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Reexamination of Uranium (IV) Phosphate Chemistry

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During the past 40 years, few papers concerning uranium (IV) phosphate chemistry have been cited as references in usual textbooks and nobody, up to now, has questioned their veracity. In our recent studies on uranium (IV) phosphates, we found that some of them, like $U_3(PO_4)_4$, do not exist or, like $(U_2O_3)P_2O_7$, were wrongly identified. Thus, the reinvestigation of uranium (IV) phosphates was decided to be necessary. Some new compounds were prepared and identified. From previously published results, this paper draws up a balance sheet of the scope concerning the complete understanding of the chemistry of tetravalent uranium phosphates. This new approach is given in terms of a survey of the literature errors to set the facts in their true light. Two synoptic schemes are given to bring forward evidence of new compounds, $U(UO_2)(PO_4)_2$ and $U_2O(PO_4)_2$, which appear to be significant in the chemistry of uranium (IV) phosphates. © 1996 Academic Press, Inc.

LITERATURE REVIEW

This paper presents a review of all uranium (IV) phosphate chemistry including our published works.

The literature concerning uranium (IV) phosphates is rather poor in comparison to that concerning uranyl ones. The first work about them was published in 1848 by Werter (1) who gave for uranium (IV) phosphate the formula $U_3(PO_4)_4$. Years later, in 1907, Colani (2) synthesized the same uranium phosphate.

In 1956, Dunn (3) classified the X-ray diffraction (XRD) data of all known uranium compounds, among them uranium (IV) phosphates. In 1963, Burdese and Borlera (4) investigated the solid system UO_2–P_2O_5 with different mole ratios U/P and obtained such compounds as uranium trioxopolyphosphate (metaphosphate) $U(PO_3)_4$, uranium diphosphate UP_2O_7, uranium oxide phosphate $(UO)_3(PO_4)_2$, uranium oxide diphosphate $(UO)_2P_2O_7$, and, of course, uranium phosphate $U_3(PO_4)_4$. The XRD data published by these authors were used as a reference by many others. Schaekers and Greybe (5) compared the XRD patterns of $(UO)_3(PO_4)_2$ with a diphosphate synthesized by them $(U_3O_5)P_2O_7$, and found no distinction between these two compounds, though they differ in 1 atom of oxygen and also in the oxidation state of uranium. It is significant that for $(UO)_3(PO_4)_2$ there are no results of chemical analysis or other characterization. Moreover, Bamberger *et al.* (6) unsuccessfully attempted to synthesize uranium phosphate $U_3(PO_4)_4$. Thus, there were two uranium phosphates with formulas that were in doubt: $U_3(PO_4)_4$ and $(UO)_3(PO_4)_2$.

A uranium oxide diphosphate, $(U_2O_3)P_2O_7$ [JCPDS File 13-64], was mentioned for the first time by Dunn (3). In 1960, Klygin and co-workers (7) synthesized the same compound. Shaekers (8), studying the thermal decomposition of uranyl phosphates, also obtained $(U_2O_3)P_2O_7$ and used this compound for quantitative determination of uranyl or phosphate ions because of its stability at high temperature (850°C) (9). Bamberger *et al.* (6) synthesized and characterized the same diphosphate but it seems that their product contained some impurities because the mole ratio U/P given in their paper is not 1 : 1 but 1 : 1.15. Surprisingly, XRD patterns of $(U_2O_3)P_2O_7$ are identical to those of uranium phosphate $U_3(PO_4)_4$, although they correspond to two very different chemical species.

In the literature concerning uranium (IV) phosphates there was no doubt about $(U_2O_3)P_2O_7$, $(U_3O_5)P_2O_7$, $(UO)_2P_2O_7$, UP_2O_7, or $U(PO_3)_4$. The existence of $(U_3O_5)P_2O_7$ was confirmed by Barten and Cordfunke (10) [JCPDS File 34-1487] but without any evidence of its purity. We have compared its XRD data with the lines of the starting compounds used by Schaekers and Greybe (5) in their synthesis, i.e., UO_2 [JCPDS File 41-1422], U_3O_8 [JCPDS File 31-1426], α-UP_2O_7 [JCPDS File 16-233], and β-UP_2O_7 [JCPDS File 9-87], as well as with those of $(UO)_2P_2O_7$ [JCPDS File 16-228]. It seems that $(U_3O_5)P_2O_7$ is a mixture of all these compounds.

The first question is about $(U_2O_3)P_2O_7$, in which a complex oxide ion $U_2O_3^{4+}$ is suggested. The existence of a such an ion, as well as the existence of $U_3O_5^{4+}$ from $(U_3O_5)P_2O_7$, is questionable, since these ions are unknown to uranium solution chemistry and appear only in solid compounds. Their identification is inconsistent with the usual oxidation states of uranium and their stability. Moreover, for $(U_2O_3)P_2O_7$, Cordfunke and Ouweltjes (11) suggested a formula like UPO_5 which can also be written as $UOPO_4$

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(1/2 $U_2O_3P_2O_7$). Taking into account this formula, uranium should be pentavalent, an oxidation state known to be very unstable even in the solid state.

The second problem concerns $(UO)_2P_2O_7$, mentioned for the first time by Dunn (3). The synthesis and crystallographic data of this compound were published also by Burdese and Borlera (4). Schaekers obtained $(UO)_2P_2O_7$ by decomposition or reduction of $(U_2O_3)P_2O_7$ by means of hydrogen or carbon in argon (8) but Barten and Cordfunke (10) did not confirm this decomposition process in a nitrogen atmosphere. Bamberger *et al.* (6) studied the same decomposition reaction without success; nevertheless, after reexamination of the system they obtained a mixture of $(UO)_2P_2O_7$ and $(U_3O_5)P_2O_7$, and finally an almost pure $(UO)_2P_2O_7$ with remnants of $(U_3O_5)P_2O_7$ was claimed to have been synthesized in an Ar–H_2 atmosphere.

Il'in *et al.* (12) reported obtaining $(UO)_2P_2O_7$ by heating uranium diphosphate in an argon–hydrogen atmosphere, but the main lines of their XRD diagram [JCPDS File 31-1433] do not agree with those of other authors (3, 4). The reaction between UP_2O_7 and UO_2 was investigated by Kirchner *et al.* (13) in argon at 1200°C also in order to synthesize uranium oxide diphosphate.

All important textbooks of chemistry (14–17) have obviously reported $U_3(PO_4)_4$, $(U_2O_3)P_2O_7$, $(U_3O_5)P_2O_7$, and $(UO)_2P_2O_7$, known from original works. Since we found their chemical formulas or XRD data wrong, we considered it necessary to clarify the controversial and doubtful situation of the chemistry of uranium (IV) phosphates.

NEW URANIUM (IV) PHOSPHATES

Syntheses in Air Atmosphere

Up to the present, $(U_2O_3)P_2O_7$ has been synthesized by dry chemistry methods at high temperature. We have studied uranium (IV) phosphate chemistry starting both from concentrated solutions of U(IV) and phosphoric acid and from solid reagents (18–21).

Uranium (IV) hydrochloric solution mixed with phosphoric acid gives a green precipitate. When the mole ratio U/PO_4 is equal to 3/4, the XRD patterns of the final product, obtained by heating this precipitate at 850–1170°C, correspond, at the same time, to the already described $(U_2O_3)P_2O_7$ and $U_3(PO_4)_4$. Chemical analysis of this compound gives a mole ratio $U/PO_4 = 1/1$ (not 3/4), and the ratio $U_{\text{total}}/U(IV)$ is equal to 2/1. Thus, there are two different oxidation states of this element, which confirms the results of Bamberger *et al.* (6) concerning uranium oxide diphosphate.

UV–visible, infrared, and Raman absorption spectroscopies, as well X-ray photoelectron spectroscopy (XPS), were performed and discussed (18). The UV–visible spectrum of the obtained solid shows the presence of the uranyl ion UO_2^{2+} in the region 350–450 nm and the presence of U^{4+} in the region 450–900 nm. These two oxidation states of uranium were confirmed by XPS taking into account the 4 $f5/2$ and 4 $f7/2$ levels. We have also observed uranyl ion bands in the Raman spectrum at 892 cm^{-1}, given for the first time for this compound by Bamberger *et al.* (6), U=O (ν_1 at 871 cm^{-1}, ν_2 at 255 cm^{-1}, ν_3 at 939 cm^{-1}) and U–O (250 cm^{-1}) bands in the IR spectra. No absorption bands characteristic for U(V) were observed in the near infrared spectrum and no signal was detected by electron paramagnetic resonance (EPR), which excludes the presence of the uranium (V) oxidation state (18, 20).

At this stage of knowledge we can say that there are two different ions, U^{4+} and UO_2^{2+}, in so-called uranium oxide diphosphate $(U_2O_3)P_2O_7$ [JCPDS File 13-64] and that it is difficult to consider as possible an ion like $U_2O_3^{4+}$ which has never been mentioned in other uranium compounds. There is also a problem with the implied diphosphate ion $P_2O_7^{4-}$. In contrast to Schaekers (8), we have not detected in the infrared spectrum any band between 700 and 800 cm^{-1}, characteristic of the symmetric stretching of the P–O–P bridge in the diphosphate group (18). Furthermore, the *ab initio* structure determination from powder diffraction data confirms the presence of isolated PO_4 and not of P_2O_7 groups. Thus, the compound in question is identified as uranium uranyl phosphate, $U(UO_2)(PO_4)_2$ (19).

Uranium uranyl phosphate is formed by heating the precipitate obtained by mixing (at room temperature) uranium (IV) hydrochloric solution with phosphoric acid. Chemical analysis, the UV–visible spectrum, and the first results of crystallographic studies of this precipitate give a formula which corresponds to uranium chloride phosphate $UClPO_4 \cdot 4H_2O$ (20). An analogous compound was also prepared from uranium (IV) hydrobromic solution and H_3PO_4, $UBrPO_4 \cdot 5H_2O$ (22). Neither uranium chloride phosphate nor uranium bromide phosphate is known in the literature up to date.

Both uranium halogenide phosphates hydrolyze, $UBrPO_4 \cdot 5H_2O$ more easily than $UClPO_4 \cdot 4H_2O$ (it was impossible to obtain $UIPO_4$ in aqueous medium), giving uranium hydroxide phosphate $U(OH)PO_4 \cdot 6H_2O$ (20). An anhydrous uranium hydroxide phosphate was already suggested by Schreyer (23, 24), but was not investigated further. $U(OH)PO_4$ mono- and dihydrates are known to exist in some uranium minerals as mixed compounds [JCPDS Files 41-1399, 38-397].

Heated in air at 1170°C, the three mentioned compounds, $UClPO_4 \cdot 4H_2O$, $UBrPO_4 \cdot 5H_2O$, and $U(OH)PO_4 \cdot 6H_2O$, always give the same product, uranium uranyl phosphate. Different intermediate compounds appear during the rise of the temperature but the mole ratio of the final product remains the same, i.e., $U/PO_4 = 1$. The reaction mechan-

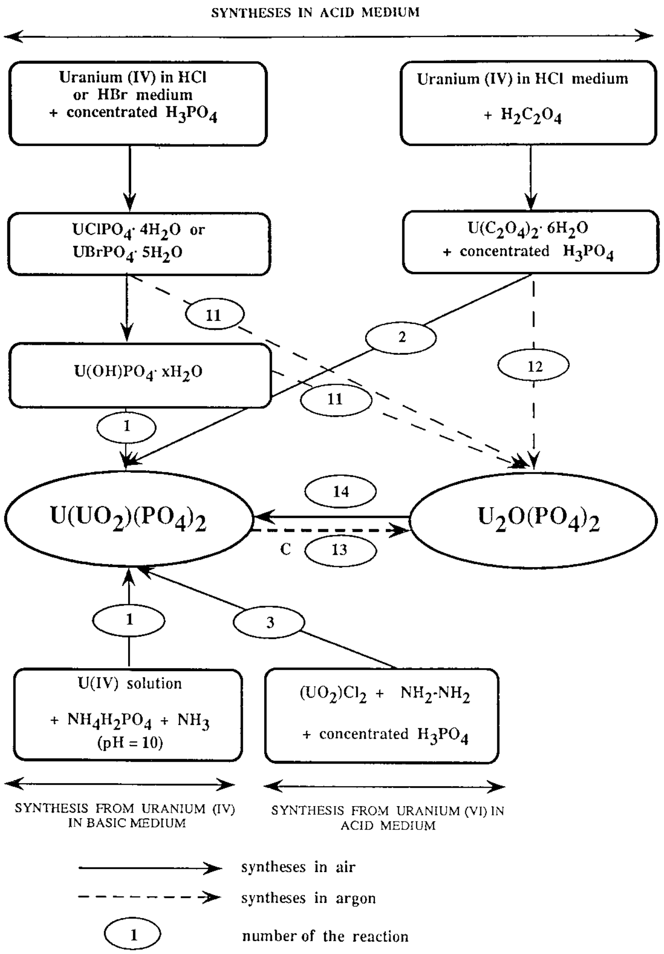

FIG. 1. Wet chemistry methods of synthesis of uranium (IV) phosphates. Numbers in blocks refer to reactions in the text.

ism of the transformation $UClPO_4 \rightarrow U(UO_2)(PO_4)_2$ was proposed elsewhere (20): uranium chloride (also bromide) phosphate is first hydrolyzed, by heating, into $U(OH)PO_4 \cdot xH_2O$ and then gives, at 800–1170°C, uranium uranyl phosphate.

We also synthesized uranium uranyl phosphate by other methods (18, 21): uranium (IV) oxalate mixed with phosphoric acid, uranyl chloride UO_2Cl_2 solution mixed with phosphoric acid in the presence (or absence) of hydrazine, uranium (IV) chloride solution mixed with ammonium dihydrogen phosphate in basic medium. All routes of synthesis that we have utilized are presented in Figs. 1 and 2 and can be represented by the reactions (their numbers correspond to those mentioned in figures)

$$2UXPO_4 \cdot nH_2O + \tfrac{1}{2}O_2 \rightarrow U(UO_2)(PO_4)_2 + 2HX\uparrow + (2n-1)H_2O\uparrow, \quad [1]$$

where X = Cl, Br, OH (in ammonia medium, NH_4X or NH_3 are evolved);

$$2U(C_2O_4)_2 \cdot 6H_2O + 2H_3PO_4 + \tfrac{5}{2}O_2 \rightarrow U(UO_2)(PO_4)_2 + 8CO_2\uparrow + 15H_2O\uparrow \quad [2]$$

$$2UO_2Cl_2 + 2H_3PO_4 \rightarrow U(UO_2)(PO_4)_2 + H_2O\uparrow + 4HCl\uparrow + \tfrac{1}{2}O_2\uparrow. \quad [3]$$

We checked that dry methods of synthesis (Fig. 2) also lead to the same final compound starting as well from uranium (IV) derivatives like (UO_2) and $NH_4H_2PO_4$ or UO_2 and UP_2O_7 (20, 21) or uranyl compounds (8, 10):

$$2UO_2 + 2NH_4H_2PO_4 + \tfrac{1}{2}O_2 \rightarrow U(UO_2)(PO_4)_2 + 2NH_3\uparrow + 3H_2O\uparrow \quad [4]$$

$$UP_2O_7 + UO_2 + \tfrac{1}{2}O_2 \rightarrow U(UO_2)(PO_4)_2. \quad [5]$$

The very well known uranium (IV) polytrioxophosphate (metaphosphate, $U/PO_4 = 1/4$) $U(PO_3)_4$ (2, 3, 26, 27) may be also used for the synthesis of $U(UO_2)(PO_4)_2$. It is decomposed, by heating, into UP_2O_7 (21, 27), while the

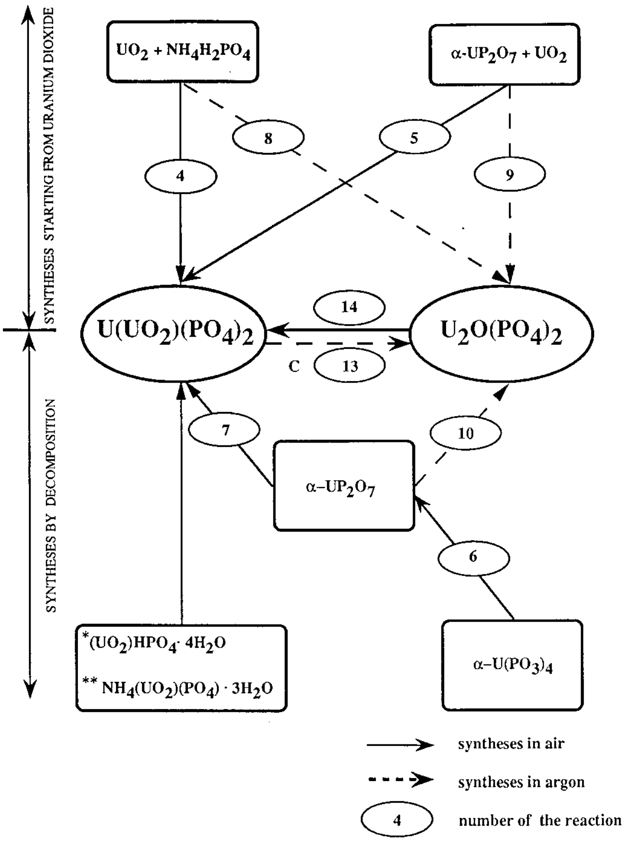

FIG. 2. Dry chemistry methods of synthesis of uranium (IV) phosphates. Numbers in blocks refer to reactions in the text. *H. Barten and Cordfunke (10). **J. M. Schaekers (8).

latter gives uranium uranyl phosphate at 1250°C (6, 20, 21):

$$2U(PO_3)_4 \rightarrow 2UP_2O_7 + P_4O_{10}\uparrow \quad [6]$$

$$4UP_2O_7 + O_2 \rightarrow 2U(UO_2)(PO_4)_2 + P_4O_{10}\uparrow . \quad [7]$$

Syntheses in Inert Atmosphere and in the Presence of a Reducing Agent

The compound identified until now as uranium oxide diphosphate $(UO)_2P_2O_7$ is very difficult to synthesize as a pure phase. It can be prepared from UO_2 and a phosphating agent such as $NH_4H_2PO_4$. Some intermediate species may be formed or may remain during the temperature rise; the most stable among them is uranium diphosphate, α-UP_2O_7, which is slowly decomposed into $(UO)_2P_2O_7$ above 1250°C (complete reaction at about 1350°C). An *ab initio* structure determination from powder diffraction data was performed and a linear bridge U–O–U, as well as isolated PO_4 (but not diphosphate) groups, was found (21, 25). Thus, the real formula of $(UO)_2P_2O_7$ should be written as diuranium oxide phosphate, $U_2O(PO_4)_2$. We achieved syntheses of this compound by dry methods (Fig. 2), starting from UO_2 and $NH_4H_2PO_4$ or UP_2O_7. They may be written as

$$2UO_2 + 2NH_4H_2PO_4 \rightarrow U_2O(PO_4)_2 + 2NH_3\uparrow + 3H_2O\uparrow \quad [8]$$

$$UO_2 + UP_2O_7 \rightarrow U_2O(PO_4)_2 \quad [9]$$

$$4UP_2O_7 \rightarrow 2U_2O(PO_4)_2 + P_4O_{10}\uparrow . \quad [10]$$

The same final compound is also obtained by heating uranium chloride phosphate, uranium bromide phosphate, uranium hydroxide phosphate, or uranium oxalate with phosphoric acid, in an argon atmosphere at about 1350°C (13, 20) (Fig. 1). The corresponding reactions are

$$2UXPO_4 \cdot nH_2O \rightarrow U_2O(PO_4)_2 + 2HX\uparrow + (2n-1)H_2O\uparrow \quad [11]$$

where X = Cl, Br, OH,

$$2U(C_2O_4)_2 \cdot 6H_2O + 2H_3PO_4 \rightarrow U_2O(PO_4)_2 + 4CO_2\uparrow + 4CO\uparrow + 15H_2O\uparrow . \quad [12]$$

TABLE 1
Uranium (IV) Phosphates Uncontested Up To Date

Compound	Reference	Compound	Reference
$U(HPO_4)_2 \cdot H_2O$	(3, 23)	UP_2O_7	(3, 4)
$U(HPO_4)_2 \cdot 2H_2O$	(3, 24)	$U(PO_3)_4$	(2–14, 26, 27)
$U(HPO_4)_2 \cdot 4H_2O$	(3, 24)	$U(OH)PO_4 \cdot H_2O$	[JCPDS 13-64]
$U(HPO_4)_2 \cdot 6H_2O$	(3, 24)	$U(OH)PO_4 \cdot 2H_2O$	[JCPDS 34-1487]
$UP_2O_7 \cdot 6H_2O$	(3, 23)	$UFPO_4 \cdot H_2O$	(3)

In the presence of carbon, in an argon atmosphere, we observed that, at 700–800°C, $U(UO_2)(PO_4)_2$ is partly reduced into $U_2O(PO_4)_2$ (20, 21):

$$U(UO_2)(PO_4)_2 + C \rightarrow U_2O(PO_4)_2 + CO\uparrow. \quad [13]$$

In air, at about 800°C, diuranium oxide phosphate is oxidized into uranium uranyl phosphate:

$$U_2O(PO_4)_2 + \tfrac{1}{2}O_2 \rightarrow U(UO_2)(PO_4)_2. \quad [14]$$

CONCLUSIONS

From our experimental results we can conclude that there are only two stable uranium phosphates at high temperature, never previously described:

—Uranium uranyl phosphate $U(UO_2)(PO_4)_2$, synthesized in air in the range 1000–1200°C (at lower temperatures it is not very well crystallized), starting from uranium (IV) (6, 8, 18–20) or uranyl compounds (6–8). This is, to our knowledge, the only mixed valence uranium phosphate.

—Diuranium oxide phosphate $U_2O(PO_4)_2$, obtained at about 1350°C in inert atmosphere (at lower temperature it contains some impurities such as UO_2 and UP_2O_7) starting from uranium (IV) compounds. Reduction of $U(UO_2)(PO_4)_2$ into $U_2O(PO_4)_2$ in argon in the presence of carbon is possible but the final product is a mixture of $U_2O(PO_4)_2$, UO_2, red phosphorus, and an excess of carbon (20, 21).

Both compounds can be obtained using different routes: wet (Fig. 1) or dry (Fig. 2) chemistry. We have carefully checked all routes described above. Details concerning techniques, synthesis conditions, and characterization of the new compounds are reported elsewhere (18–22).

All these methods of synthesis lead to the conclusion that $U(UO_2)(PO_4)_2$ or $U_2O(PO_4)_2$ can be obtained whatever the initial reagents are if the ratio U/PO_4 is in the range from 1/4 to 1/1. When the phosphating agent is in excess with respect to uranium, the decomposition of this excess of phosphate is observed at high temperatures. The deficiency of phosphates (mole ratio $U/PO_4 < 1/1$) leads to a polyphase system composed of $U(UO_2)(PO_4)_2$, UO_2, and U_3O_8 when heated in air or of $U_2O(PO_4)_2$ and UO_2 if treated in an argon atmosphere.

To prepare pure and well-crystallized products, the temperature and length of calcination are also decisive parameters. Uranium uranyl phosphate may be obtained in the interval 1000–1250°C while diuranium oxide phosphate needs 1350–1380°C. Above these limits both decompose into volatile phosphoric anhydride and refractory uranium oxides.

On the other hand, all our attempts to synthesize the uranium phosphate $U_3(PO_4)_4$ were unsuccessful, which confirms the doubts of other authors (6). Now, we can consider that this compound does not exist. Schaeckers' compound of the formula $(U_3O_5)P_2O_7$ (5) might also be questioned, mainly whether it is a mixture of different species.

Hydrated uranium (IV) hydrogen phosphates, stable only at lower temperatures (3, 23, 24), that are not discussed in this paper and some other uncontested uranium (IV) diphosphates are listed in Table 1. From the reexamination of uranium (IV) phosphate chemistry, the main modifications brought by our works are summarized in Table 2.

TABLE 2
Contested and New Uranium (IV) Phosphates

Contested compounds	References	JCPDS File	New compounds to be considered	References
$U_3(PO_4)_4$	(1, 4)	16-225	$U(UO_2)(PO_4)_2$	(18–21)
$(U_2O_3)P_2O_7$	(3, 5–10)	13-64		
$(U_3O_5)P_2O_7$	(5, 10)	30-1390; 34-1487	Polyphase systems	
$(UO)_3(PO_4)_2$	(4, 5)	16-229		
$(UO)_2P_2O_7$	(3, 4, 6, 12)	16-228; 31-1433	$U_2O(PO_4)_2$	(21, 25)
			$UClPO_4 \cdot 4H_2O$	(18, 21, 22)
			$UBrPO_4 \cdot 5H_2O$	(22)
			$U(OH)PO_4 \cdot 6H_2O$	(20, 22)

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