# HYDROTHERMAL URANOTHORITE IN FLUORITE BRECCIAS FROM THE BLUE JAY MINE, JAMESTOWN, BOULDER COUNTY, COLORADO[1]

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## Abstract

In the course of thin-section and heavy-mineral studies of fluorite breccias from Jamestown, Colorado, the mineral thorite, variety uranothorite, was identified on the basis of chemical, spectrographic, optical, and *x*-ray data. This uranothorite is compared with uranothorite from South Westland, New Zealand, that was described by Hutton in 1950, and with similar material from an Alaskan placer sample studied by the writers. These uranothorites are in turn contrasted with the uranothorites described in the older literature, all of which represent hydrated material. Thorium halos in fluorite are described, probably for the first time. The uranothorite associated with the fluorite breccias is clearly of hydrothermal origin—unlike all previously described thorites and uranothorites, with one very doubtful exception.

## Introduction

The Blue Jay mine is one of the larger fluorite producers in the Jamestown district, Boulder County, Colorado. George Phair visited the second level of this mine in September 1949, guided by R. U. King and H. C. Granger of the U. S. Geological Survey's Denver office, and collected some 30 pounds of the breccia ore for mineralogic and chemical studies of the radioactive constituents. A preliminary binocular study of the heavy-mineral contents of this ore revealed scattered grains of an unknown glassy green mineral. Qualitative chemical and spectrographic tests showed that the mineral resembled uranothorite in chemical composition. Although the uranothorite (?) accounted for only a small part of the total radioactivity of this ore, its occurrence in a mineral assemblage which is definitely of hydrothermal origin seemed unique. Largely for this reason the mineral was considered of sufficient interest to justify the numerous separations and the tedious hand-picking of grains for its positive identification. Moreover, the fact that a similar-appearing green mineral had been found in a placer sample from the Ruby district, Alaska, emphasized the need for the specific determination. This mineral was identified tentatively as thorite, variety uranothorite, by Kiyoko Shimamoto; its physical properties, however, depart widely from those of the dozen or so thorites described in the literature prior to 1950.

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## METHODS OF SEPARATION

To obtain enough uranothorite for analyses, the parts of the fluorite breccia selected for high radioactivity were crushed to −120, +200 mesh and the heavy minerals separated in methylene iodide. These heavy minerals consisted chiefly of deep-purple fluorite containing heavy impurities; these were impure carbonates, pyrite, galena, sphalerite, iron oxides, uraninite, and uranothorite. The light fractions consisted chiefly of light-purple fluorite, quartz, carbonate, clay minerals, and altered feldspar; in bulk samples the light fractions showed negligible radioactivity. Some slight additional concentration of the heavy-mineral fractions was obtained by passing them through the Frantz isodynamic separator; the uranothorite tended to accumulate in the moderately magnetic fraction. The desired material was hand-picked from these concentrates under the binocular microscope, and this sample, in turn, was hand-picked a second time for the reasons described later.

## IDENTIFICATION OF THE URANOTHORITE

Preliminary optical studies had shown that the green mineral in the fluorite breccias, like that in the Alaskan placer sample, was completely metamict (isotropic) with $n=1.84$. The specific gravity of several crystals of the Alaskan mineral determined on the Berman microbalance was found to be $6.5 \pm 0.2$. It was impossible to reconcile the green color, the high refractive index, and the high density of these minerals with the properties of thorite and uranothorite reported in the literature prior to 1950 ($n=1.68$ to 1.72, sp. gr. 4.1 to 5.2). Nevertheless both unknown minerals had the typical thorite form, tetragonal with the prism $\{110\}$ terminated by the pyramid $\{111\}$. Like most completely metamict minerals, prior to ignition they gave the $x$-ray pattern of an amorphous solid. Unlike many completely metamict minerals, the isotropic thorites do not revert to their original crystalline condition after being heated. Instead, as noted by Robinson (1950), uranothorites after ignition at 800° C. for half an hour in an inert atmosphere give an anomalous face-centered cubic powder pattern; neither the unknown green mineral from Jamestown, Colorado, nor that from the Ruby district, Alaska, was an exception to this rule. According to J. Berman of the Geological Survey, who is at present engaged in *x*-ray diffraction studies of the different members of the thorite group, our uranothorites after ignition gave powder patterns nearly identical with the pattern of a thorianite having $a_0 = 5.60$ Å and similar to that given by synthetic $ThO_2$ prepared by igniting $Th(NO_3)_4$ in a stream of nitrogen. The patterns of heated thorianite and of our heated uranothorites are nearly identical with respect to the relative intensities and spacings of the major lines; they differ in only one particular, namely, several weak lines present in the thorianite pattern are absent from the less intense uranothorite pattern.

Preliminary qualitative spectrographic analyses were made on a few nearly pure grains of each of the two green minerals. Additional separations yielded, after a single hand-picking, a sample of the Jamestown mineral large enough for the semiquantitative work planned, but because of mineral intergrowths, its over-all purity was lower than was thought desirable. In contrast to the Alaskan mineral, pure samples of which could be obtained with little difficulty, the hand-picked Jamestown material consisted largely of grains of the green mineral more or less intergrown with a brown alteration product of much lower refractive index. Grains containing other mineral intergrowths were less abundant but common. The bulk sample was subdivided by a second hand-picking as follows:

1. Mixed green and brown phases free of other impurities, about 30 mg.
2. Green mineral alone plus impurities, about 5 mg.
3. Brown mineral alone plus impurities, about 5 mg.

All mixed green and brown grains containing other impurities were discarded.

The small size of the samples of the separate brown and green phases (2 and 3 above) permitted only a qualitative spectrographic analysis of each plus a quantitative chemical analysis for uranium. The results of these analyses showed that both the green mineral and its brown alteration product were thorium minerals of similar composition (Table 1). The presence of much intergrown sphalerite in both samples accounts for: (1) the high zinc content, (2) the high refractive index (over 2.00) of some of the intergrown material, and (3) the weak sphalerite powder pattern given by the less pure grains of the green and of the brown minerals before ignition. The brown alteration product contained much less uranium (4.2 per cent) than the green (20.0 per cent). It was weakly birefringent, with a mean index of refraction close to 1.64 in white light. After ignition for half an hour in the flame of a blast lamp, it showed a large increase in

TABLE 1. CHEMICAL COMPOSITION, IN WEIGHT PER CENT, OF URANOTHORITES

| | Ranges of 4 earlier anal.[1] | South Westland, N.Z. (Hutton 1950)[1] | Placer, Ruby, Alaska. Phair and Shimamoto[2] | Green and brown minerals in fluorite from Blue Jay mine, Colo. Phair and Shimamoto[2] |
|---|---|---|---|---|
| Th | 40.6 –56.6 *c*[3] | 55.1 *c* | 56.6 *c* | $\gg$10.0 *s*[4] |
| U | 6.7 –14.6 *c* | 10.1 *c* | 8.2 *c* | 11.8 *c* |
| Si | 6.1 – 9.1 *c* | 9.1 *c* | >10.0 *s* | >10.0 *s* |
| Fe | 0.9 – 5.3 *c* | 1.6 *c* | 0.1–1 *s* | 1–10 *s* |
| Ce | 0.07– 1.18 *c* | 0.9 *c* | Close to 0.1 *s* | <0.1 *s* |
| Ca | 0.7 – 3.1 *c* | 0.2 *c* | Close to 0.1 *s* | 1–10 *s* |
| Pb | 0.4 – 1.5 *c* | 0.5 *c* | Not detected *s* | 0.1–1 *s* |
| $H_2O+$<br>$H_2O-$ | 9.24–11.31 *c* | 1.93 *c* | Very low by qual. test | Very low by qual. test |
| | | | | *Green mineral plus inclusions*<br>U 20.0 *c*<br>Th, Zn major *s* (qual.) |
| | | | | *Brown mineral plus inclusions*<br>U 4.2 *c*<br>Th, Si, Zn major *s* (qual.) |

[1] Analyses listed by Hutton (1950, p. 679) converted to percentages of elements.

[2] Analyses by following members of U. S. Geological Survey: chemical analyses by F. S. Grimaldi, Mary H. Fletcher, Irving May, and Harry Levine; semiquantitative spectrographic analyses by C. L. Waring; qualitative spectrographic analyses by Jules Stich.

[3] *c* indicates data obtained by chemical analysis.

[4] *s* indicates data obtained by semiquantitative spectrographic analysis except where followed by (qual.), which indicates that constituents were determined only as major, minor, or trace.

mean refractive index ($\Delta n = +0.14$), which was probably caused by a loss of water, and it turned greenish brown. In its mean index, color, high thorium and silicon contents, low uranium content, probable high water content, and its association with other thorium minerals the brown mineral fits the descriptions of the simple hydrated species (?), hydrothorite, $ThSiO_4 \cdot 4H_2O$(?).

The analytical data obtained on the sample of mixed brown and green thorium minerals free of other impurities are shown in Table 1, last column. Also shown are the corresponding data for (1) the Alaskan green mineral, column 4; (2) definite uranothorite of similar composition described by Hutton (1950) column 3; (3) the ranges in composition shown by four analyses of other uranothorites listed in the older literature column 2. The results of the analyses indicated that the green Alaskan mineral and the green Jamestown mineral (together with its hydrated brown alteration product) were chemically very similar. Each contained only the constituents typical of uranothorite in amounts within the ranges shown by chemical analyses of uranothorites from other localities. As might be expected, the uranium content of the bulk sample of the Jamestown material (11.8 per cent) was intermediate between the uranium contents of its separate green and brown mineral constituents. The percentage of uranium (20.0 per cent) is high even for the uranium-rich variety, uranothorite, but not excessive. Uranothorites containing as much as 17 per cent uranium (20.0 per cent $U_3O_8$) are listed in a table of Canadian radioactive minerals compiled by Lang (1950).

Hutton's description (1950, p. 677) of a definite nonmetamict placer uranothorite from South Westland, New Zealand, which had a maximum index of refraction, color, and specific gravity similar to those shown by the Alaskan and Jamestown thorium minerals, provided a useful standard of comparison and explained the differences in physical properties between these and the uranothorites previously described. Hutton pointed out that the earlier descriptions of thorite and uranothorite were based on hydrated metamict material that contained on the average about 10 per cent water. It is not surprising that such material had low indices (generally in the range 1.68 to 1.72) and low specific gravities (generally in the range 5.19 to 5.40). Larsen (1921, p. 144) reported that several thorites from Norway showed a marked increase in index of refraction after ignition for half an hour over a blast lamp, with resulting indices as high as 1.85. Neither the green uranothorite from the Alaskan placer nor that from the Blue Jay mine in Colorado showed an increase in refractive index after ignition for half an hour over a blast lamp; the Alaskan mineral actually showed a slight but probably real decrease in index. Presumably these uranothorites, like Hutton's, are relatively anhydrous; but unlike Hutton's, they are metamict. Recently George (1951, p. 129) described a green uranothorite from several California placers that has physical properties (color, refractive indices, and specific gravity) almost identical with those of the two uranothorites described in this paper; moreover, like these, it is completely metamict and is intergrown with a brown alteration product of lower mean index. The physical properties of the four comparable uranothorites are summarized in Table 2.

Of 18 thin sections of parts of the fluorite breccia from the Blue Jay mine selected for high radioactivity, 6 showed one or more euhedra of green uranothorite partly replaced by pseudomorphs of yellow-brown hydrothorite. Nearly all of these uranothorite euhedra form inclusions in fluorite. The square basal sections range in length from 0.02 to 0.10 mm., and the prismatic sections are only slightly longer. Within large grains of fluorite, halos that have maximum widths of 41 microns corresponding to the calculated range in fluorite of high-energy alpha particles emitted by $Po^{212}$ (Th C′) serve as conspicuous indicators of uranothorite (Fig. 1). Alpha-sensitive nuclear emulsions applied to uncovered thin sections and developed in the manner described by Stieff and Stern (1950, p. 9) showed, under suitably high magnification, swarms of alpha tracks directed radially outward from the uranothorite cores of the halos. Thorium halos in fluorite, unlike uranium halos, have not been previously reported. These halos, together with the more abundant uranium halos (maximum widths of 31 microns) were found to be especially numerous in parts of the fluorite darkened by radioactivity.

TABLE 2. COMPARISON OF PHYSICAL PROPERTIES OF FOUR URANOTHORITES

| | S. Westland, N. Z. (Hutton 1950) | California (George 1951) | Ruby, Alaska (Phair, Shimamoto) | Blue Jay mine, Colo. (Phair, Shimamoto) |
|---|---|---|---|---|
| System | Tetragonal | Tetragonal | Tetragonal | Tetragonal |
| Specific gravity | 6.7±0.05 | 6.36 | 6.5±0.2 | — |
| Color in oils | Green (dichroic) | Blue green | Greenish | Green |
| Optical characteristics | Uniaxial + | Isotropic (metamict) | Isotropic (metamict) | Isotropic (metamict) |
| Refractive indices | $nX=1.815$<br>$nY(\max)=1.850$ | $n=1.82$–$1.87$ | $n=1.86\pm0.01$ | $n=1.86\pm0.01$ |
| $X$-ray diffraction patterns | — | — | Anom. $f$-$c$ cubic $a=5.60$ Å | Anom. $f$-$c$ cubic $a=5.60$ Å |

## DISCUSSION

In thin section most of the uranothorite is associated with relatively unsheared fluorite and is almost completely unsheared, retaining its sharp euhedral outlines (Fig. 1). The lack of visible crushing indicates that the uranothorite crystals were not introduced into the fluorite mechanically in the course of the brecciation. The close association of the uranothorite with a fluorite-carbonate-sulfide assemblage, and in particular the tendency of the uranothorite to form inclusions in the fluorite, is strong evidence of a hydrothermal origin. Apparently all thorites and uranothorites previously described in the literature have been found either as residual concentrates in placers or in situ in granitic igneous rocks, especially pegmatites. The one exception to this rule is a very doubtful occurrence of a single microscopic crystal of thorite (?) noted by Gordon (1944, p. 329) in a sample from the high-temperature tin veins of Llallagua, Bolivia. Its tentative identification as thorite was based on morphological measurements; its interfacial angles were intermediate between thorite and xenotime but closer to thorite.

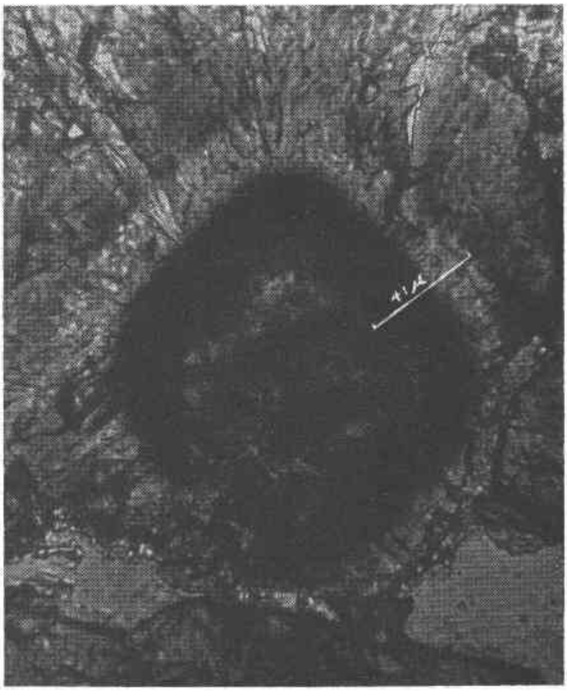

FIG. 1. Thorium halo surrounding euhedral uranothorite inclusion in fluorite. A basal section of uranothorite forms the center of a thorium halo consisting of a semiopaque inner "ring" and an outer bleached "ring." The width of the halo is 41 microns as measured from the inner boundary of the darkened zone to the outer boundary of the bleached zone. (Uncrossed nicols.)

The temperatures at which the Jamestown uranothorite was deposited may have reached the mesothermal range but were certainly no higher. The Jamestown fluorite deposits are at the northern end of the Front Range mineral belt—a region wherein the ore deposits assume many epithermal characteristics in contrast to the characteristics of deposits at the southern end of the belt, where mesothermal conditions prevailed (Lindgren, 1933, p. 635). Lindgren lists the Jamestown fluorite deposits with mesothermal ores, and Goddard (1946, p. 19) noted that enargite and tennantite were among the early sulfides in many of the ores. However, the brecciation that accompanied the latest stages of fluorite mineralization left open spaces and could have taken place only under relatively near-surface conditions.

Previously thorite has been considered a rare mineral, but it seems likely that, once the properties of the unaltered mineral become more widely known, it will be found rather widely distributed not only in "high-temperature" granitic pegmatites and in placers but also in many hydrothermal veins.

The rare-earth content of many fluorites is relatively high; samarium, neodymium, and cerium contents in a fluorite described by Chang (1945) ranges from 0.1 to 1.0 per cent. Heinrich (1948, p. 64) found that "fluorite and rare-earth minerals are associated in 19 of the 22 pegmatite districts in North America from which fluorite has been reported." $Th^{4+}$ has many chemical properties in common with the rare earths, and its ionic radius is in the same range. The oxides $UO_2$, $ThO_2$, and $CeO_2$ and the fluoride $CaF_2$ all have the face-centered cubic "fluorite" lattice with the unit cell close to 5.50 Å. The preference of the uranothorite and fluorite for the same geochemical environment is, therefore, readily explained by the Goldschmidt rule. It seems probable that thorium minerals as well as rare-earth minerals will prove to be of widespread, but scattered, distribution not only in fluorite-bearing pegmatites but also in many fluorite-rich hydrothermal deposits.

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