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Solid solution formation in the metatorbernite-metazeunerite system ($Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x.nH_2O$) and their stability under conditions of variable temperature.

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Summary

Mineral phases which can be thought of as members of a metatorbernite -metazeunerite solid solution $(Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x.8H_2O$ have been identified in radioactive samples from spoil heaps at the uranium mine site in South Terras, Cornwall (grid reference *SW935523)*. A complete solid solution ($0<x<2$) was synthesised by precipitation from solution using uranium (VI) nitrate and copper (II) chloride and phosphoric acid/arsenic acid in the appropriate molar proportions. Refined unit cell parameters determined by Pawley fitting of powder X ray Diffraction data, showed a linear variation in the *a* unit cell parameter according to Vegard's Law, allowing the composition of the natural mineral phases found at South Terras to be determined from measurement of their unit cell parameters. High resolution variable temperature synchrotron powder X ray diffraction studies were carried out at the Diamond Light Source on three members of this solid solution (x = 0, 1, 2) and showed different structural behaviour as a function of composition and temperature. Metatorbenite (x=0) retains its tetragonal symmetry at low temperatures and dehydrates to an amorphous phase at 473K, whereas metazeunrite (x=2) transforms to an orthorhombic phase at low temperatures, regains its tetragonal symmetry on heating to 323K and undergoes a further transition to an, as yet, unidentified phase at 473K.

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Introduction

Metatorbernite ($Cu(UO_2)_2(PO_4)_2.8H_2O$), is a common secondary mineral resulting from pitchblende (UO_2) alteration and can be considered as a significant host for uranium in both natural and anthropogenically contaminated environments [1]. Uranyl phosphates, such as metatorbernite, are known for their low solubility at circumneutral pH and are considered important for the control of uranium mobility in the environment under oxidising conditions [2]. It has been suggested that U-contaminated groundwater may be decontaminated through the application of polyphosphates to form sparingly soluble uranyl phosphate phases, such as metatorbernite [3].

The disused uranium mine in South Terras, Cornwall, has been abandoned for nearly a century, but discarded spoil heaps at the site still retain significant levels of activity [4]. The interest in this site is part of a larger study into the fate of radionuclides in the environment (NERC Long-lived Radionuclides In the Surface Environment (Lo-RISE) project). While previous studies have indicated that uranium in these spoil heaps is relatively immobile [5, 6], there are no published studies reporting the exact composition and stability of the uranium solid-state phases present in the spoil heaps. Metatorbernite has been reported to be present in areas of this locality [4, 5], along with the arsenate analogue of this mineral phase, metazeunerite ($Cu(UO_2)_2(AsO_4)_2.8H_2O$). A 2017 study indicated the possibility of a phosphate containing metazeunerite phase existing at this locality [7].

Metatorbernite is a member of the autunite family of minerals, which are some of the most widespread and abundant secondary uranium minerals known [8]. The composition of this family of minerals is variable with the ideal formula $A(UO_2)_2(XO_4)_2.nH_2O$, where A is a divalent cation, X is arsenic or phosphorus and n is in the region of 10-16 for the autunite group and 6-8 for the meta-autunite group [9]. The mineral autunite has the ideal composition $Ca(UO_2)_2(XO_4)_2.10\text{-}12H_2O$ and is less stable than the phase meta-autunite, $Ca(UO_2)_2(PO_4)_2.8H_2O$ [10]. There are other known mineral phases related to autunite with monovalent or,

more rarely, trivalent cations. The ideal formula for these phases is slightly altered to $M^{+}(UO_2)(XO_4).nH_2O$ or $M^{3+}(UO_2)(XO_4).nH_2O$ [9, 11].

The structures of autunite and meta-autunite minerals are mostly reported to crystallise in primitive tetragonal space groups. However, there are also reports of phases crystallising in orthorhombic, monoclinic and triclinic space groups as well [11]. The structure can be described as sheets of uranyl arsenate/phosphate, with the composition $[(UO_2)_2(XO_4)_2]^{2-}$, X = P or As, stacked along the *c* axis with the cations and varying numbers of water molecules situated between the sheets (figure 1) [12, 13].

The published structural models for metatorbernite and metazeunerite are all primitive tetragonal, however, there are inconsistences in the reported unit cell parameters and a number of different space groups have been used to describe their structures. Previous structural studies on metatorbernite and metazeunerite phases have been carried out on mineral samples using X ray diffraction techniques [12, 14-21]. The work presented in this paper focuses on refinement of unit cell parameters of synthetic phases only and further work on full structural characterisation is underway [22].

In this paper we report the synthesis and characterisation of a metatorbernite-metazeunerite ($Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x.8H_2O$) solid solution for $0 < x < 2$. Powder X ray Diffraction (PXRD) data collected on these synthetic samples are compared with PXRD data collected on spoil heap samples removed from the disused uranium mine in South Terras, Cornwall to determine the composition of the naturally occurring mineral metatorbernite-type phases identified. Variable temperature studies carried out on the high resolution powder diffraction beamline I11 at the Diamond Light Source [23] on three solid solution compositions, $Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x.8H_2O$ (x = 0,1, 2) are also reported and show different behaviour according to the value of x .

Methods

(a) Sampling

Sampling of the South Terras site was carried out in July 2015. Two sites of interest were identified using a handheld LB124 Berthold monitor; these were named Mine Spoil (MS) and Ore Processing Floor (OPF). About 10 litres of soil and/or spoil were removed from the surface of each site using a hand shovel to a depth of about 20-30 cm. The samples were packed and stored in clean, polypropylene boxes before being transported to Loughborough University. All samples were dried in an oven at 80 ºC before being gently crushed with a pestle and mortar. They were then placed into a laboratory sieve shaker and separated into size fractions: > 2 mm and < 2 mm. The > 2 mm fraction from the MS sample was spread out in a tray and monitored using a Geiger-Müller counter. Individual samples of especially high activity (≥100 cps) were separated and labelled as high activity (HA) samples for further analysis.

(b) Synthesis

Metatorbernite was synthesised by adapting a method described by Cretaz [2]. 2.5g Uranyl nitrate hexahydrate (Aldrich) was dissolved in 25 mL of a 0.5 x 10^{-2} mol L^{-1} solution of nitric acid. 0.44 g copper (II) chloride dihydrate (reagent grade Sigma Aldrich) was added and shaken until dissolved. 2.5 mL of a 2 M solution of phosphoric acid (reagent grade Sigma Aldrich) was then added. After approximately one hour, pale green crystals were observed to form. The crystals were left on a shaker at room temperature for 1 h before being left to settle for 48 h. The product was then filtered under vacuum using a 0.1 μm cellulose membrane and washed three times with deionised water. The crystals were left to dry in an oven at 40ºC until a constant weight was achieved.

Metazeunerite was prepared using the same method but replacing the phosphoric acid with a 2 M solution of arsenic acid. The arsenic acid was prepared by dissolving 2.5 g arsenic (V) oxide (sigma Aldrich reagent grade) in 10 mL of deionised water.

Members of the solid solution were prepared using different ratios of phosphoric and arsenic acid in the synthetic mixture to produce the compositions $Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x.nH_2O$, x = 0.2, 0.4, 0.5, 0.6, 0.8, 1.0, 1.2, 1.4, 1.5, 1.6 and 1.8.

(c) Powder X Ray Diffraction

Powder X-ray diffraction data were collected using a Bruker D8 Discover X-ray diffractometer in transmission geometry using Co Kα_1 radiation, selected using a Ge 111 single crystal monochromator and a Braun Position Sensitive detector. For phase identification of samples, data were collected over the 2θ range 5-60° with a step size of 0.0072334° 2θ and a count time of 0.5s per step. For refinement of structural parameters, data were collected over the 2θ range 9-80° with a step size of 0.0072334° 2θ and a count time of 5.2s per step.
Synchrotron powder diffraction data were collected using a Si-calibrated wavelength of λ = 0.82603 Å on the high-resolution powder X-ray diffraction beamline I11 at the Diamond Light Source, UK [23]. The samples were packed into 0.5 mm borosilicate capillary tubes and secured with Kapton tape. Data were collected in transmission geometry using multi-analysing crystal detectors over an angular range of 1 – 150º 2θ. The PXRD data were collected at 293 K for 30 minutes. Samples were then cooled using the Cryostream Plus to 105-110 K and a new dataset was collected for 30 minutes. Data were collected on heating at 50K intervals until a temperature of 500K was reached.
For the purposes of phase identification, the PXRD data patterns were compared to known end-member phases in the International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF2) database using the search match software contained in the software suite WinXPow. For the refinement of structural parameters, data were analysed using the software Topas Academic V6 [24].

(d) ICP-OES

0.2 g of either the solid solution phase or mineral sample was weighed into a 15 mL polypropylene centrifuge tube. It was then dissolved in 2 mL 50% HNO_3. A 0.1 mL aliquot of sample was removed and added to a 15 mL centrifuge tube, this was then diluted to 10 mL using more 2% HNO_3 in deionised water. Elemental analysis was carried out using a Thermo Scientific 6000 series ICAP-6500 duo ICP-OES .

Results and Discussion

PXRD data collected on the samples from South Terras which were shown to have high activity (≥100 cps), identified the presence of metatorbernite-type phases. Figure 2 shows an example of one of the datasets collected on sample HR 001, which was found to contain quartz as an impurity phase. The powder diffraction data did not match exactly with any of the metatorbernite diffraction patterns contained in the database (ICDD PDF2) as the observed peak positions were found to be shifted relative to the database patterns. We confirmed this was a sample effect and not due to misalignment of the diffractometer or the sample preparation method by adding a silicon internal standard (not shown in this dataset). We propose that the composition of the sample deviates from that of metatorbernite and could be a member of a solid solution between metatorbernite and metazeunerite as the observed peak positions were found to lie between the reflection positions of metatorbernite, (ICDD PDF 36-406 [15]) and metazeunerite (ICDD PDF 17-146 [25]). ICP-OES analysis confirmed the presence of As in these samples. The results from the sample HR 001 are presented in supplementary figure 1 and show the presence of Cu, U, As and P, which can be related to an As-containing metatorbernite-type phase. Fe, Al, Pb and Si are observed in small quantities due to the presence of impurity phases, present in quantities below the detection limits of PXRD techniques. There are only a few reports in the literature regarding the cross-substitution of phosphorus and arsenic in the metatorbernite-type system in nature [3]. Corkhill *et al* reported a phosphate containing metazeunerite phase at South Terras, present as a thin crust on minerals such as muscovite and jarosite. [7]. The only report of similar solid solution behaviour is in the related system $H(UO_2)(PO_4)_{1-x}(AsO_4)_x.3H_2O$ [26, 27].

To confirm the hypothesis that a solid solution between metatorbernite and metazeunerite exists, a synthetic study was carried out. We prepared compositions of the proposed solid solution $Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x.nH_2O$, $0 < x < 2$, in 0.2 increments. PXRD data were collected on the samples and found that a complete solid solution existed with no evidence for the presence of any impurity phases. Synchrotron PXRD data collected on selected samples of the solid solution are presented in supplementary information figure 2.

Pawley refinements of the lab PXRD data in space group P4/n were carried out and the refined unit cell parameters as a function of composition, x, are presented in figure 3. The refined unit cell parameters are *a* = 6.9736 (9) Å and *c* = 17.341 (2) Å for metatorbernite and *a* = 7.1204 (9) Å and *c* = 17.442 (3) Å for metazeunerite. Comparison with the reported unit parameters for the end member phases by Locock *et al*, of *a* = 6.98 (5) Å and *c* = 17.35 (2) Å for metatorberinte and a = 7.11 (1) Å and c = 17.42 (1) Å for metazeunerite show our findings are consistent with previous studies [12]. It should be noted that the reported unit cell parameters for both metatorbernite and metazeunerite show some variation, with a wider range found for reported *c* parameters. For metatorbernite, *a* was found to range between 6.95 Å [19] and 6.98 Å [17, 12] and *c* between 17.28 Å [20] and 17.41 Å [17], whereas for metazeunerite the range of refined *a* unit cell parameters was between 7.10 Å [17] and 7.13 Å [14] and a wider range for *c* of between 17.38 Å [17] and 17.70 Å [16].

The variation in reported values could be due to compositional variations away from the ideal (i.e. $Cu(UO_2)_2(XO_4)_2.8H_2O$, X = P or As) as all studies were carried out on mineral samples and there is a possibility that the X site is not pure P or As, and/or Cu may have been replaced with other metal cations (e.g. Ca, Fe) as well as the water content not being exactly 8 molecules per formula unit. [12, 14 – 21]. The refined unit cell parameters of the solid solution members show a (nearly) linear trend as a function of composition, which is more obvious in terms of the *a* parameter than the *c* parameter. Due to the layered nature of the structure (figure 1), a change in the number water molecules per formula unit between the layers would have more impact on *c* than *a*. All the synthetic samples were dried at 40 °C to ensure the transformation from torbernite-type to metatorbernite-type phases was complete. The torbernite-type samples are more hydrous, with a reported twelve water molecules per formula unit and are less stable than the metatorbernite-type samples (with eight water molecules per formula unit), on which this study focuses. It was found that the compositions containing more arsenate ions required longer times to fully complete the transformation. Further investigations are underway to establish what variability exists in terms of water content.

Using the linear correlation between the *a* parameter and the AsO_4/PO_4 ratio (equation 1, figure 3), the formulae of two natural samples taken from South Terras were determined (Table 1). A comparison of the observed data collected on the natural samples to the observed data on the solid solution member with the same approximate composition, showed good agreement. (Supplementary information figures 3 and 4)

Our results show that the abundance of arsenic on the South Terras site is significant and natural samples contain mixtures of the two species where arsenate is significant and possibly dominant. While the stability of the phosphate end member in the natural environment has been documented [2], much less is known about the arsenate material or samples with a mixed composition of the AsO_4/PO_4 species, which appear to be present naturally. This suggests stability studies on the mixed anion materials will be of major interest in assessing the stability of the mine spoil on a long term basis.

$$y = 0.0778x + 6.9707$$

Equation 1: Relationship between refined *a* parameter and composition in terms of x for the solid solution $Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x.nH_2O$

The scatter in the refined unit cell *c* parameter between metatorbernite and metazeunerite could be due to several reasons, variation in the water content, as highlighted above or differences in the space group between the two systems. We have carried out preliminary structural refinements of the high resolution synchrotron data collected on metatorbenite, which refined well in space group P4/n and metazeunerite, with data fitting better in space group P4/ncc [22]. However, there are real difficulties with refining these structures by X-ray diffraction due to the dominant scattering of uranium compared to all other species, anion disorder and the complexity of this structure. Powder neutron diffraction data will be required to resolve these issues.

Variable temperature studies on three solid solution compositions, $Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x.8H_2O$ (x = 0,1, 2) over the temperature range 110K-500K were also carried out. There was noticeable variability in the behaviour of different compositions as a function of temperature. The metatorbernite sample remained tetragonal on cooling and decomposed on heating, showing an amorphous signature at temperatures > 473K, which recrystallized on cooling to produce an as yet unidentified phase. The high resolution synchrotron powder diffraction data are presented in supplementary figure 5 and the refined unit cell parameters plotted as a function of temperature are shown in figure 4. The unit cell parameters were refined in space group P4/n over

the temperature range 105 – 443K. Both unit cell parameters were found to expand linearly, with *c* expanding more than *a*. A plot of *a*/*c* versus temperature (supplementary figure 6) shows the linear expansion up to 373K and then a deviation from linearity, which could indicate the beginnings of a dehydration process.

The composition $Cu(UO_2)_2(PO_4)(AsO_4).8H_2O$ was studied over the temperature range 110 – 473K and its behaviour was found to be different to that of the end member phases. The sample remains tetragonal on cooling, as in the case of metatorbernite but on heating to 423K, the diffraction pattern shifts to higher 2 theta values and can be indexed in space group P4/n, with smaller unit parameters refined as $a = 7.08224$ (4) Å and $c = 16.7862$ (2) Å (figure 4). On further heating to 473K, the diffraction pattern changes completely forming a new structure that is still to be identified. The variable temperature data collected on this composition are given in supplementary information (supplementary figure 7) and a plot of the *a*/*c* ratio as a function of temperature (supplementary figure 8). As with the metatorbernite phase, a linear expansion with temperature is observed up to 323K and the trend is found to be non-linear above these temperatures, which could indicate the start of the dehydration process.

Figure 4 presents the refined unit cell parameters from the high temperature PXRD studies of metatorbernite and the composition $Cu(UO_2)_2(PO_4)(AsO_4).8H_2O$ compared to published unit cell parameters from a high temperature PXRD study carried out on a mineral sample [28]. The composition of this mineral sample was determined to be $Cu(UO_2)_2(PO_4)_{1.9}(AsO_4)_{0.1}.2H_2O$ by EPMA. Their findings show that at 129 °C (402K), the diffraction pattern can be indexed in space group P4/n with a smaller unit cell ($a = 6.9551$ (3) Å, $c = 16.6604$ (9) Å) than the parent metatorbernite phase. This trend is similar to our results, whereby the mixed arsenate/phosphate composition shows a decrease in *a* and *c* unit cell parameters at 423K. We suggest the deviation between the two studies are due to the different compositions of the phases analysed.

The metazeunerite sample was studied over the temperature range 110 – 473K and exhibits different behaviour on heating and cooling, whereby on cooling the symmetry of the sample is lowered and the diffraction pattern can be indexed on an orthorhombic unit cell with proposed space group Pccn, $a = 7.1138$ (2) Å, $b = 7.1584$ (3) Å, $c = 17.5439$ (9) Å. On heating back to room temperature, the structure remains orthorhombic until 323K, with the room temperature dataset refined as a mixture of tetragonal and

orthorhombic phases. It may be that a more controlled heating rate would allow the sample to transform to the tetragonal phase at room temperature and this needs further investigation. The sample remains tetragonal until 373 K and above this temperature forms a new phase, with an unknown structure. The variable temperature data collected on metazeunerite are presented in supplementary figure 9 and figure 5 shows a plot of the refined lattice parameters as a function of temperature. The reversible tetragonal to orthorhombic phase transition is clearly shown on the refined unit cell parameter versus temperature plot (figure 5). Over the temperature range 110 – 373 K, a linear expansion in the unit cell volume is observed.

The phase changes that occur in metatorbenite and metazeunerite at high temperature have been studied previously using X ray diffraction, thermogravimetric analysis and Raman spectroscopy [28-33]. Most of the studies have been carried out on mineral samples and there is a lack of consistency in the findings due to the compositional variation in the samples.

Suzuki *et al* carried out HTXRD and TGA on a mineral sample of metatobernite and reported a weight loss at 86°C that equated to 4 or 5 molecules of H_2O per formula unit [29]. The XRD pattern collected at 100°C showed a shift in two theta positions when compared to the dataset collected at room temperature, with the basal spacing decreasing from 8.61Å to 8.07Å. The authors claim that the dehydrated phase at this temperature is likely to have the composition $Cu(UO_2)_2(PO_4)_2.4H_2O$, losing water molecules from between the uranyl phosphate sheets, but retaining the layered structure. On further heating the sample showed another weight loss and change in diffraction pattern at ~200°C and Suzuki and co-workers stated that the dehydrated phase at this temperature has the likely composition $Cu(UO_2)_2(PO_4)_2.2H_2O$, with a basal spacing of 6.58 Å. On heating further to 300 °C, there are two reflections with *d* spacings of 6.52 and 5.60 Å; the authors interpret the appearance of the these reflections as being due to the presence of two different hydration states with likely compositions $Cu(UO_2)_2(PO_4)_2.H_2O$ and anhydrous $Cu(UO_2)_2(PO_4)_2$. There is no evidence from their HT PXRD study of any amorphous phase forming under these conditions, as we observed with the synthetic metatorbernite phase at temperatures greater than 423K. It should be noted, that they only reported the *d* spacings of the basal spacing of the phases formed on heating with no refined unit cell parameters given.

Suzuki *et al* compare their findings with that of Vochten *et al* [30], who carried out TGA studies on metatorbernite and found weight loss steps at 120 °C, 150 °C and 150-400 °C, which they stated were the temperatures where the compositions $Cu(UO_2)_2(PO_4)_2.4H_2O$, $Cu(UO_2)_2(PO_4)_2.2H_2O$ and $Cu(UO_2)_2(PO_4)_2$ formed.

Stubbs *et al* [28] studied a mineral sample, that was shown to have the composition $Cu(UO_2)_2(PO_4)_{1.9}(AsO_4)_{0.1}.2H_2O$ by EPMA, using HT XRD over the temperature range RT to 315 °C. These authors carried out more in depth structural analysis on the phases formed on dehydration than Suzuki and reported preliminary structural models for two of the dehydrated phases. Their findings state that at 129 °C, a phase crystallising in the space group P4/n with a smaller unit cell than the parent metatorbernite phase was formed with a suggested formula of $Cu(UO_2)_2(PO_4)_2.6H_2O$, on further heating to 173 °C, the sample dehydrates to $Cu(UO_2)_2(PO_4)_2.3H_2O$ and recrystallises in space group P21. There is a further phase which formed at higher temperatures (209-315 °C), but at the maximum temperature used in this study there was still evidence for the presence of the phase $Cu(UO_2)_2(PO_4)_2.3H_2O$; no structural model or suggested composition was given for this phase. Stubbs *et al* compared their work to that of Frost *et al* [31], who carried out controlled rate thermal analysis on a mineral sample of metatorberntite, whereby the heating rate was varied according to whether the sample was undergoing a dehydration event or not. Frost found three mass losses which they equated to the compositions $Cu(UO_2)_2(PO_4)_2.6.5H_2O$ (at 138 °C), $Cu(UO_2)_2(PO_4)_2.2H_2O$ (at 155°C) and $Cu(UO_2)_2(PO_4)_2$ (at 291°C).

Our PXRD study on the synthetic analogue of the pure metatorbernite composition at elevated temperatures, does not follow the dehydration profile of either of the reported HT XRD studies on mineral samples of metatorbernite [28, 29]. We suggest that the differences are due to several factors. Firstly the sample environment is different, in this study the sample is in a sealed capillary and therefore its dehydration behaviour is different to that of a sample which is heated in an open system. Secondly, the compositional variations are key. This synthetic sample is a pure copper uranyl phosphate, whereas the mineral samples were shown to be either two phase by PXRD [29] or contain arsenate as well as phosphate through EPMA [28]. As discussed above, the dehydration behaviour of the mixed phosphate arsenate composition ($Cu(UO_2)_2(AsO_4)_2.8H_2O$) is more in line with that of Stubbs [28], see figure 5.

Two studies of the high temperature behaviour of metazeunerite have been reported [32, 33], both studies analyse metazeunerite samples using TGA techniques, but neither carry out any *in situ* HTXRD studies. The study by Frost is on a mineral sample that is stated to be a mixture of zeunerite and metazeunerite, as determined by PXRD analysis. The results of the TGA study, which were carried out under a N_2 atmosphere, are discussed in terms of the sample being single phase metazeunerite and are linked to a HT Raman study carried out on the same sample. Frost *et al* [32] show three weight losses that are claimed to be the loss of water, which would give the following compositions on heating $Cu(UO_2)_2(AsO_4)_2.6H_2O$ (48 °C), $Cu(UO_2)_2(AsO_4)_2.2H_2O$ (88 °C) and $Cu(UO_2)_2(AsO_4)_2$ (125-250 °C).

Vochten *et al* [33] carried out a TGA study, under a flow of air, on a synthetic sample of metazeunerite, prepared under different conditions to the synthetic samples in our study. They showed four stages of dehydration which would give the following compositions on heating, $Cu(UO_2)_2(AsO_4)_2.7H_2O$ (108 °C), $Cu(UO_2)_2(AsO_4)_2.3H_2O$ (130 °C), $Cu(UO_2)_2(AsO_4)_2.2.5H_2O$ (185 °C) and $Cu(UO_2)_2(AsO_4)_2$ (230 °C). Our study did not use a flow of gas, the samples were sealed in borosillicate capillaries and therefore the dehydration behaviour is shown to be different, with only one change in structure observed at 150 °C, to an as yet unidentified phase.

All these studies highlight the variability in the behaviour of metatorbernite-type phases as a function of temperature. The heating rate and atmosphere will play a role in how theses phases dehydrate, but the composition is key too, with differences between mineral and synthetic samples shown as well as differences between metatorbernite and metazeunerite.

Conclusions

We have shown the presence of a complete solid solution between the end member phases metatorbernite and metazeunerite ($Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x.8H_2O$) through a controlled synthetic study. Refinement of the lattice parameters confirmed all the solid solution members crystallised in a primitive tetragonal unit cell. The scatter of the *c* unit cell parameter as a function of composition, was suggested to be due to the variable water content

of these samples as well as structural differences between the end member phases, whereby metatorbernite crystallises in space group P4/n, but metazeunerite crystallises in space group P4/ncc. However, we found a linear correlation between the *a* unit cell parameter and the AsO_4/PO_4 ratio (x in the solid solution $Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x.8H_2O$).

We have refined the lattice parameters of mineral samples of metatorbernite type phases, found to be present at the South Terras site and compared to the synthetic samples to predict their compositions using the relationship established between *a* and the AsO_4/PO_4 ratio. Our results on the natural samples obtained from the South Terras site, show they may contain mixtures of arsenate and phosphate where arsenate is significant and possibly dominant. While the stability of the phosphate end member, metatorbernite, in the natural environment has been documented, much less is known about the arsenate material or compositions containing mixtures of AsO_4 and PO_4 species, which appear to present naturally. This suggests stability studies on the mixed anion materials will be of major interest in assessing the stability of the mine spoil on a long term basis.

The stability of the two end member phases and the composition $Cu(UO_2)_2(PO_4)(AsO_4).8H_2O$ were studied using high resolution synchrotron powder diffraction data as a function of temperature. These phases have been found to have different behaviour as a function of temperature. On cooling metatorbernite remains primitive tetragonal and on heating above 373 K the sample becomes amorphous to X rays. The composition $Cu(UO_2)_2(PO_4)(AsO_4).8H_2O$ remains tetragonal on cooling and on heating, with a noticeable decrease in unit cell parameters at 423K before transforming to a new structure type at 473K. In the case of metazeunerite, on cooling the symmetry lowers and the data were indexed on a primitive orthorhombic unit cell. The sample transforms to the tetragonal phase on heating above RT and on continued heating under goes a phase transition likely due to water loss to a new phase which is still to be identified.

This preliminary study shows that natural samples of metatorbernite-type phases can have variable compositions, which may effect their stability in nature. Uranium is an environmental contaminant throughout the world, especially in areas where mining and milling of U were carried out, such as South Terras. Uranyl phosphate phases are key in controlling U-mobility and studies have suggested using the

precipitation of metatorbernite-type phases to decontaminate groundwater contaminated by U through addition of polyphosphate. However, as we have shown, their stability is variable, dependent upon the composition. Therefore, understanding any stability changes as a function of composition will be key to their use as remediation materials. Ongoing studies into the structures and stabilities of phases in the metatorbernite-metazeunerite solid solution is underway.

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Tables

Sample	*a* (Å)	*c* (Å)	X
HR001	7.060 (4)	17.400 (1)	1.2
Bulk HA sample	7.018 (6)	17.394 (2)	0.6

Figure and table captions

Figure 1. *ac* projection of the structure of metatorbernite: Red CuO_6 octahedra, green UO_6 square bipyramids and yellow PO_4 tetrahedra are shown, small and large blue spheres represent O atoms. Structure reproduced after [12] using the ATOMS V6.1 atomic structure display package [13].

Figure 2. PXRD pattern of spoil heap sub sample with high activity compared to ICDD PDF for metatobernite, (ICDD PDF 36-406 [15]) and metazeunerite (ICDD PDF 17-146 [25]) and quartz (ICDD PDF 46-1045). Data were collected on a laboratory X ray diffractometer using Co $K\alpha_1$ radiation.

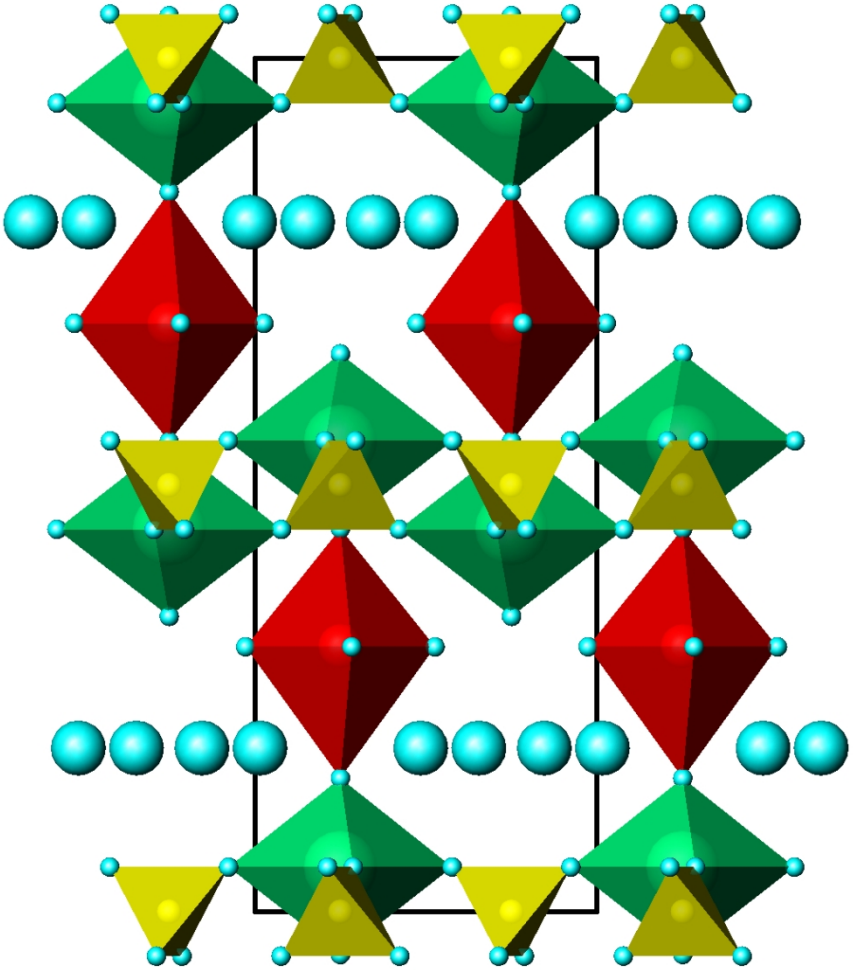
Figure 3. Comparison of unit cell parameters of the metatorbernite-metazeunerite ($Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x.nH_2O$) solid solution refined from laboratory PXRD data. Filled blue circles refined unit cell parameter *a* (bottom), filled orange triangles refined unit cell parameters *c* (top).

Figure 4. Refined lattice parameters from variable temperature study of metatorbernite ($Cu(UO_2)_2(PO_4)_2.8H_2O$) and the composition $Cu(UO_2)_2(PO_4)(AsO_4).8H_2O$ compared with reported unit cell parameters from a variable temperature study on a mineral sample of metatorbernite [27]. Grey filled circles metatorbernite *a*, yellow filled triangles metatorbernite *c*, blue filled diamonds $Cu(UO_2)_2(PO_4)(AsO_4).8H_2O$ *a*,

green filled squares $Cu(UO_2)_2(PO_4)(AsO_4).8H_2O$ *c*, blue open circles reported metatorbernite *a*, red open triangles reported metatorbernite *c* [28]. Note, error bars on the refined parameters were smaller than the markers used.

Figure 5. Refined lattice parameters from variable temperature study of metazeunerite ($Cu(UO_2)_2(AsO_4)_2.8H_2O$). Blue filled circles metazeunerite *a* in tetragonal space group, red filled triangles metazeunerite *c* in tetragonal space group, green filled crosses metazenerite *a* in orthorhombic space group, purple filled diamonds metzeunerite *b* in orthorhombic space group, blue filled squares metazeunerite *c* in orthorhombic space group. Note, error bars on the refined parameters were smaller than the markers used.

Table 1. Refined unit cell parameters from two natural samples of metatorbernite-type phases and the calculated x value from equation 1.



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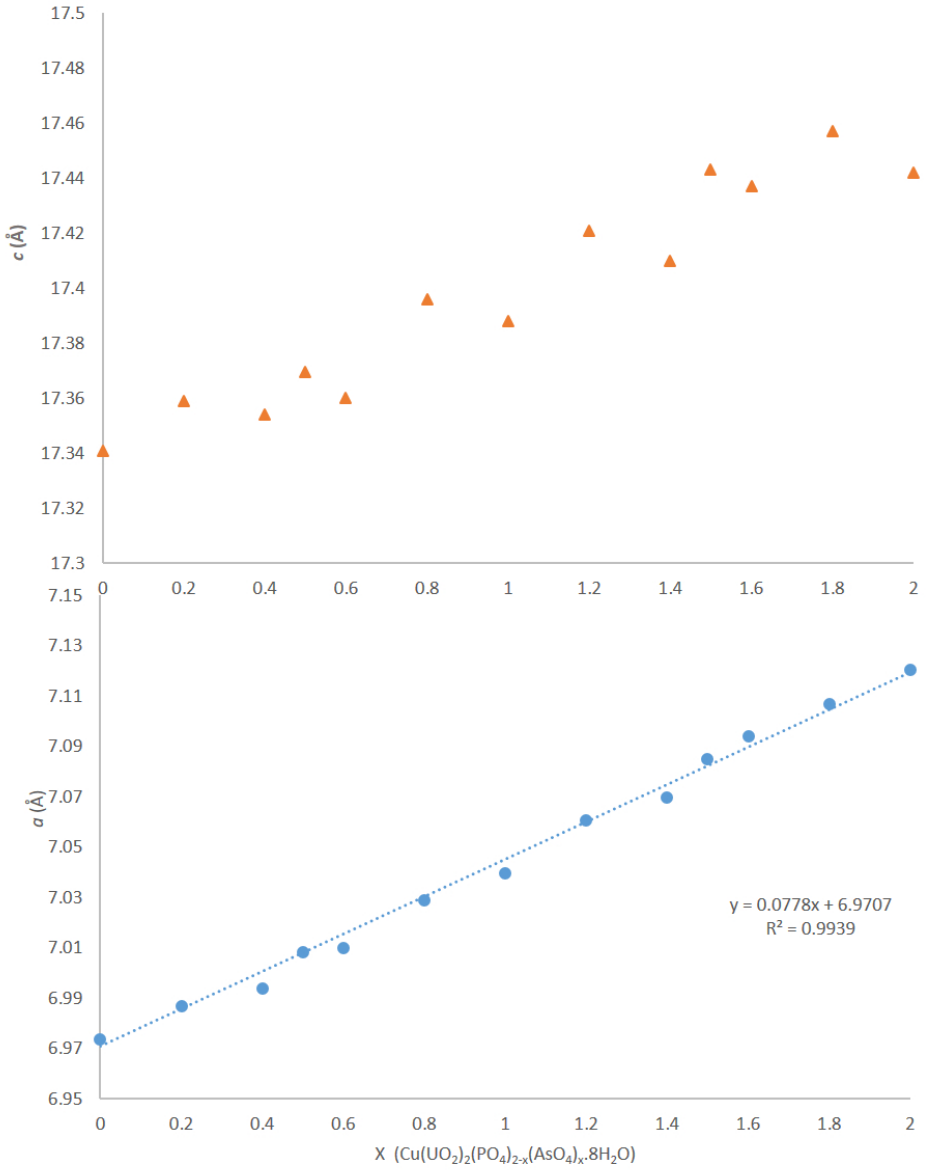

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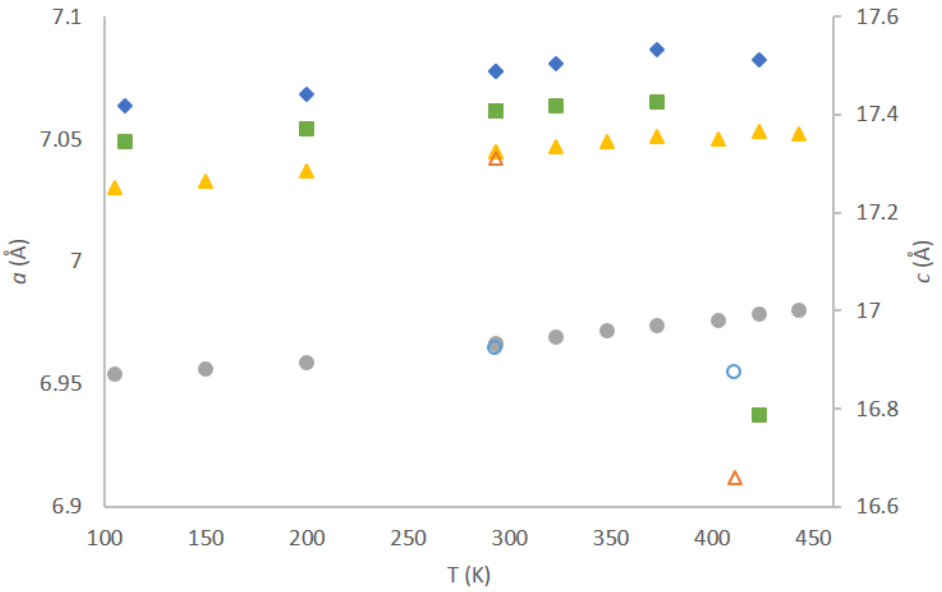

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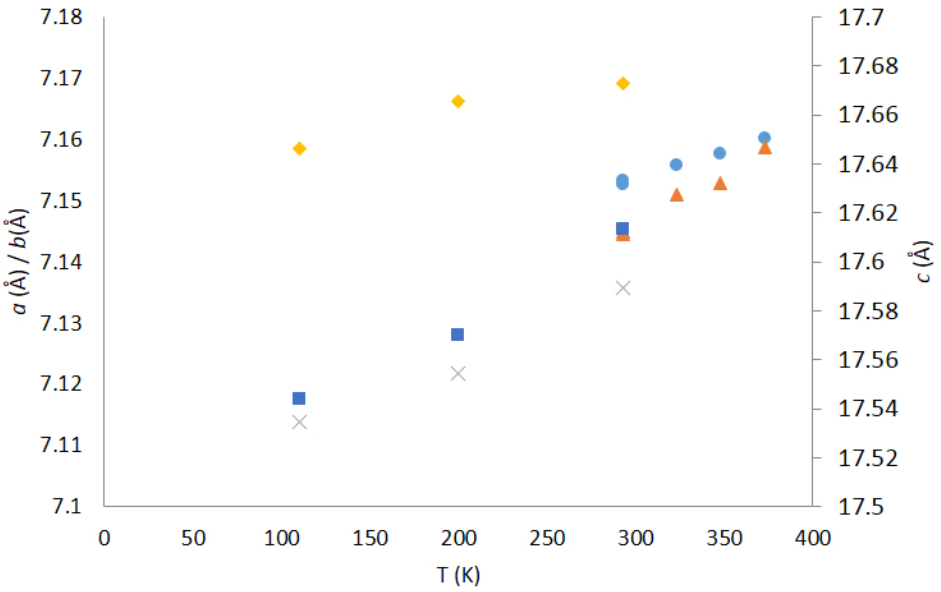

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