THE AMERICAN MINERALOGIST, VOL. 44, SEPTEMBER-OCTOBER, 1959

THE PREPARATION AND PROPERTIES OF URANIUM (IV) SILICATE*

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ABSTRACT

Uranium (IV) orthosilicate, corresponding to the mineral coffinite, has been synthesized by a hydrothermal procedure. Preparative conditions including precipitation techniques, temperature, pH and uranium oxidation state have been investigated. $USiO_4$ is a blue microcrystalline compound isostructural with thorite and zircon. The infrared spectrum of $USiO_4$ shows an absorption maximum at 11.1 μ, characteristic of isolated SiO_4^{4-} tetrahedra. No evidence was found for hydroxyl substitution in the synthetic material. $USiO_4$ is stable to 1000° C. in a vacuum and to 500° C. in air.

INTRODUCTION

Zircon and thorite are well-known mineral constituents and procedures have been established for their synthesis in the laboratory. The two orthosilicates are isostructural, crystallizing with tetragonal symmetry. Until recently the uranium (IV) analogue had not been found in nature nor prepared in the laboratory. Partial substitution of uranium for thorium is frequently observed (uranothorites), but the uranium content rarely exceeds 10%.

Recently a preliminary announcement by Stieff, Stern and Sherwood (1955) reported the discovery of a new uranium mineral in the LaSal No. 2 mine on the Colorado Plateau. The mineral, isostructural with zircon and thorite, was given the name coffinite. A later more detailed, description (1956) characterized the substance as a uranous silicate (ideally $USiO_4$) with partial substitution of $(OH)_4^{4-}$ for $(SiO_4)^{4-}$. At approximately the same time Hoekstra and Fuchs (1956) announced the synthesis of $USiO_4$ in the laboratory. Fuchs and Gebert (1958) have subsequently reported detailed *x*-ray diffraction results on coffinite, thorite and uranothorite. The present paper will describe in greater detail the preparation of coffinite and some of its properties.

PREPARATION OF $USiO_4$

According to Iler (1955) an insoluble metal silicate is usually precipitated as a gelatinous amorphous mass when a solution of a polyvalent metal salt is added to a solution of a soluble alkali metal silicate. Maurice (1949) reported the hydrothermal preparation of zircon by heating amorphous zirconium silicate in acid or weakly alkaline solutions. We have used an analogous procedure for the synthesis of coffinite, but find that the uranium compound is obtained only in basic solutions. The uranium-

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* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

silicate solution is prepared by dissolving equimolar quantities (one millimole each) of uranium (IV) tetrachloride and sodium metasilicate in distilled water (10 ml). Sodium hydroxide solution (1 *M*) is then added dropwise until a stiff green gel forms near the neutral point. The gel is broken by adding a few additional drops of base with shaking. When sufficient base has been added to make the solution slightly alkaline, the gelatinous precipitate is centrifuged and the supernate decanted to a total volume of approximately 6 ml. The preparation is then buffered to a pH 8.3 by adding sufficient sodium bicarbonate to make a 0.5 *M* solution. Excess silica is provided by adding powdered vitreous silica (0.25 gm.). The slurry is poured into a platinum cup which is then inserted into an Inconel hydrothermal reaction vessel (11 ml. capacity) fitted with a compression seal. All operations are performed in a nitrogen atmosphere to prevent oxidation of tetravalent uranium. The sealed reaction vessel is heated 24 hours at 250° C. or 120 hours at 200° C. The pressure in the reaction vessel has not been determined, but is assumed to be approximately equal to the vapor pressure of water at the given temperatures (15 atm. at 200° C., 40 atm. at 250° C.). The synthetic coffinite is obtained as a microcrystalline solid which may be separated from the bulk of the excess silica (as quartz) by gravitational methods in water. Despite its lower density the bulk of the quartz settles more rapidly than the extremely finely-divided coffinite.

FACTORS INFLUENCING COFFINITE SYNTHESIS

Precipitation Technique

It has been shown (Iler, 1955) that most solutions of soluble silicates contain a mixture of polysilicate ions. Since these ions are not of uniform size, they cannot form a regular crystal lattice when precipitated with metal ions. In order to obtain a crystalline silicate the polysilicate ions must be depolymerized in order to rearrange themselves into a regular lattice. Thus, precipitation of a metal silicate solution at ordinary temperature usually results in a colloidal mixture of metal ions on gelatinous silica or as a mutual coagulation of positively charged colloidal metal hydroxide and negatively charged colloidal silica. Britton (1927) also concluded that mutual coagulation rather than compound formation occurs on precipitation of metal hydroxides with sodium silicate. Based on these observations, it appears that depolymerization of the polysilicate and formation of $USiO_4$ occurs during the heating process rather than during the precipitation step. Co-precipitation of uranium and silica is necessary for the synthesis, since the mixing of freshly prepared uranium (IV) hydroxide and silica results in the formation of uraninite and quartz, even though all other conditions of the experiment are identical. This suggests that coffinite in nature is not likely to be formed by the reaction of finely-divided UO_2 and colloidal silica. Instead, the reaction probably involves dilute solutions containing soluble monomeric silica. The frequent association of coffinite with organic material also suggests that reduction of solutions containing hexavalent uranium, followed by precipitation as the orthosilicate may occur.

pH and Buffers

An alkaline environment appears to be essential for the laboratory synthesis of coffinite. Because of the uncertainty of pH maintenance in non-buffered solutions, synthesis could be repeated effectively only when buffering was provided. The effect of pH and various buffering agents is illustrated in Table 1. The pH limits for successful preparation of $USiO_4$ lie between 8 and 10.5.

TABLE 1. EFFECT OF pH AND BUFFERING AGENTS ON COFFINITE PREPARATION

Solutions heated 115 hours at 250° C.

Buffer	pH before heating	pH after heating	Products
None	10	8.9	diffuse UO_2
None	6.6	7.3	diffuse UO_2
None	6.7	6.6	diffuse UO_2
None	7.5	8.7	mostly coffinite+diffuse UO_2
None	9.9	10.1	coffinite
0.5 M $Na_2B_4O_7$	9.3	9.0	mostly coffinite+diffuse UO_2
0.1 M Na_2CO_3	10.7	10.2	mostly coffinite+diffuse UO_2
0.2 M Na_2CO_3	10.7	9.5	mostly coffinite+quartz+UO_2
0.1 M Na_2SiO_3	11.4	11.2	no coffinite, unknown compound
0.1 M $NaHCO_3$	8.8	8.8	mostly coffinite+diffuse UO_2
0.5 M $NaHCO_3$	8.4	8.1	mostly coffinite+quartz
0.6 M KH_2PO_4 0.04 M $Na_2B_4O_7$	8.2	8.6	diffuse UO_2+quartz
0.05 M KH_2PO_4 0.05 M $Na_2B_4O_7$	8.6	8.6	diffuse UO_2+quartz

Temperature

Coffinite is crystallized after heating a standard preparation (as described above) for 24 hours at 250° C., and a mixture of coffinite with trace amounts of UO_2 is obtained after 120 hours at 200° C. Reduction of the heating temperature to 150° C. produced only diffuse UO_2 x-ray patterns after 720 hours; a preparation heated 120 hours at 177° C. also produced only UO_2. These results would appear to set 200° C. as the lower limit for the preparation of coffinite by our procedure. However, coffinite was formed when a standard preparation was heated 120 hours at 120° C. then heated an additional 120 hours at 225° C. This result seems to conflict with that obtained by precipitating the uranium (IV) hydroxide separately and suggests that uranium dioxide can, under proper conditions, be converted to coffinite. If, however, the UO_2 crystallization in the 150° and 177° preparations occurs during the drying step, the formation of coffinite at the lower temperatures becomes strictly a rate problem and the apparent conflict of results is resolved.

A coffinite preparation at 360° C. gave a product with an unidentified *x*-ray powder pattern. The temperature limits for the formation of coffinite by the conditions outlined are thus 200° C. to $<$360° C.

Atmosphere of Preparation

Practically all of the tetravalent uranium in a standard preparation heated at 250° C. forms coffinite, as evidenced by the color of the product and the weak-to-absent lines of uranium dioxide in the powder pattern. If the precipitation steps are carried out in air, instead of in an inert atmosphere, a black product results, and the powder pattern shows the presence of a much larger fraction of uranium oxide with the coffinite. The coffinite-uraninite mixture can be partially fractionated by suspension in water. The uraninite settles much more rapidly than coffinite, and the latter can be obtained relatively pure by decanting and centrifuging the suspended material after the bulk of the uranium oxide has settled.

These results indicate that partially oxidized uranium does not take part in the formation of coffinite, Since freshly precipitated $U(OH)_4$ is very susceptible to oxidation, exposure to the atmosphere must be severely restricted. However, the presence of a reducing agent might permit the preparation of pure coffinite without the necessity of operating in an inert atmosphere. We have not investigated this possibility in detail, as yet.

ANALYIS OF COFFINITE

One of our coffinite samples analyzed 71.33% UO_2 and 29.20% SiO_2 as compared with a theoretical 81.80% UO_2 and 18.20% SiO_2 for $USiO_4$. From this result it is apparent that an 11% excess of silica remained in the coffinite concentrate after the gravity separation. Our best sample, analyzing 24.8% SiO_2 contained only 6.6% excess silica. This sample contained less than 1% moisture after vacuum drying at 70° C. Approximately 75% of this water was removed below 400° C. in a vacuum.

PROPERTIES OF COFFINITE

As differentiated from the black naturally-occurring coffinite, the synthetic material is a blue microcrystalline solid. A sample of natural coffinite, AE1019 (obtained from Prof. Gruner) turned from black to a grey-green color when ignited to 400° C. in air. The black color appeared to be due, at least in part, to organic matter. The coffinite *x*-ray pattern was improved as a result of this treatment. Further heating in air to 500° C. however, resulted in a gradual decomposition of the sample to U_3O_8 and SiO_2.

The structure of synthetic coffinite is tetragonal with $a = 6.981 \pm 0.004$ kX, $c = 6.250 \pm 0.005$ kX. Like natural coffinite, all synthetic material is finely divided as evidenced by the diffuse character of the back reflection lines. No anisotropic crystals can be seen under the microscope. No apparent change in crystallite size was observed when a preparation was heated at 250° C. for as long as 410 hours. Seeding of preparations had no noticeable effect on the size of coffinite crystals, thus emphasizing the necessity for intimate mixing of the constituents to affect crystal formation.

The refractive index of our coffinite dried at 75° C. was 1.83, vacuum ignition to 1000° C. increased this value to 1.88.

INFRARED SPECTRUM

Infrared spectra were obtained of synthetic coffinite as well as of synthetic thorite and natural zircon. Fig. 1 illustrates the similarity of the three orthosilicate spectra.

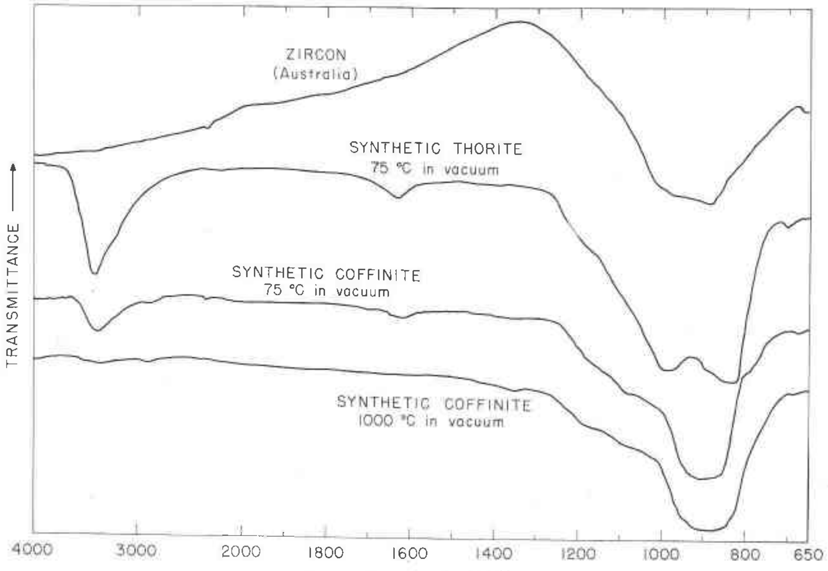

FIG. 1. Infrared spectra of synthetic coffinite, thorite, and natural zircon.

The spectrum of synthetic coffinite vacuum-dried at 75° C. shows moderate O—H absorption in addition to the characteristic isolated SiO_4 tetrahedra absorption reported by Launer (1952) in the region of 11.2 μ. The O—H absorption may be associated with excess silica, coffinite, or both. No rigorous correlation of the frequency of the O—H absorption could be made with other known hydroxyl-containing crystallographic structures. A similar conclusion was reached by Roy and Roy (1957) in their studies on the hydroxyl region of the infrared spectra of brucite, gibbsite and the clay minerals. The spectra of synthetic coffinite showed a steady decrease in the O—H absorption of samples which had been heated in vacuo for several hours at progressively increasing temperatures, until at 1000° C. virtually no trace of the O—H absorption remained. A room temperature *x*-ray powder photograph of the sample heated to 1000° C. in vacuo showed no change in cell dimension or line intensities compared with the unheated material, which suggests that the synthesized product is $USiO_4$ without an essential hydroxyl component. Since several per cent of excess silica was present, it seems likely that the water was present as hydrated silica rather than as a hydroxyl-substituted orthosilicate.

THERMAL STABILITY

Synthetic coffinite heated in a vacuum of 10^{-5} mm. Hg for 25 hours at 1000° C. shows no change in its *x*-ray powder pattern taken at room temperature. Patterns taken at elevated temperatures of a sample sealed in an evacuated vitreous silica capillary show that no phase changes occur during 3 to 4 hour exposures at 200, 400, 600 and 800° C. However, a sample heated in vacuo at 1245° C. for $2\frac{1}{4}$ hours turns brown, the decomposition products are UO_2 and amorphous silica. It is apparent from this observation that coffinite cannot easily be synthesized by a high temperature fusion of UO_2 and SiO_2. Heating a sample in air at 500° C. for 20 hours results in the fading of the back reflection lines of the powder pattern, and an additional 20 hours at 750° C. produces a U_3O_8-like pattern with no traces of coffinite lines remaining. The stability limits of $USiO_4$ are thus placed at 1000° C. in vacuum, and 500° C. in air.

ACKNOWEDGMENTS

We are indebted to Ralph Telford for the analytical results, and to Elizabeth Sherry and Dr. Stanley Siegel for the *x*-ray diffraction studies.

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Manuscript received January 28, 1959.