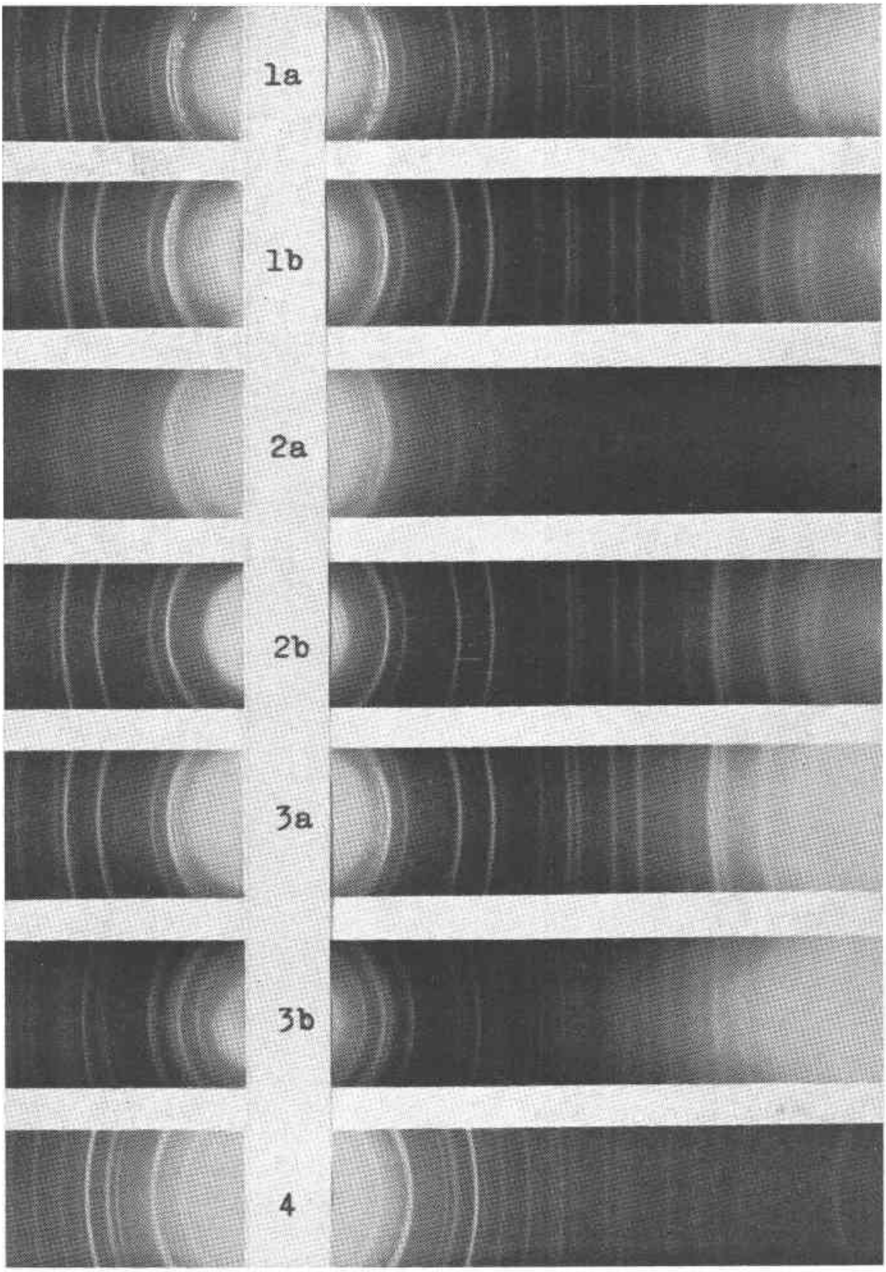
FIGS. 1–4. *X*-ray powder photographs with Cu/Ni radiation; camera radius $360/4\pi$ mm. (1 mm. on film $=1°\theta$); full size reproductions of contact prints. FIGS. 1a, b. Pitchblende, Great Bear Lake, Northwest Territories, representing type 1. 1a, before ignition: UO_2; 1b, after ignition: UO_2. FIGS. 2a, b. Pitchblende, Ace Lake, Saskatchewan, representing type 2A. 2a, before ignition: metamict UO_2; 2b, after ignition: crystalline UO_2. FIGS. 3a, b. Pitchblende, Black Lake, Saskatchewan, representing type 3, 3a, before ignition: UO_2; 3b, after ignition: U_3O_8. FIG. 4. Synthetic U_3O_8.


1a
1b
2a
2b
3a
3b
4

2B. Metamict UO_2, partly oxidized; faint UO_2 pattern before ignition, moderately strong UO_2 and U_3O_8 patterns after; samples 4 and 7.

2C. Metamict UO_2, largely oxidized; faint UO_2 pattern before ignition, moderately strong U_3O_8 and faint UO_2 pattern after; samples 2 and 5.

3. Crystalline UO_2, largely oxidized; strong UO_2 pattern before ignition, strong U_3O_8 pattern after with no appreciable UO_2; sample 8 (Figs. 3a, 3b).

The powder patterns representative of types 1, 2A, 3 are reproduced as Figs. 1, 2, 3 respectively, and for comparison, Fig. 4 shows the pattern of synthetic U_3O_8 prepared by R. J. Arnott by heating $UO_2(NO_3)_2 \cdot 6H_2O$ and then reducing the product with lampblack. The spacings and intensities of this pattern and those of the pitchblendes which gave U_3O_8 lines, are in substantial agreement with the data for U_3O_8 in the ASTM Card Index (1945, II-585). Some of the photographs which are reproduced show, in addition to the uranium oxide patterns, a few very weak lines due to impurities.

The question arises as to whether the oxidation from UO_2 to U_3O_8 is due to oxygen within the pitchblende, or to the addition of oxygen during heating. As all specimens were heated under uniform conditions it would be expected, if oxygen were added during heating, that all specimens would have changed in part to U_3O_8. As this is not the case it is inferred that the chemical changes are due to the state of oxidation of the pitchblende itself, prior to heating, or to the presence of oxygen in solid solution.

With the small number of specimens examined, it is difficult to make generalizations relating the degree of oxidation and the metamict character to any one of the cell edge, the locality, or the color of the streak. The cell edges, ranging from 5.39 to 5.45 A, fall a little outside the range given by Goldschmidt & Thomassen, 5.43 to 5.46 A, but almost within the range given by Arnott in a paper elsewhere in this issue, 5.403 to 5.475 A. Regarding locality, all the metamict pitchblendes come from the Goldfields area and show varying degrees of oxidation, whereas the specimens from both Black Lake and Great Bear Lake are crystalline and differ strongly in their degrees of oxidation.

Most of the samples showed a noticeable change in the color of the powder after ignition and, as indicated at the foot of the table, the colors were matched with those in the *Rock Color Chart.* The *Handbook of Chemistry and Physics* (1948, p. 514) gives the following colors for the uranium oxides; UO_2, brownish-black; U_3O_8, olive-green; and UO_3, yellowish-red. Our observed colors show limited correlation with these. The unoxidized pitchblendes (1, 3, 6, and 9) are mainly brownish-gray, most of them turning to a dark gray after ignition. The olive-green color of pure U_3O_8 is suggested by only one of the specimens containing

TABLE 1

No.	Locality	*Color of Unheated Powder	*Color of Ignited Powder	Strength of Pattern	a, A (± 0.01) of UO_2	Remarks
1a	Ace Lake	Brownish-gray	....	Faint	....	Metamict UO_2
1b	Ace Lake	....	Dark gray	Moderately strong	5.43	UO_2 structure restored
2a	Ace Lake	Brownish-gray	....	Very faint	....	Metamict UO_2
2b	Ace Lake	....	Dark Yellowish-brown	Moderately strong	....	Mainly U_3O_8, some UO_2
3a	Ace Lake	Dark greenish-gray	....	Faint	....	Metamict UO_2
3b	Ace Lake	....	Dark gray	Strong	5.39	UO_2 structure restored
4a	Christie Lake	Olive-gray	....	Very faint	....	Metamict UO_2
4b	Christie Lake	....	Dusky Yellowish-brown	Moderately strong	5.42	UO_2 and U_3O_8
5a	Christie Lake	Brownish-gray	....	Faint	....	UO_2
5b	Christie Lake	....	Grayish-brown	Faint	....	Mainly U_3O_8, some UO_2
6a	Christie Lake	Brownish-gray	....	Faint	....	Metamict UO_2
6b	Christie Lake	....	Grayish-brown	Strong	5.41	UO_2 structure restored
7a	Beaverlodge Lake	Brownish-gray	....	Faint	....	Metamict UO_2
7b	Beaverlodge Lake	....	Dusky brown	Moderately strong	5.42	UO_2 and U_3O_8
8a	Black Lake	Dark greenish-gray	....	Strong	5.45	UO_2
8b	Black Lake	....	Dark greenish-gray	Strong	....	Mainly U_3O_8
9a	Great Bear Lake	Med. dark gray	....	Strong	5.45	UO_2
9b	Great Bear Lake	....	Dark gray	Strong	5.41	UO_2

* Colors of the powders are close to those given in the *Rock Color Chart* (National Research Council, Washington, D. C.).

it, number 8, although the brownish shade assumed by 2, 4, 5, and 7 after ignition may be due to the development of U_3O_8 in these powders. In general, however, our observations indicate that no definite deductions regarding the state of oxidation of the uranium in a given pitchblende can be made from the color of its powder either before or after ignition.

SUMMARY

(1) The work of Goldschmidt & Thomassen (1923) and the present study indicate that a convenient way of determining the approximate degree of oxidation of the uranium in a given pitchblende is to

make *x*-ray patterns of the powder before ignition and after ignition in a closed crucible. Specimens not oxidized give a UO_2 pattern in both cases; specimens highly oxidized give a UO_2 pattern before ignition and a U_3O_8 pattern after; and specimens partly oxidized give UO_2 before and both UO_2 and U_3O_8 after.

(2) Nine specimens of pitchblende studied in this way showed examples representing all stages of oxidation.

(3) Seven pitchblendes from the Goldfields area, Saskatchewan, are shown to be metamict, apparently the first metamict pitchblendes to be described. These varied widely in their degree of oxidation.

(4) On the basis of their crystalline or metamict character, and their degree of oxidation as described under (1), the nine specimens examined have been classified into five types. An extension of this classification might prove useful in describing all uraninites and pitchblendes.

(5) The streak of a given pitchblende does not, in general, give definite evidence concerning the state(s) of oxidation of the constituent, uranium.

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