The Canadian Mineralogist
Vol. 35, pp. 135-144 (1997)

THE CHEMICAL EVOLUTION AND PARAGENESIS OF URANIUM MINERALS FROM THE RUGGLES AND PALERMO GRANITIC PEGMATITES, NEW HAMPSHIRE

STANLEY L. KORZEB

13993 East Arizona Avenue, Aurora, Colorado 80012, U.S.A.

EUGENE E. FOORD[1]

U.S. Geological Survey, Denver Federal Center, Box 25046, Mail Stop 905, Denver, Colorado 80225, U.S.A.

FREDERICK E. LICHTE

U.S. Geological Survey, Denver Federal Center, Box 25046, Mail Stop 973, Denver, Colorado 80225, U.S.A.

ABSTRACT

A study of the chemical evolution and paragenesis of the uranium minerals at the Palermo No. 1 and Ruggles granitic pegmatites, Grafton County, New Hampshire, revealed four stages of secondary mineralization. A total of eight uranium minerals were identified in the four stages. The first stage is a mixture of uranyl oxide hydroxide-hydrates represented by mineral "A", which surrounds and replaces a uraninite core. The second stage is a carbonate stage found only at the Palermo No. 1 pegmatite, and is represented by rutherfordine. The third stage is represented by uranyl silicates. At the Palermo No. 1 pegmatite, this stage consists of β-uranophane, and at the Ruggles pegmatite, it consists of soddyite and β-uranophane. A final fourth stage is a phosphate stage represented by phosphuranylite and meta-autunite I. The first three stages of mineralization developed from hydrothermal and meteoric processes. With dropping temperatures, hydrothermal fluids reached meteoric temperatures and acquired the characteristics of meteoric water. The pH shifted from acidic (pH less than about 6 at 100°C) to alkaline (pH > 7 at 25°C). Since mineral "A" contains hydroxyl and a low amount of molecular water, it probably formed at a temperature greater than 100°C in the acidic environment. After the first stage, the hydrothermal fluids likely reached the temperatures of meteoric water. The initial pH of the meteoric water was acidic (pH less than about 6 at 25°C) and then slowly shifted to alkaline. The mineralizing fluids became oversaturated in CO_3, Ca, K, and Si. Uraninite and mineral "A" became unstable and were replaced by rutherfordine and uranyl silicates. The fourth or phosphate stage developed from the introduction of groundwater. The uranyl phosphate minerals precipitated from an acidic fluid (pH < 7 at 25°C) that was oversaturated with Ca, K, U, and P.

Keywords: uraninite, Ruggles granitic pegmatite, Palermo granitic pegmatite, schoepite, rutherfordine, soddyite, β-uranophane, compreignacite, phosphuranylite, meta-autunite-I, New Hampshire.

SOMMAIRE

Nous avons étudié l'évolution chimique et la paragenèse des minéraux uranifères des pegmatites granitiques de Palermo No. 1 et de Ruggles, dans le comté de Grafton, au New Hampshire, et nous en déduisons quatre stades de minéralisation secondaire. En tout, huit minéraux uranifères ont été identifiés dans ces quatre stades. Le premier est un mélange d'oxydes-hydroxydes hydratés d'uranyle, représentés par le minéral "A", qui entoure et remplace un coeur d'uraninite. Le second stade, décelé à Palermo No. 1 seulement, implique le minéral carbonaté rutherfordine. Le troisième stade implique des silicates à uranyle. Dans la pegmatite de Palermo No. 1, ce stade comprend l'uranophane-β, et dans celle de Ruggles, cette dernière est accompagnée de soddyite. Une stade final, à phosphates, est représenté par la phosphuranylite et la méta-autunite I. Les trois premiers stades de minéralisation se sont développés à partir de processus hydrothermaux et météoriques. Avec une diminution de la température, la phase fluide a atteint la température de météorisation, et a acquis les caractéristiques de l'eau météorique. Le pH s'est déplacé du côté acidique (pH inférieur à environ 6 à 100°C) vers le côté alcalin (pH supérieur à 7 à 25°C). Comme le minéral "A" contient de l'hydroxyle et une faible quantité d'eau moléculaire, il s'est probablement formé à une température supérieure à 100°C, dans le milieu acidique. Après ce premier stade, la température a probablement convergé sur celle de l'eau météorique. La phase fluide est progressivement devenue alcaline, et sursaturée en CO_3, Ca, K et Si. L'uraninite et le minéral "A" sont devenus instables, et ont été remplacés par la rutherfordine et les silicates à uranyle. Le quatrième stade, à phospahtes, s'est développé suite à l'introduction de l'eau météorique. Les phosphates d'uranyle ont été précipités d'un fluide acidique (pH inférieur à 7 à 25°C) qui était sursaturé en Ca, K, U et P.

(Traduit par la Rédaction)

Mots-clés: uraninite, pegmatite granitique de Ruggles, pegmatite granitique de Palermo, schoepite, rutherfordine, soddyite, uranophane-β, compreignacite, phosphuranylite, méta-autunite-I, New Hampshire.

---

[1] *E-mail address*: efoord@usgs.gov

INTRODUCTION

The chemical evolution of uranium minerals has not been as well studied in the granitic pegmatite environment as in sandstone-hosted uranium deposits. In this paper, we present a detailed investigation of the chemical evolution and paragenesis of the secondary uranium minerals in two granitic pegmatites, the Palermo No. 1 and Ruggles. Our investigation was stimulated by recent findings of Finch & Ewing (1992) on alteration and geochemistry of uraninite.

The Palermo No. 1 pegmatite is located near North Groton Village, Groton, Grafton County, and the Ruggles mine is located in Grafton, Grafton County, both in New Hampshire (Fig. 1). These pegmatites were chosen because the internal zoning is well documented from past investigations and well exposed from past mining efforts, and because specimens are readily available for study. The internal zonation of both pegmatite bodies was thoroughly investigated by Cameron *et al.* (1954) and Page & Larrabee (1962). At the Palermo No. 1 pegmatite, relationships of the accessory minerals to the internal zonation of the pegmatite have been well established from past studies on the phosphate minerals by Segeler *et al.* (1981).

PREVIOUS INVESTIGATIONS

The occurrence of uraninite in granitic pegmatite has long been recognized. Uraninite and associated secondary minerals were identified at Haddam Neck, Connecticut (Ingerson 1938), but their origin was not discussed. Shaub (1938) described the habit and composition of uraninite from the Ruggles mine, and determined an age of 304 Ma for the pegmatite on the basis of the U–Pb method on uraninite. The mineralogy of primary and secondary uranium minerals in granitic pegmatites was discussed by Page (1950). Ford (1955) described the zonation and mineralogy of a uraninite-bearing pegmatite in Lac La Ronge, Saskatchewan, and recognized two stages of uraninite deposition.

The most comprehensive work covering the mineralogy of uranium in granitic pegmatites was done by Frondel (1956). He recognized three zones of secondary

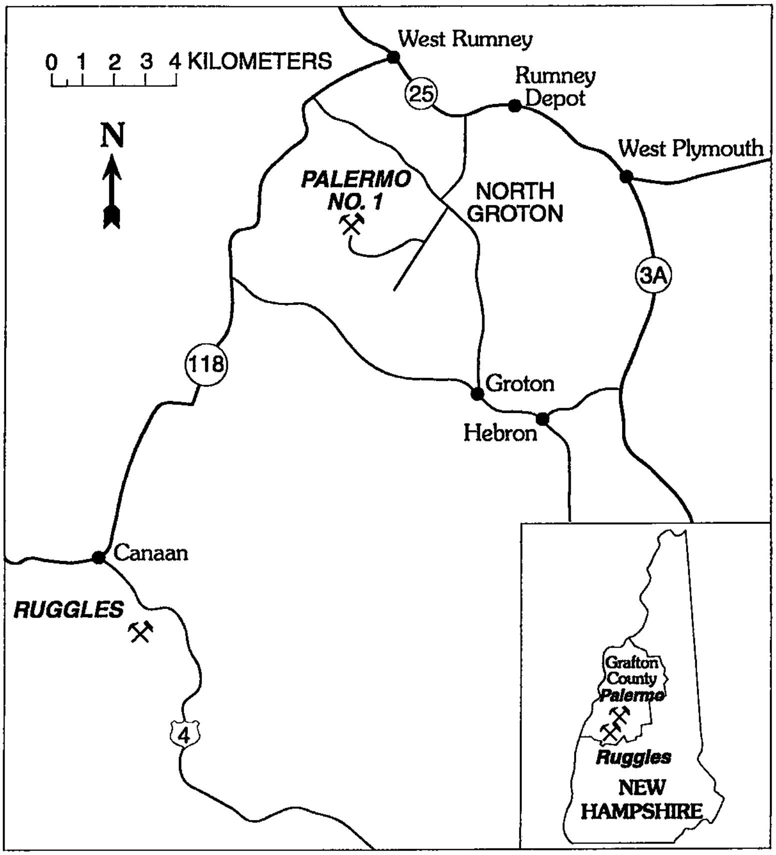

FIG. 1. Index map showing the location of the Palermo No. 1 and Ruggles granitic pegmatites.

uranium minerals resulting from the alteration of uraninite, and described three unknown minerals, among which was phase "A", documented here and in Foord *et al.* (1997) in greater detail. Frondel (1956) found that the uraninite core is surrounded by 1) a zone of hydrated uranyl oxides, 2) a uranyl silicate zone, and 3) an outer uranyl silicate + phosphate zone. The minerals in the outer zone also are deposited in fractures in the immediate vicinity of the earlier-deposited minerals. This outer zone results from a period of leaching of the earlier-deposited minerals.

METHODS OF INVESTIGATION

Specimens used for the mineral identifications and paragenesis were sought from the Mineralogical Museum collection at Harvard University, and from Mr. Robert Whitmore, Weare, New Hampshire, to complement field studies by the first author to determine the position of the unmined pods of uranium minerals in the various zones of the Palermo No. 1 pegmatite. Mineral identifications were made using SEM–EDS (scanning electron microscopy – energy dispersion spectrometry), LAM – ICP – MS (Laser-ablation microprobe – inductively coupled plasma – mass spectrometry), TGA (thermogravimetric analysis), and X-ray powder diffractometry (Straumanis method).

GEOLOGICAL SETTING AND MINERALOGY

Palermo No. 1 pegmatite

The Palermo No. 1 pegmatite is hosted by the Devonian Littleton Formation, which consists of a quartz – mica – sillimanite schist. The pegmatite body is 85 m long, 42 m wide, and concordant with the host rock; it contains six zones: a quartz – muscovite – plagioclase border zone, a plagioclase – quartz – muscovite wall zone, a plagioclase – quartz – perthite intermediate zone, a quartz – plagioclase – perthite intermediate zone, a plagioclase – quartz – muscovite – perthite core-margin zone, and a quartz – perthite core. The core-margin zone contains the uranium minerals, along with phosphates and beryl. This zone is a fine-to coarse-grained pegmatite that is 9 m thick on the footwall side of the core. On the hanging-wall side, this unit forms discontinuous lenses.

The core-margin zone consists of 30% plagioclase, 25% quartz, 25% muscovite, and 20% perthite. Plagioclase occurs as oval aggregates of "cleavelandite" 3 m long by 2.2 m wide, rimmed by greenish yellow muscovite. Medium-grained muscovite and massive quartz form equally large aggregates. The quartz is similar to the massive quartz in the core, and the uranium minerals are embedded in muscovite.

Ruggles pegmatite

The Ruggles granitic pegmatite, 14.5 km southwest of the Palermo No. 1, also is hosted by the Littleton Formation. The pegmatite body is 500 m long, with a maximum width of 100 m and a thickness of 50 m. The main body forms a northeast-trending tabular sheet that has an extremely variable dip to the southeast. A lobe-like eastward dipping extension is attached to the north end of the main body.

This pegmatite shows thirteen well-defined zones: a plagioclase – quartz – muscovite border zone, a plagioclase – quartz wall zone, a muscovite – quartz – plagioclase first intermediate zone, a plagioclase – perthite – quartz – biotite – tourmaline second intermediate zone, a quartz – plagioclase third intermediate zone, a plagioclase – muscovite – quartz – perthite fourth intermediate zone, a perthite – quartz – plagioclase fifth intermediate zone, a graphic granite core of the east-dipping extension, a perthite – quartz sixth intermediate zone, a perthite core of the main pegmatite body, quartz lenses and veins, muscovite – plagioclase replacement bodies, and a sericitized perthite – plagioclase – quartz replacement body.

Uraninite and associated secondary minerals occur in irregular bodies of massive quartz and late veins adjacent to the perthite core. Uraninite also occurs in the perthite – quartz sixth intermediate zone, near the contact with the perthite core. Shaub (1938) described uraninite and associated secondary minerals of uranium in the sixth intermediate zone.

Mineralogy

A total of eight uranium minerals were identified, seven from the Palermo No. 1, and six from the Ruggles pegmatite (Table 1). Uraninite is the only primary uranium mineral; the rest are secondary. Of the eight uranium minerals, only meta-autunite shows a fluorescence response to either long- or short-wave ultraviolet light. The secondary minerals were deposited as concentric bands or zones around a central core of partially to completely replaced uraninite and in fractures and along cleavage planes of the host minerals [Figs. 1 and 2 of Foord *et al.* (1997)]. Mineral "A" and rutherfordine are confined exclusively to concentric bands around a uraninite core, with each band dominated by a different species. Depending on the degree of alteration and transport of elements, these bands of uranium minerals are less than 5 cm across. Secondary minerals deposited in fractures and cleavage planes can cover zones up to 0.6 m across.

Frondel (1956) reported vandendriesscheite occurring at both Palermo No. 1 and Ruggles pegmatites. Parsonsite was reported to occur on three specimens from the Ruggles pegmatite by Frondel (1950). These two minerals are rare, and were not identified during this study.

TABLE 1. PARAGENESIS OF URANIUM MINERALS FOR THE PALERMO NO. 1 AND RUGGLES PEGMATITES, NEW HAMPSHIRE

		Palermo No. 1 pegmatite						
		TIME ——						
UO_2	uraninite	—						
$(UO_2)(OH)_2 \bullet \frac{1}{2}H_2O$ to $(UO_2)(OH)_2$	mineral "A"		—					
$UO_2(CO_3)$	rutherfordine			—				
$Ca(UO_2)_2[SiO_3(OH)]_2 \bullet 5H_2O$	β-uranophane				—			
$K_2(UO_2)_6O_4(OH)_6 \bullet 8H_2O$	compreignacite					-		
$KCa(H_3O)_3(UO_2)_7(PO_4)_4O_4 \bullet 8H_2O$	phosphuranylite						—	
$Ca(UO_2)_2(PO_4)_2 \bullet 2\text{-}6H_2O$	meta-autunite I							—
		Ruggles pegmatite						
		TIME ——						
UO_2	uraninite	—						
$(UO_2)(OH)_2 \bullet \frac{1}{2}H_2O$ to $(UO_2)(OH)_2$	mineral "A"		—					
$(UO_2)_2SiO_4 \bullet 2H_2O$	soddyite			—				
$Ca(UO_2)_2[SiO_3(OH)]_2 \bullet 5H_2O$	β-uranophane				—			
$KCa(H_3O)_3(UO_2)_7(PO_4)_4O_4 \bullet 8H_2O$	phosphuranylite						—	
$Ca(UO_2)_2(PO_4)_2 \bullet 2\text{-}6H_2O$	meta-autunite I							—

COMPOSITION OF URANINITE

Uraninite compositions are controlled by the geochemical conditions during crystallization. Pure uraninite with the stoichiometry UO_2 has never been reported; this fact indicates the existence of U^{6+} in the structure, which was caused by processes other than post-depositional oxidative alteration (Finch & Ewing 1992). Uraninite in granitic pegmatites typically contains significant concentrations of Th, Pb and the rare-earth elements (*REE*), and lesser amounts of Ca, Si, and Fe.

Uraninite generally occurs as unaltered, euhedral crystals in both pegmatite bodies, but it also occurs as dendritic growths in albite and K-feldspar. Crystals vary in size from 1 to 10 mm, but most crystals are less than 3 mm across. Where partially altered, uraninite forms a black, massive core enclosed by mineral "A", rutherfordine or soddyite. The dendrites can likewise be altered to secondary minerals.

Unaltered uraninite is associated with hematite, which occurs as a thin crust covering the crystal faces. Iron oxide stains the surrounding grains of feldspar hosting the uraninite. This iron oxide staining also occurs with the associated secondary minerals.

THE DECOMPOSITION OF URANINITE

The decomposition of uraninite takes place in an oxidizing environment, where U^{4+} is oxidized to U^{6+}. During the initial stages of oxidation, the crystal structure of uraninite remains stable. The stability of uraninite depends on the ability of the structure to accommodate additional oxygen [see Frondel (1958) for discussion]. The chemical composition of the initial uraninite determines the redox conditions under which it is stable (Finch & Ewing 1992).

Uraninite from a pegmatitic environment can have U^{6+} in excess of U^{4+}, thereby reducing the unit-cell parameter a_0. However, the presence of Th in uraninite from a pegmatitic environment will increase a_0 (Berman 1957). Grandstaff (1976) reported that unaltered uraninite from pegmatites can have high concentrations of U^{6+} in its structure, with concentration ratios of $U^{6+}:U^{4+} \approx 1:1$.

In a pegmatitic environment, uraninite may incorporate U^{6+} during its formation. One atom of oxygen per unit cell ($Z = 4$) is the maximum amount of "excess" oxygen that can be incorporated into the structure. The amount of oxygen that can be incorporated into uraninite is controlled by the availability of interstitial sites that are compatible with the cubic structure [see Frondel (1958) and Finch & Ewing (1992) for discussion]. Thus the limit of oxidation for uraninite is $UO_{2.25}$. For uraninite with $U^{6+}:U^{4+}$ in excess of 1:3, charge balance is maintained by incorporating Ca, Ba, Mg, Fe, K, Na and *REE* ions in the structure rather than incorporating oxygen (Finch & Ewing 1992).

The ratio of $U^{6+}:U^{4+}$ in the uraninite from the Palermo No. 1 and Ruggles pegmatites has not been determined, but can be inferred from results of the LAM–ICP–MS analyses [see Foord *et al.* (1997) on mineral "A"). LAM–ICP–MS data of the uraninite from both pegmatites show small amounts (<1 wt.% each) of Ca, Si, Mg, Mn, Na, and Th, and from 2.2 to 2.6 wt.% K_2O and from 4.6 to 5.9 wt.% PbO. The presence of these elements in uraninite from both pegmatites suggest a $U^{6+}:U^{4+}$ in excess of 1:3.

Finch & Ewing (1992) noted that the alteration of uraninite in an oxidizing environment is inhibited by an increased oxidation state of the primary uraninite, which can reach a $U^{6+}:U^{4+}$ value of 2:1. Alteration can also be inhibited by the saturation of interstitial sites, especially with O and Pb. The uraninite from the Palermo and Ruggles pegmatites contains several wt.% Pb, but the interstitial sites are not saturated with Pb and O. Therefore, these samples of uraninite are susceptible to further oxidation as a result of increasing Eh.

Mineral "A"

Mineral "A" was described as an unknown mineral by Frondel (1956). It is the only mineral of the first stage of mineralization, and is a common component of orange "gummite". We found it to be the principal phase in pure unaltered orange "gummite" at the Palermo and Ruggles pegmatites, where it replaces uraninite as fine-grained, orange, waxy masses [see Figs. 1 and 2 of Foord *et al.*

(1997)]. Additional studies were done on this mineral in an attempt to define it as a new species. These studies revealed mineral "A" to be a mixture of different types of dehydrated schoepite and related compounds. Results of electron-microprobe and TGA analyses reveal that mineral "A" is a uranyl-oxide hydroxyl-hydrate. The compounds forming this mixture can have the formulas $(UO_2)(OH)_2 \cdot \frac{1}{2}H_2O$ and $(UO_2)(OH)_2$.

Frondel (1956), Smith (1984) and Finch & Ewing (1992) noted that uranyl oxide hydrates are the first phases to form during the corrosion of uraninite under oxidizing conditions. Mineral "A" was the first phase to form during the alteration of uraninite at both pegmatites. A simplified oxidation reaction that developed mineral "A" may be written as

$$UO_{2(cr)} + 2H^{+}_{(aq)} \rightarrow UO_2^{2+}{}_{(aq)} + H_{2(g)} \quad (1)$$

$$UO_2^{2+}{}_{(aq)} + 2\tfrac{1}{2}H_2O \rightarrow (UO_2)(OH)_2 \cdot \tfrac{1}{2}H_2O_{(cr)} + 2H^{+}_{(aq)} \quad (2)$$

The $2H^{+}_{(aq)}$ that is generated in reaction 2 may continue to react with the primary uraninite, causing additional replacement of uraninite by mineral "A". This reaction will continue as long as water can reach the mineral "A" – uraninite interface. However, this infiltration of water was of limited extent, leaving unaltered cores of uraninite.

Rutherfordine

Rutherfordine is found only at the Palermo No. 1 pegmatite and was the next phase to develop after mineral "A", *i.e.*, during stage 2. Rutherfordine occurs as fine-grained earthy yellow masses replacing mineral "A" or orange "gummite", forming pseudomorphs representing the shape of the original crystals of uraninite. Rutherfordine can be partially replaced by, and associated with, β-uranophane.

At the Palermo No. 1 pegmatite, rutherfordine formed from H^{+} and HCO_3^{-} reacting with mineral "A". The following reactions are proposed for the development of rutherfordine from mineral "A":

$$(UO_2)(OH)_2 \cdot \tfrac{1}{2}H_2O_{(cr)} + 2H^{+}_{(aq)} \rightarrow UO_2^{2+}{}_{(aq)} + 2(OH)^{-}_{(aq)} + \tfrac{1}{2}H_2O + H_{2(g)} \quad (3)$$

$$UO_2^{2+}{}_{(aq)} + HCO_3^{-}{}_{(aq)} \rightarrow UO_2(CO_3)_{(cr)} + H^{+}_{(aq)} \quad (4).$$

The development of rutherfordine first required the decomposition of mineral "A" by hydrogen into a uranyl complex (eq. 3). This uranyl complex in turn reacted with carbonate, producing rutherfordine (eq. 4). The hydrogen produced from the reaction in (4) can continue reacting with mineral "A" in the presence of carbonate, thus continuing the replacement of mineral "A". This reaction will continue as long as waters can reach the mineral "A" – rutherfordine interface.

Soddyite

Soddyite is found only at the Ruggles pegmatite and was the next phase to form at the expense of mineral "A". Soddyite replaces mineral "A", mimicking the shape of the original crystals of uraninite that mineral "A" originally replaced. In addition, soddyite crystallized in fractures and cleavage planes in muscovite, quartz and perthite in the immediate vicinity of the replaced mineral "A" phase. In fractures and open spaces, soddyite occurs as well-developed, light yellow, orthorhombic, needle-like crystals a few micrometers long. Soddyite is associated with β-uranophane within the pseudomorphs of mineral "A" and in fractures. The interval of crystallization of soddyite and β-uranophane overlaps, and β-uranophane dominates over soddyite in the fractures.

Soddyite developed from solutions with dissolved silica and hydrogen reacting with mineral "A". Acid water containing dissolved hydrogen will react with mineral "A", placing uranium in solution (eq. 2). The products of this reaction could be expected in turn to react with dissolved silica, producing soddyite. The following reaction is proposed for the development of soddyite from the components of decomposition of mineral "A":

$$2[UO_2^{2+}{}_{(aq)}] + H_4SiO_{4(aq)} + 2(OH)^{-}_{(aq)} \rightarrow (UO_2)_2SiO_4 \cdot 2H_2O_{(cr)} + 2H^{+}_{(aq)} \quad (5).$$

Sufficient hydrogen is put into solution from this reaction to continue the decomposition of mineral "A". In addition, concentrations of uranium and silica in solution were sufficient to precipitate soddyite beyond the immediate vicinity of mineral "A".

β-Uranophane

The most common secondary uranium mineral found at both pegmatites is β-uranophane. It was the next phase to form during stage 3, after rutherfordine and soddyite. At the Palermo No. 1 pegmatite, β-uranophane replaces uraninite and rutherfordine, and is part of the pseudomorphs after mineral "A". At the Ruggles pegmatite, β-uranophane crystallized with and after the soddyite. It replaces uraninite and mineral "A".

At both pegmatites, β-uranophane is abundant in fractures and along cleavages of the adjacent minerals. It forms a light yellow band around the replaced uraninite; β-uranophane can completely replace uraninite, rutherfordine and mineral "A", and also can be formed as well-developed crystals (5 mm across) lining cavities that were once occupied by uraninite.

Before β-uranophane can precipitate, uraninite, mineral "A" and rutherfordine need to be placed into solution. The earlier-developed minerals will be broken down by hydrogen (equations 1 and 3). The components placed in solution from this decomposition will react with Ca and silica also in solution to produce β-uranophane. The following reaction is proposed for the development of β-uranophane from the components of decomposition of uraninite and mineral "A":

$$2(UO_2^{2+})_{(aq)} + 2(H_4SiO_4)_{(aq)} + Ca^{2+}{}_{(aq)} + 4(OH^-)_{(aq)} + H_2O \rightarrow Ca(UO_2)_2[SiO_3(OH)]_2 \cdot 5H_2O_{(cr)} + 2H^+{}_{(aq)} \quad (6).$$

Since rutherfordine is stable in solutions with a pH of 6, it should decompose in an alkaline solution (pH greater than approximately 7) containing hydroxyl and hydrogen. The following reaction is proposed for the decomposition of rutherfordine:

$$UO_2(CO_3)_{(cr)} + 2(OH^-)_{(aq)} + 2H^+{}_{(aq)} \rightarrow UO_2^{2+}{}_{(aq)} + HCO_3^-{}_{(aq)} + H_2O \quad (7).$$

Uranium placed in solution by this reaction will react with calcium and silica, producing β-uranophane (eq. 6). The H^+ produced in (6) in conjunction with OH^- will continue decomposing rutherfordine, causing β-uranophane to replace rutherfordine. This replacement will continue as long as the rutherfordine – β-uranophane interface is accessible to these reactive fluids.

Concentrations of uranium, calcium and silica in solution were sufficient to be transported into fractures and cleavages. The following reaction is proposed for the precipitation of β-uranophane from a fluid that was transported into fractures:

$$2[UO_2(OH)_3^-]_{(aq)} + 2(H_4SiO_4)_{(aq)} + Ca^{2+}{}_{(aq)} \rightarrow Ca(UO_2)_2[SiO_3(OH)] \cdot 5H_2O_{(cr)} + H_2O \quad (8).$$

In equation 8, uranium is transported as the uranyl complex $UO_2(OH)_3^-$. This complex is being proposed for uranium transport because it is most abundant at a pH above 7 (Finch & Ewing 1992), which favors the precipitation of β-uranophane. In addition, hydroxyl and hydrogen are generated from the decomposition of mineral "A" (eq. 3), which can generate a uranyl-hydroxyl complex.

Compreignacite

Compreignacite is a rare phase that was identified on three specimens from the Palermo No. 1 pegmatite. This mineral formed during stage three after β-uranophane and occurs as a translucent glassy yellow coating on uraninite, mineral "A", rutherfordine and β-uranophane. The yellow coating consists of orthorhombic crystals a few µm across. It was not found in association with the phosphate phases.

Compreignacite precipitated from saturated solutions that were transported into fractures. The following reaction is proposed for the precipitation of compreignacite from a solution:

$$6[UO_2(OH)_3]^-{}_{(aq)} + 2K^+{}_{(aq)} + 4H^+{}_{(aq)} \rightarrow K_2(UO_2)_6O_4(OH)_6 \cdot 8H_2O_{(cr)} \quad (9).$$

The equation shows that uranium was transported as the uranyl complex $UO_2(OH)_3^-$. Compreignacite precipitated from the same fluid as β-uranophane, at similar conditions of pH. For these reasons, the same complex was used as in equation 8 to account for the precipitation of compreignacite.

Phosphuranylite

After β-uranophane and compreignacite crystallized, phosphuranylite formed during stage 4. Phosphuranylite is found in both pegmatites, in fractures and cleavages of muscovite, plagioclase, quartz, and perthite. The mineral occurs as a dark yellow crust that shows well-developed orthorhombic crystals a few µm across. Phosphuranylite also occurs as a pseudomorph after β-uranophane; it can coat earlier phases, and can be associated with meta-autunite I. At the Ruggles pegmatite, phosphuranylite is associated with fluorapatite in the sixth intermediate zone adjacent to the perthite core.

Phosphuranylite precipitated from an aqueous fluid containing uranium, phosphorus, potassium, and calcium. Uranium was placed in solution from the decomposition of the earlier phases and transported to fractures, where phosphuranylite precipitated. The following reaction is proposed for the development of phosphuranylite from an aqueous solution:

$$7(UO_2)^{2+}{}_{(aq)} + 4(HPO_4)^{2-}{}_{(aq)} + K^+{}_{(aq)} + Ca^{2+}{}_{(aq)} + 5(OH)^-{}_{(aq)} + 10H_2O \rightarrow KCa(H_3O)_3(UO_2)_7(PO_4)_4O_2 \cdot 8H_2O_{(cr)} + 4H^+{}_{(aq)} \quad (10).$$

In equation 10, the transport of uranium is attributed to the $UO_2^{2+}{}_{(aq)}$ complex. This complex was used because it is the predominant complex of uranium in acidic solutions [pH less than about 7 at 25°C: Langmuir (1978)], which favors the precipitation of phosphuranylite. Phosphorus is transported as $(HPO_4)^{2-}$, which can occur over a wide range of pH depending on concentration, and is the most important ligand in natural groundwaters (Finch & Ewing 1992). Equation 10 demonstrates the high concentrations of phosphate needed to produce uranyl phosphates.

The replacement of β-uranophane by phosphuranylite is not common, and will only take place in the presence of high concentrations of phosphate (Finch & Ewing 1992). At both pegmatites, phosphuranylite replaced β-uranophane, but is of minor importance. β-uranophane is first decomposed in the presence of hydrogen in an acidic aqueous fluid before it is replaced by phosphuranylite. The following reaction is proposed for the decomposition of β-uranophane:

$$\begin{aligned}&Ca(UO_2)_2[SiO_3(OH)]_2{\cdot}5H_2O_{(cr)} + H^+_{(aq)} \rightarrow\\ &2(UO_2)^{2+}_{(aq)} + Ca^{2+}_{(aq)} + 2(H_4SiO_4)_{(aq)}\\ &+ 5(OH)^- \qquad (11).\end{aligned}$$

The products of equation 11, with the exception of silica, will react with potassium and phosphate and produce phosphuranylite (eq. 10). Silica entering the solution in equation 11 will remain in solution because the pH is too acidic to produce uranyl silicate minerals, and calcium is being used to precipitate phosphuranylite. A sufficient amount of hydrogen ions is produced during the precipitation of phosphuranylite (eq. 10) to continue reacting with β-uranophane at the phosphuranylite – β-uranophane interface. The replacement reaction will continue as long as fluids can reach this interface.

Meta-autunite I

Meta-autunite I is the last phase to crystallize during stage 4. At both locations, the mineral coats fractures and cleavages in plagioclase, perthite, muscovite and quartz. Meta-autunite I is most abundant in bands surrounding the phosphuranylite band; it is rarely associated with the earlier secondary minerals, but where present, it coats the earlier-formed phases along fractures. The mineral occurs as well-developed yellow-green tetragonal plates that vary in size from a few μm to 2 mm across and as light gray scaly coatings.

Meta-autunite I precipitated in isolated locations in and adjacent to the pegmatite core. At the Palermo No. 1 pegmatite, meta-autunite I is found in hydrothermal quartz veins in the core with smoky quartz (Segeler *et al.* 1981). Meta-autunite I, the first dehydration phase of autunite, is the most stable mineral in this series with respect to autunite (Takano 1961).

Meta-autunite I precipitated from an acidic aqueous fluid containing uranium, phosphorus and calcium ions. The following reaction is proposed for the precipitation of meta-autunite I:

$$\begin{aligned}&2(UO_2)^{2+}_{(aq)} + 2(HPO_4)^{2-}_{(aq)} + Ca^{2+}_{(aq)} + 6H_2O \rightarrow\\ &Ca(UO_2)_2(PO_4)_2{\cdot}6H_2O_{(cr)} + 2H^+_{(aq)} \qquad (12).\end{aligned}$$

Both meta-autunite I and phosphuranylite precipitated from the same aqueous fluid. Therefore, both minerals will precipitate as a result of similar reactions. All the K was used when phosphuranylite precipitated, leaving the excess Ca in solution, which in turn precipitated as meta-autunite I in the last phase.

DISCUSSION

There has been much discussion in the literature as to whether the secondary alteration of uraninite in pegmatites resulted from reactions with a late-stage hydrothermal fluid or meteoric water. Ross *et al.* (1931) suggested that uraninite alteration in the Spruce Pine pegmatites was caused by reactions with a late-stage hydrothermal fluid. Frondel (1956) pointed out that uranium deposits in sandstone undergo a similar sequence of alteration as in granitic pegmatites under weathering conditions. In granitic pegmatites in India, uraninite near the surface is altered into "uranium ocher" and grades downward into unaltered uraninite (Frondel 1956). Frondel (1956; W.R. Griffitts, pers. comm., 1990) suggested that the alteration of uraninite in granitic pegmatites is the result of chemical reactions with circulating meteoric waters and perhaps some hydrothermal waters.

At the Palermo No. 1 and Ruggles pegmatites, the bulk of the evidence presented is consistent with early hydrothermal interaction with uraninite and a later development of the secondary uranium minerals at a meteoric stage. When a hydrothermal fluid cools, it could be expected to converge onto the same chemical and physical characteristics as meteoric water. At both pegmatites, the development of the secondary uranium minerals is a kinetic as well as a temperature problem. However, kinetics and pH are more important at temperatures typical of meteoric processes.

The first stage of uraninite alteration produced a uranyl hydroxyl hydrate (mineral "A"), which is a mixture of nearly completely dehydrated forms of schoepite. Completely hydrated schoepite forms from the weathering of uraninite and is typically the first uranyl phase to precipitate from water in contact with the atmosphere (Finch & Ewing 1992). Moore (1973) noted that phosphate minerals with a low degree of hydration crystallized at higher temperatures than those with a high degree of hydration. The same inference can be applied to explain the precipitation of mineral "A" and fully hydrated schoepite. Since mineral "A" is nearly dehydrated, it could not have formed from the weathering of uraninite by meteoric waters in contact with the atmosphere. Instead, mineral "A" likely formed in a closed system from late-stage hydrothermal fluids.

From investigations of phosphate minerals at the Palermo No. 1 pegmatite, Segeler *et al.* (1981) suggested that the late-stage hydrothermal fluids might have been active over the temperature range 350° to 50°C. Mineral "A" crystallized at the beginning of this hydrothermal stage, probably somewhat above 300°C.

The precipitation of uranyl-hydroxide hydrates requires large oversaturations, and may involve solutions with significant concentrations of silica (Finch & Ewing 1992). Mineral "A" developed from a fluid that was oversaturated not only with respect to mineral "A", but also probably with silica. Uranyl silicates did not precipitate from this solution with mineral "A" because the pH was too acidic (pH less than about 6), and the temperature was above 25°C.

After mineral "A" crystallized, the residual late-stage hydrothermal fluids cooled to the temperature of meteoric water (25°C). Thus this remaining fluid converged onto the same pH and chemical characteristics as meteoric water. The pH is temperature-dependent; at 100°C, neutral pH is 6; in other words, with dropping temperature, a neutral pH for the same fluid would shift toward 7 (Romberger 1984). When the hydrothermal fluid cooled to temperatures of meteoric water, the initial pH remained acidic and with time, slowly shifted toward neutral (pH 7 at 25°C) to alkaline when the uranyl silicates precipitated.

At the Palermo No. 1 pegmatite, the second stage of alteration produced the uranyl carbonate rutherfordine. This pegmatite contains abundant carbonate minerals, mostly siderite. Water reacting with siderite will contain dissolved carbonate as HCO_3^-. Where the partial pressure of CO_2 exceeds $10^{-2.2}$ atm. in meteoric waters, dehydrated schoepite becomes unstable, and rutherfordine will form (Finch & Ewing 1992). When the hydrothermal fluid that developed mineral "A" cooled to meteoric temperatures, it became oversaturated with carbonate, and the partial pressure of CO_2 exceeded $10^{-2.2}$ atm. Mineral "A" became unstable in this fluid and was partially to completely replaced by rutherfordine.

In uranium-rich aqueous solutions [$\Sigma U = 10^{-4}$M, $P(CO_2) = 10^{-2}$ atm. at 25°C], rutherfordine is dominant at a pH of 6 (Finch & Ewing 1992) and can be stable at a pH ranging from <6 to 7 (Sergeyeva *et al.* 1972). The precipitation of rutherfordine at the Palermo No. 1 pegmatite took place in near-neutral to acid waters (pH less than about 6 at 25°C).

At the Ruggles pegmatite, carbonate is absent, and soddyite was the next phase to crystallize. Soddyite is the first uranyl silicate phase to crystallize during the silicate or third alteration stage. The precipitation of uranyl silicates from a solution requires oversaturations of silica and calcium (Finch & Ewing 1992).

The stability boundaries for soddyite, schoepite, and uranophane at 30°C have been proposed by Finch & Ewing (1992). They are dependent on the activity of Ca^{2+}, H_4SiO_4 and pH. Schoepite is stable in environments with low activities of dissolved Ca and silica. With increasing activities of dissolved silica and at low activities of Ca, soddyite becomes stable at the expense of schoepite. At 30°C, the stability boundary between schoepite and soddyite is defined by an activity of H_4SiO_4 greater than $10^{-4.2}$ and an activity ratio $a\mathrm{Ca}^{2+}/a2\mathrm{H}^+$ less than 10^4, as illustrated in Figure 2.

Soddyite precipitated from an aqueous fluid that had an activity of dissolved H_4SiO_4 greater than $10^{-4.2}$ and a low value of $a\mathrm{Ca}^{2+}/a2\mathrm{H}^+$ ($<10^4$) with a near-neutral to acid pH (pH greater than about at 25°C). Mineral "A", unstable in this solution, was replaced by soddyite. Solution saturations were sufficient for uranium and silica to be transported into fractures and cleavage planes, where soddyite precipitated.

Beta-uranophane, found at both pegmatites, was the next mineral to precipitate during the third stage of alteration. The stability diagram for soddyite, schoepite, and uranophane (Fig. 2) shows uranophane becoming stable at $a\mathrm{Ca}^{2+}/a2\mathrm{H}^+$ between $10^{6.5}$ and 10^{12}, depending on the activity of H_4SiO_4. This demonstrates that the pH required for the precipitation of β-uranophane is higher than for the precipitation of soddyite. Whereas soddyite

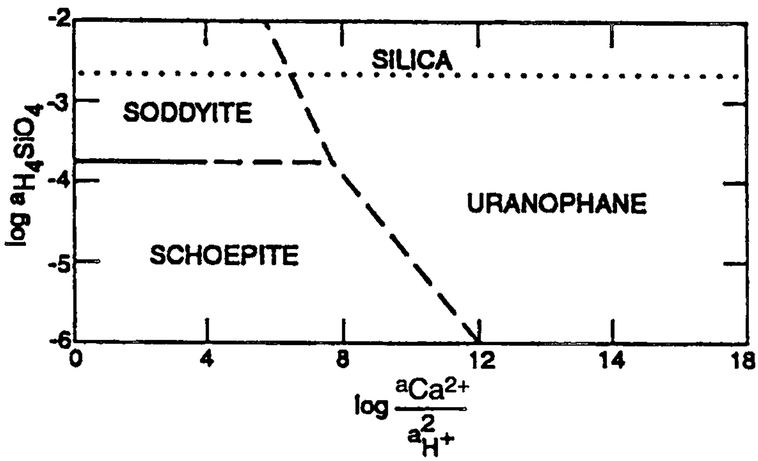

FIG. 2. Stability fields of uranophane, schoepite and soddyite at 30°C as a function of $a\mathrm{H_4SiO_4}$, $a\mathrm{Ca}^{2+}$ and pH. Lines dashed where metastable with respect to becquerelite. Diagram modified from Finch & Ewing (1992).

precipitated at an acidic to near-neutral pH, β-uranophane crystallized at an alkaline pH (≥7 at 25°C). Beta-uranophane can crystallize over a wide range of silica activities, ranging from 10^{-2} to 10^{-6}.

At the Palermo No. 1 pegmatite, conditions were not favorable for the precipitation for soddyite. Either the calcium activities and pH were too high, or it was the silica activity that was too high. Instead, β-uranophane precipitated. However, in the Ruggles pegmatite, both minerals precipitated.

At the Ruggles pegmatite, β-uranophane and soddyite deposition overlapped, which places some constraints on the activities of Ca and silica and on pH. Soddyite is expected where the activity of H_4SiO_4 is greater than $10^{-4.2}$, the activity ratio Ca^{2+}/H^+ is below 10^8, and the pH is near-neutral to acidic. Beta-uranophane can be expected to form at the same activity of silica as soddyite if the ratio of activity of Ca^{2+} to that of H^+ is greater than 10^8 and the pH is alkaline (Fig. 2) (Finch & Ewing 1992). Based on the above constraints, the initial crystallization of β-uranophane probably took place where H_4SiO_4 activity exceeded $10^{-4.2}$ at a pH of less than about 7 at 25°C. Later, with increased activity of H_4SiO_4, increased ratio of Ca^{2+} to H^+ activities and increase of the pH to the alkaline range, the deposition of β-uranophane was favored over soddyite.

At the Palermo No. 1 pegmatite, compreignacite precipitated at the close of the third stage of alteration. Since compreignacite crystallized with β-uranophane, it probably precipitated under the same alkaline conditions as β-uranophane. Because compreignacite is so rare, it probably crystallized under restricted chemical conditions, *i.e.*, only where the pH and concentrations of K^+ and U^{6+} were sufficiently high to favor its precipitation.

The fourth and final stage of alteration is characterized by the precipitation of uranyl-phosphate minerals. Phosphuranylite was the first phase to precipitate, followed by meta-autunite I.

Uranyl phosphate minerals precipitate from an acidic aqueous fluid with high concentrations of phosphate. On the basis of previous experimental work, Finch & Ewing (1992) suggested that phosphate concentrations need to be high, at about 10^{-2} M, with an acid pH, to precipitate uranyl phosphate in the absence of a catalyst. At a pH exceeding approximately 7, fluorapatite should maintain phosphate concentrations below those required for the precipitation of uranyl phosphates. At a pH below 7, fluorapatite is increasingly soluble, possibly allowing phosphuranylite to precipitate.

At the Ruggles pegmatite, fluorapatite associated with uranyl phosphate minerals is etched. This etching suggests the presence of acidic solutions at the stage the uranyl phosphate minerals were precipitated. The replacement of β-uranophane by phosphuranylite further indicates the acidic conditions needed to precipitate uranyl phosphates. Uranyl silicates can be replaced by uranyl phosphates when phosphorus concentrations in groundwater are elevated (Finch & Ewing 1992). Beta-uranophane is unstable in acidic groundwater and will decompose. If this decomposition takes place in the presence of high concentrations of phosphorus, then β-uranophane can be replaced by phosphuranylite.

Minerals of the phosphuranylite group have higher solubilities than those of the autunite group (Finch & Ewing 1992). Therefore, the precipitation of phosphuranylite will require higher degrees of saturation of the solution than for meta-autunite I. Equation 10 shows that higher proportions of $UO_2^{2+}{}_{(aq)}$ and HPO_4^{2-} are needed to generate phosphuranylite than is the case for meta-autunite I, as shown in equation 12. Since higher concentrations of the solution are needed to generate phosphuranylite, it is more closely associated with uraninite and the earlier secondary minerals than with meta-autunite I.

CONCLUSIONS

The paragenetic sequence determined for the Palermo No. 1 and Ruggles pegmatites (Table 1) confirms the sequence of alteration observed by Frondel (1956). The secondary uranium minerals at the Ruggles and Palermo No. 1 pegmatites developed from the alteration of primary uraninite by hydrothermal fluid and groundwater. At the Palermo No. 1 pegmatite, four stages of alteration took place: uranyl oxide hydrate, uranyl carbonate, uranyl silicate and uranyl phosphate. At the Ruggles pegmatite, the uranyl carbonate stage is missing.

The first three mineralizing stages and mineral paragenesis represent continuous changes in pH and fluid saturations in a closed system. Initial alteration took place at temperatures above or near 300°C, with an acidic pH. After stage one, the initial hydrothermal fluid cooled and, with time, the pH shifted to approximately 7 at 25°C. During the carbonate or second stage, the fluid remained acidic, with a pH closer to 6 at 25°C, and was oversaturated with carbonate. The third or silicate stage had an initial acidic pH that shifted to slightly alkaline at the close of this stage. Initially, the Ca and Si saturations and pH favored the deposition of soddyite. Later, Ca and Si saturations increased along with the pH, and β-uranophane precipitated.

The fourth stage represents alteration by the introduction of groundwater in an open system. During this stage, phosphuranylite and meta-autunite I precipitated from an oversaturated, acidic aqueous fluid. After the close of the third stage, the remaining aqueous fluid was alkaline; the introduction of groundwater shifted the pH of this fluid to the acidic range.

Phosphuranylite and meta-autunite I precipitated from an acidic solution with oversaturations in uranium, phosphorus, calcium, and potassium. After the precipitation of phosphuranylite, the solution became oversaturated with respect to meta-autunite I, and this final phase precipitated.

The alteration of uraninite and precipitation of secondary uranium minerals under late-stage hydrothermal and meteoric conditions in a pegmatite are not well understood. Most work has been concentrated on the alteration and precipitation of these minerals under weathering conditions in sandstone deposits. Much experimental work remains to be done to determine Eh and pH constraints for the precipitation of these minerals in a pegmatite-forming environment.

ACKNOWLEDGEMENTS

Carl A. Francis (Harvard University) provided the samples originally studied by C. Frondel, as well as some additional specimens. Reviews were provided by P.J. Modreski (USGS) and Vandall T. King (Rochester, N.Y.). Additional reviews by W.B. Simmons and Alexander U. Falster (University of New Orleans) are gratefully acknowledged. Robert J. Finch (University of Manitoba) added valuable suggestions and comments that made the completion of this manuscript possible. Robert F. Martin (McGill University) also reviewed the manuscript and provided suggestions on its presentation.

REFERENCES

BERMAN, R.M. (1957): The role of lead and excess oxygen in uraninite. *Am. Mineral.* **42**, 705-731.

CAMERON, E.N., LARRABEE, D.M., MCNAIR, A.H., PAGE, J.J., STEWART, G.W. & SHAININ, V.E. (1954): Pegmatite investigations 1942–45, New England. *U.S. Geol. Surv., Prof. Pap.* **255**.

FINCH, R.J. & EWING, R.C. (1992): The corrosion of uraninite under oxidizing conditions. *J. Nucl. Mater.* **190**, 133-156.

FORD, R.B. (1955): Mineralogy of a uraninite-bearing pegmatite, Lac La Ronge, Saskatchewan. *Econ. Geol.* **50**, 196-205.

FOORD, E.E., KORZEB, S.L., LICHTE, F.E. & FITZPATRICK, J.J. (1997): Additional studies on mixed uranyl oxide–hydroxide-hydrate alteration products of uraninite from the Palermo and Ruggles granitic pegmatites, Grafton County, New Hampshire. *Can. Mineral.* **35**, 145-151.

FRONDEL, C. (1950): Studies of uranium minerals. 1. Parsonsite and randite. *Am. Mineral.* **35**, 245-250.

________ (1956): Mineral composition of gummite. *Am. Mineral.* **41**, 539-568.

________ (1958): Systematic mineralogy of uranium and thorium. *U.S. Geol. Surv., Bull.* **1064**.

GRANDSTAFF, D.E. (1976): A kinetic study of the dissolution of uraninite. *Econ. Geol.* **71**, 1493-1506.

INGERSON, E. (1938): Uraninite and associated minerals from Haddam Neck, Connecticut. *Am. Mineral.* **23**, 269-276.

LANGMUIR, D. (1978): Uranium solution–mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta* **42**, 547-569.

MOORE, P.B. (1973): Pegmatite phosphates: descriptive mineralogy and crystal chemistry. *Mineral. Rec.* **4**, 103-130.

PAGE, J.J. & LARRABEE, D.M. (1962): Beryl resources of New Hampshire. *U.S. Geol. Surv., Prof. Pap.* **353**.

PAGE, L.R. (1950): Uranium in pegmatites. *Econ. Geol.* **45**, 12-34.

ROMBERGER, S.B. (1984): Transportation and deposition of uranium in hydrothermal systems at temperatures up to 300°C: geological implications. *In* Uranium Geochemistry, Mineralogy, Geology, Exploration and Resources (B.D. Vivo, F. Ippolito, G. Capaldi & P.R. Simpson, eds.). Institution of Mining and Metallurgy, London, U.K. (12-17).

ROSS, C.S., HENDERSON, E.P. & POSNJAK, E. (1931): Clarkeite, a new uranium mineral. *Am. Mineral.* **16**, 213-220.

SEGELER, C.G., ULRICH, W., KAMPF, A.R. & WHITMORE, R.W. (1981): Phosphate minerals of the Palermo No. 1 pegmatite. *Rocks and Minerals* **56**, 197-214.

SERGEYEVA, E.I., NIKITIN, A.A., KHODAKOVSKIY, I.L., NAUMOV, G.B. & VERONASKIY, V.I. (1972): Experimental investigation of equilibria in the system UO_3–CO_2–H_2O in 25–200°C temperature interval. *Geochem. Int.* **9**, 900-910.

SHAUB, B.M. (1938): The occurrence, crystal habit and composition of the uraninite from the Ruggles mine, near Grafton Center, New Hampshire. *Am. Mineral.* **23**, 334-341.

SMITH, D.K. (1984): Uranium mineralogy. *In* Uranium Geochemistry, Mineralogy, Geology, Exploration and Resources (B.D. Vivo, F. Ippolito, G. Capaldi & P.R. Simpson, eds.). Institution of Mining and Metallurgy, London, U.K. (43-71).

TAKANO, Y. (1961): X-ray study of autunite. *Am. Mineral.* **46**, 812-822.

Received October 18, 1995, revised manuscript accepted October 9, 1996.