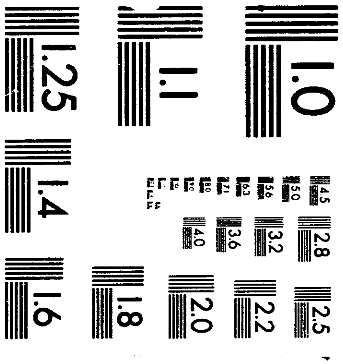
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DISTRIBUTION OF URANIUM-BEARING PHASES IN SOILS FROM FERNALD*

E. C. Buck, N. R. Brown, and N. L. Dietz
Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

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E. C. Buck, N. R. Brown, and N. L. Dietz, Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439.

ABSTRACT

Electron beam techniques have been used to characterize uranium-contaminated soils at the Fernald Site, Ohio. Uranium particulates have been deposited on the soil through chemical spills and from the operation of an incinerator plant on the site. The major uranium phases have been identified by electron microscopy as uraninite, autunite, and uranium phosphite [$U(PO_3)_4$]. Some of the uranium has undergone weathering resulting in the redistribution of uranium within the soil.

INTRODUCTION

The soils from the Fernald processing plant became contaminated with uranium after decades of defense-related activities [1]. Identification of the uranium-bearing solid phases which control the solubility of uranium in the environment is necessary both for remediation efforts and determining the long-term behavior of the radionuclide. This paper describes electron beam analysis study of uranium-contaminated soils from the Fernald site. These detailed characterization studies have yielded interesting observations on the nature of uranium in soils which have implications for the transportability of uranium in the environment. Much of the uranium has been found in particulate form, which conventional soil washing methods will not be able to remove.

Location of Contamination at Fernald

Fernald is located northwest of Cincinnati, by the Great Miami river. Surveys of the site, conducted using a portable gamma spectrometer, have located the regions of high uranium contamination (Fig. 1). Initial site surveys found a number of highly contaminated regions, where the uranium content was up to 5000 ppm. These sites have been sampled and were labeled SP4, SP2-3, SP5, and A14. Area SP4 possessed the highest level of contamination. The contamination at these sites was caused by; product spills (SP4 and SP5) and incinerator ash (A14); SP2-3 was an area that has been exposed to failed remediation efforts.

Soil Description and Gamma Spectroscopic Analysis

Fernald site soils have been size fractionated by Lee and Marsh [1], who determined the distribution of uranium by size fraction. The largest concentration of uranium was found with the smaller soil size-fractions, although the clay fraction (<2 μm) did not contain the highest levels of contamination in all soil samples. Areas SP4, SP9, and SP2-3 had the highest uranium contamination in the 2-0.053 mm sand fraction, with about 50% of the total uranium content. In SP5 the gravel fraction was the largest contributor to the uranium contamination. The silt and clay both had high uranium contents but were lower than the sand fraction.

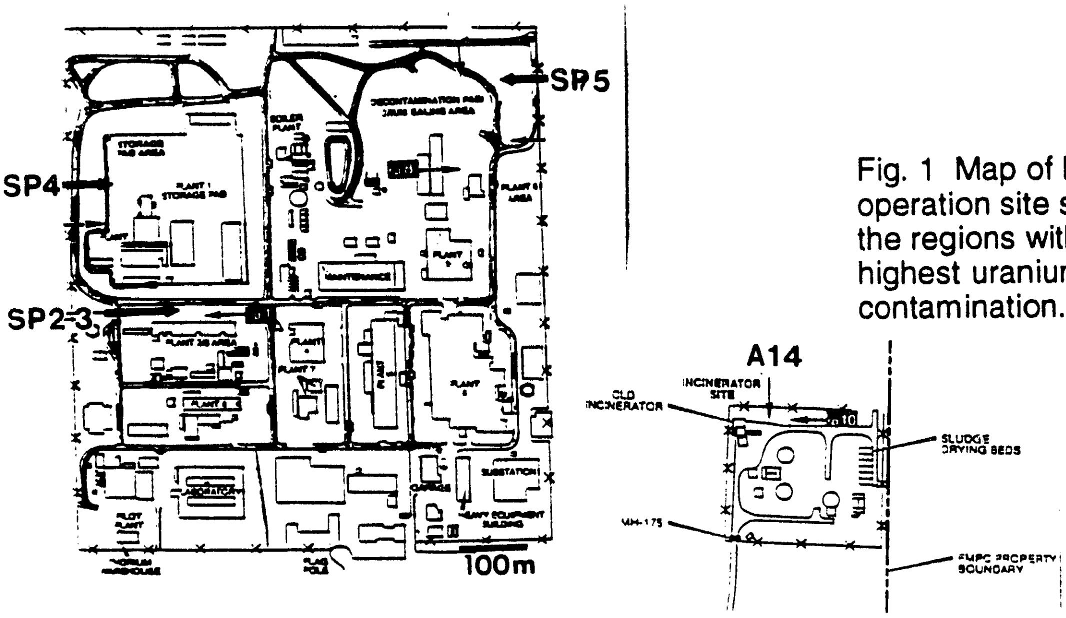

Fig. 1 Map of Fernald operation site showing the regions with the highest uranium contamination.

Characterization Studies

The soil fractions containing the largest uranium contents have been further characterized by a variety of techniques including electron beam methods [2]. Lee and Marsh [1] performed x-ray diffraction and scanning electron microscopy (SEM) of soils to try to describe the nature of the uranium in soils. Investigations showed that uranium was in particulate form within the soil. These particles of uranium have been more closely examined by analytical electron microscopy (AEM) [3]. AEM has allowed detailed characterization of the soil, including the distribution of uranium. Morris et al. have used Synchrotron x-ray absorption spectroscopy (XAS) to determine uranium oxidation state of bulk soil samples from Fernald [4]. The position of the x-ray absorption uranium L_{III} edge indicated that 80% of the uranium was in the [U(VI)] oxidation state. Micro-beam XAS by Bertsch et al. [5] was more effective at determining oxidation state of uranium in soils, as the distribution of uranium in soils is inhomogeneous.

EXPERIMENTAL PROCEDURE

Fernald soil samples were infiltrated with a water soluble melamine resin and uranium-rich particles were located by SEM combined with backscattered electron (BSE) imaging. These particles were isolated and prepared into transmission electron microscopy (TEM) thin sections by ultramicrotomy (see Fig. 2). This method of sample preparation allowed direct comparison between SEM and TEM images, which enabled characterization of TEM samples to be representative of the bulk sample. The samples were analyzed in a JEOL 2000 FXII TEM operated at 200 kV and equipped with x-ray energy dispersive spectrometers (EDS). Phases were identified by a combination of EDS, selected area electron diffraction (SAED) and convergent beam electron diffraction (CBED).

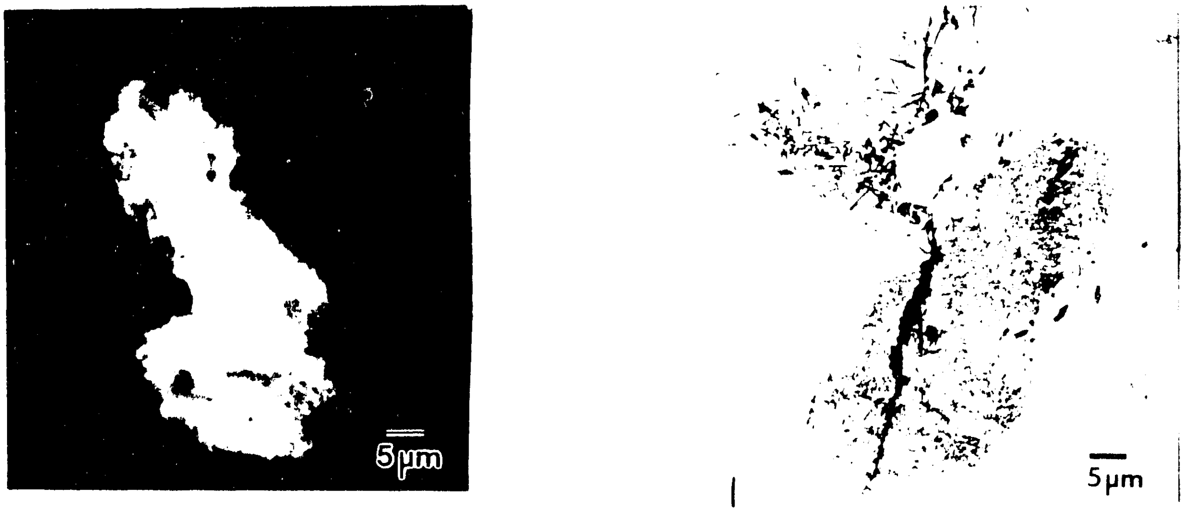

Fig. 2. (a) SEM/BSE micrograph showing an uranium-bearing particle, which can also be seen in (b) the TEM image. The uranium-contaminated regions can be identified by the white BSE contrast. The particles are similar in shape because the SEM mount has been sectioned nearly parallel to the plane of the paper.

RESULTS AND DISCUSSION

Recent investigations have provided new information on the fate of uranium at Fernald. SEM studies showed that uranium is contained within particles typically 1 to 100 μm in diameter. Further analysis with AEM has shown that weathering and redistribution of uranium resulted in the formation of secondary uranium-bearing phases similar to those observed at naturally occurring weathered uranium deposits, often described as natural analogues for waste disposal sites.

At the macroscopic level much of the uranium was associated with the small sized fractions of the soil; however, SEM analysis revealed that uranium was in a particulate form, and further detailed analysis with TEM showed that the uranium was present as discrete phases. In this paper, we report on recent AEM studies concerning the distribution of uranium phases found in some soil samples.

Characterization of Soil Phases

While the general mineralogy of the soil samples has been described by Lee and Marsh [1], we sought to identify the specific phases in the current samples which would help us to describe the distribution of uranium within the clay fraction of the soil.

Examination of the soils by TEM revealed two major components, quartz and layer silicates. Quartz does not section well, so shattered particles of quartz were often found displaced from their original sites. The major layer silicate minerals in SP4, SP2-3, and SP5 were identified as illite and chlorite based on SAED and EDS analysis; however, specific phyllosilicate minerals could not be positively identified with the method of analysis used. Lattice images were taken with an objective aperture that excluded all *hkl* reflections except the basal {00*l*} (Fig. 3). Other phases were found in the soil samples, including feldspar, rutile, maghemite, apatite, cerium phosphate, and zircon.

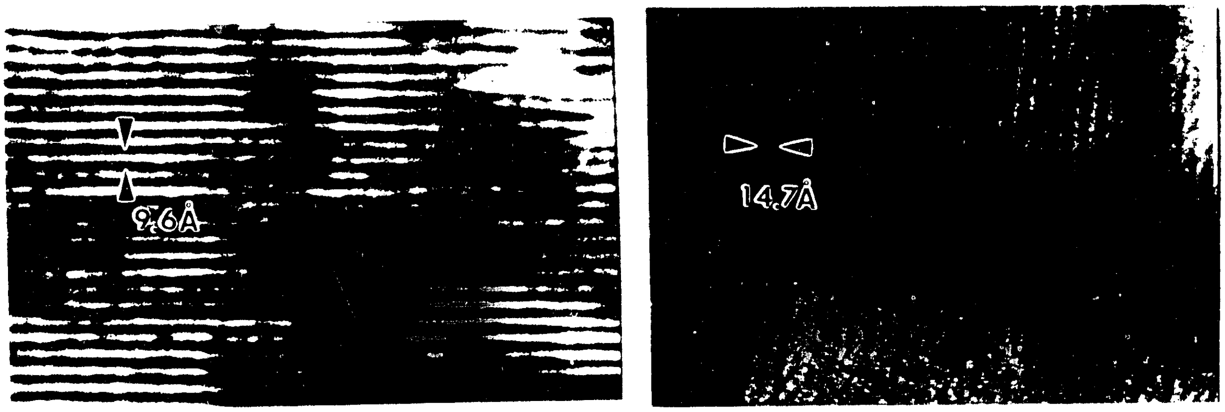

Fig. 3a. Lattice images of (i) illite and (ii) chlorite with c-axis spacings of ~10 Å and ~15 Å, respectively.

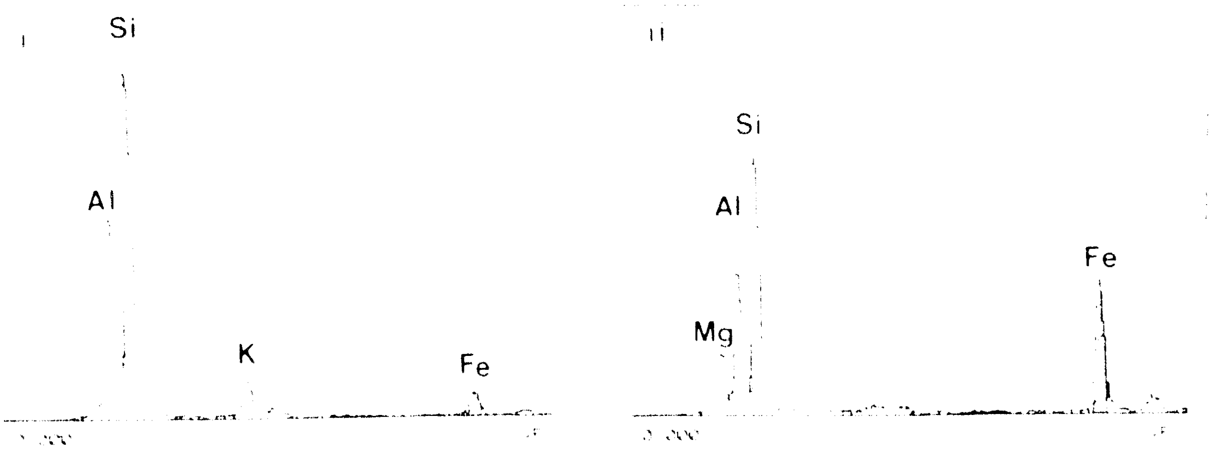

Fig. 3b. EDS analysis of the layer silicate phases (i) mica and (ii) chlorite

Uranium-Bearing Phases

Uranium has been found in a number of different forms in Fernald soils [3]. Uranium has been found in the form of uranium silicide ($USi_{1.6}$), uranium silicate (soddyite), and uranium associated with calcium fluoride and with iron oxides. Uranium is known to have a strong affinity for adsorption onto iron oxides, particularly amorphous iron oxyhydroxides [6].

Uranium was commonly found associated with iron oxides in SP4, but was also found in the form of uranium oxides, see Fig. 4 [3]. SP2-3 and SP5 samples contained significant amounts of uranium phosphate (autunite), which was isolated within the soils, as if it had precipitated from solution. The SP2-3 sample also contained quantities of calcium phosphate (apatite). A14 contained uranium oxide, uranium phosphate (autunite), and particles of uranium phosphite [$U(PO_3)_4$], a high temperature phase. The uranium phosphite phase was not beam sensitive (a converged beam would not induce amorphization), suggesting that this phase was dehydrated and, therefore, probably formed in the incinerator. Uranium has also been found in the form of calcium uranium oxide, uranium silicate, and uranium silicide. Some of these phases suggest that the uranium has been redistributed through weathering.

Fig. 4 Major uranium-bearing phase found in SP4, an amorphous iron oxide phase. The micrograph shows the arrangement of the colloidal-sized iron phases and clay which can only be detected with TEM.

Electron Diffraction Characterization of Uraninite

Uraninite (UO_2) is normally a non-stoichiometric phase (UO_{2+x}) possessing a fluorite structure. UO_2 will readily undergo oxidation, resulting in changes in the unit cell parameters which can be detected by use of x-ray diffraction [7] or electron diffraction [8]. Electron diffraction data of uranium oxide particles found at Fernald can be used to distinguish between UO_2 and certain oxidized forms (see Fig. 5).

Identification of Autunite Phase

Many uranium minerals are beam sensitive in the microscope and will undergo rapid amorphization which makes structural characterization difficult. The figure below shows a uranium phosphate phase found in SP2-3, which was identified as tetragonal autunite, ideally [$Ca(UO_2)_2(PO_4)_2 \cdot xH_2O$]. The phase consists of spiny needles, which could be recognized in the SEM images (Fig. 6a). The electron diffraction was taken along the [001] zone axis (Fig. 6b).

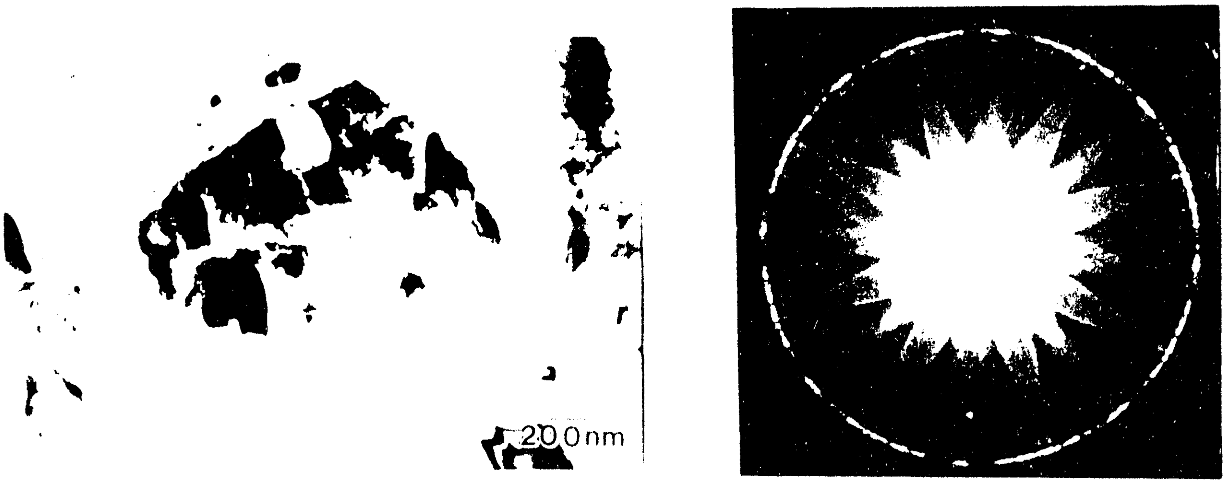

Fig. 5. TEM image of uranium oxide particle (left) and CBED pattern (right), showing four-fold symmetry, taken along the [010] zone axis.

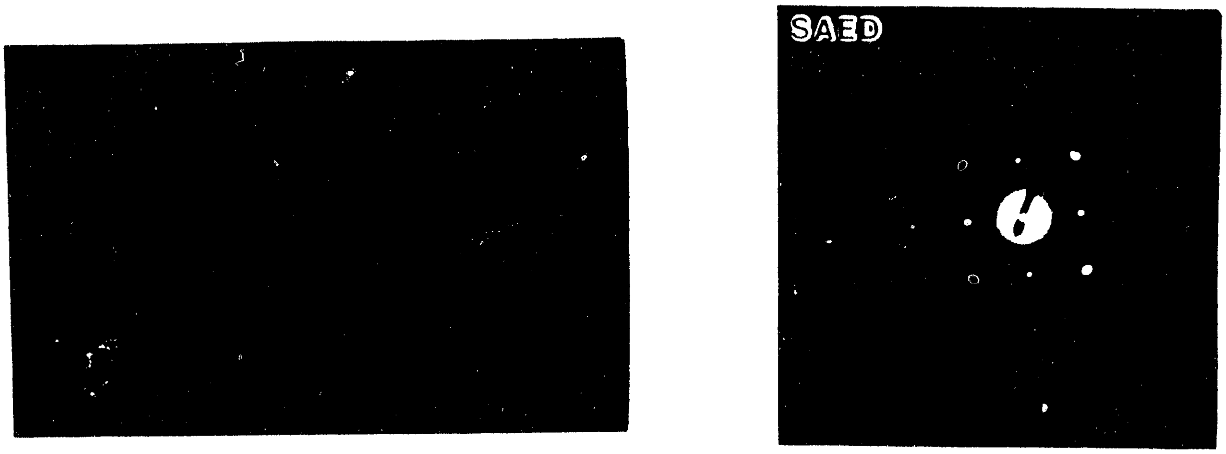

Fig. 6 Electron beam analysis of uranyl phosphate phase found in SP2-3 (a) SEM image showing isolated nature of particles and (b) SAED analysis.

The uranyl phosphates constitute a very diverse group of uranium-bearing minerals. The most common type, autunite, is characterized by a U:P ratio of 1:1. Phosphuranylites are another group of uranyl phosphates and have a U:P ratio of 3:2. They are often closely associated with uraninite in natural systems. Uranyl phosphates will control the uranium concentration in groundwaters, as they have solubilities below those of uranyl silicates. In groundwaters, where

$$\lg\frac{[CO_3]}{[PO_4]} < 3.5,$$

uranyl phosphates dominate [9].

Finch and Ewing [9] believe that the formation of autunite requires the presence of a lead-containing uranyl hydrate, curite, which acts as a catalyst for the formation of uranyl phosphate, at least in groundwaters with a low phosphate concentration. However, uranyl phosphates will precipitate if a high phosphate concentration exists (> 10^{-7} M), therefore, the question is whether such a high [PO_4^{3-}] concentration exists in Fernald soils. Apatite controls the [PO_4^{3-}] concentration in many natural waters and will keep phosphorus levels below 10^{-7} M when the pH exceeds 7. In the Fernald soils we have observed the presence of calcium phosphate and iron phosphate, which are sources for phosphorus in the soil. Much of this phosphate may have come from fertilizers used in farming or during weathering of rocks. According to Lee and Marsh [1], the soil pH was around 8 for all soil samples, suggesting that [PO_4^{3-}] concentrations will be low. Therefore, at Fernald we have observed the formation of uranyl phosphates without visible evidence of a precursor curite or apparently high [PO_4^{3-}] concentrations.

Alteration of Uranium Phases at Fernald

Examination of Fernald soils indicates that large changes have occurred to the initial uranium-bearing phases due to interaction with other elements in the soil. In Fig. 7, a cross-section through a soil particle shows the presence of a uranium phosphate, which was composed of final crystallites, next to an iron phosphate phase, which was composed of much coarser grains. A more convincing case of uraninite (UO_2) alteration is shown in Fig. 8, which shows an occluded uranium oxide particle

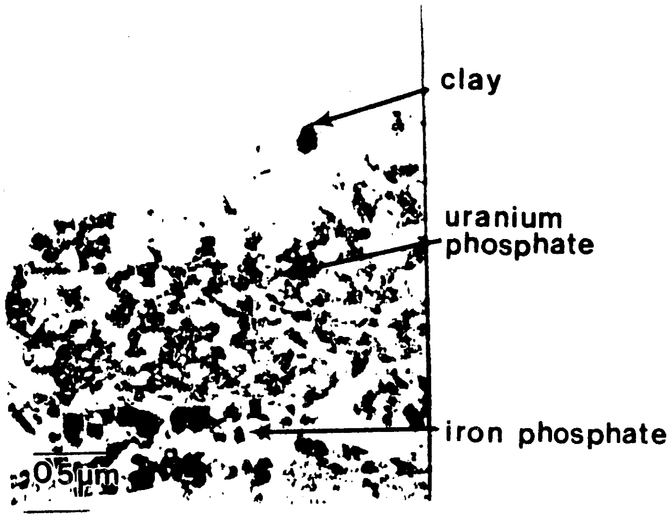

Fig. 7. TEM image of iron phosphate and uranium phosphate in A14.

Fig. 8. SEM/ BSE images showing uranium oxide, which is surrounded by a calcium phosphate phase, undergoing alteration into uranyl phosphates in A14.

surrounded by calcium uranium phosphate in soil sample A14 (incinerator site). TEM analysis of similar samples (see Fig. 9) shows how the uranium phosphate phase is attached to the uranium oxide crystallites.

Autunite is commonly observed associated with the dissolution of natural uraninite [9, 10] but it has not been observed during the dissolution of spent fuel [11].

The distribution of uranium in Fernald soils appeared to be strongly affected by the presence of phosphorus. This observation is similar to that made at the uranium deposit at Koongarra [10], in spite of the apparently large differences between the Ohio farmland site and the tropical Koongarra site.

CONCLUSION

Uranium at Fernald has been found in many diverse forms, which will impede clean-up efforts, as any single remediation technique will probably be unable to remove all the different forms of uranium in the soils. Over the 40-year period that the Fernald operation site was in use, uranium, present in the soil has undergone significant changes. Weathering of the originally deposited materials has redistributed the uranium and changed its transportability.

Electron beam analysis of these contaminated soils has provided information on the uranium in soils that is useful for developing innovative cleanup technologies, as it has enabled both phase identification and relationship of the uranium-bearing phase to other phases in the soil.

Fig. 9. TEM image showing autunite attached to uranium oxide in soil sample A14. The darker clumps were identified as uranium oxide, and attached to them were uranium phosphate crystallites.

ACKNOWLEDGMENTS

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