INVESTIGATIONS OF THE AUTUNE AND META-AUTUNE GROUPS: CRYSTAL STRUCTURE REFINEMENTS OF SYNTHETIC ZEUNERITE, METATORBERNITE, TRÖGERITE AND CHERNIKOVITE. A. J. Locock1 and P. C. Burns1, 2, 1, 2Department of Civil Engineering and Geological Sciences, 156 Fitzpatrick Hall, University of Notre Dame, Notre Dame, Indiana, 46556, alocock@nd.edu, pburns@nd.edu

The minerals of the autunite and meta-autunite groups are the most numerous of the uranyl arsenates and uranyl phosphates. The minerals of these groups are widespread, relatively insoluble and may control the concentration of U in many groundwaters [1].

The autunite and meta-autunite groups consist mainly of hydrated uranyl phosphates and arsenates with tetragonal or pseudo-tetragonal structures and the general formulas: \( \text{A}[(\text{UO}_2\text{O}_2)\text{X}(\text{AsO}_4)\text{Y}](\text{H}_2\text{O})\text{Z} \) and \( \text{A}[(\text{UO}_2\text{O}_2)\text{X}(\text{PO}_4)\text{Z}](\text{H}_2\text{O})\text{Y} \) respectively, where \( \text{X} = \text{P}^{5+}, \text{As}^{5+} \), and \( \text{A} = (\text{Al}^{3+} \text{H}^{+})^{1/2}, \text{Ba}^{2+}, \text{Ca}^{2+}, \text{Cu}^{2+}, \text{Fe}^{2+}, (\text{H}_3\text{O})^2, \text{K}^+, \text{Mg}^{2+}, \text{Mn}^{2+}, \text{Na}^+, (\text{NH}_4)^2, \text{Zn}^{2+} \). Not all of these chemical substituents have been found as mineral species in both groups. Varying degrees of hydration have been reported for these minerals. The meta-autunite group can be related to the autunite group by dehydration.

The crystal structures have been refined only for a few species from these groups. These have the autunite-type sheet that consists of \( \text{(UO}_2\text{O}_2)\text{PO}_{4-10} \) square bipyramids and phosphate/arsenate tetrahedra. The sharing of equatorial vertices of the uranyl square bipyramids with tetrahedra results in infinite sheets. The divalent interlayer cations are octahedrally coordinated and an extensive hydrogen-bonding network is present [2].

In an ongoing examination of the details of the interlayers and hydrogen bonding in the autunite and meta-autunite groups, selected species were synthesized and their crystal structures refined. In each of these three successful refinements, hydrogen atoms were located by difference-Fourier synthesis and were refined to occupancies of 0.75 and 0.25, respectively. Chernikovite is a fast-proton solid conductor [5].

The crystal structure of synthetic zeunerite, \( \text{Cu}[(\text{UO}_2\text{O}_2)\text{AsO}_4](\text{H}_2\text{O})_{12} \), \( Z = 2 \), tetragonal, \( a 7.1797(3), c 20.8571(13) \), space group \( P4/ncc \), was solved by inspection and refined by full-matrix least-squares techniques to an agreement index \( (R1) \) of 1.6%, calculated for 568 unique observed reflections \((|F| \geq 4\sigma(|F|)) \) collected using MoKa radiation and a CCD-based area detector.

The structure of copper-deficient synthetic twinned metatorbernite, \( \text{Cu}_{0.88}[(\text{UO}_2\text{O}_2)\text{PO}_4](\text{H}_2\text{O})_{8} \), \( Z = 2 \), tetragonal, \( a 6.9756(5), c 17.3491(16) \), space group \( P4/n \), was solved by direct methods and refined by full-matrix least-squares techniques to an agreement index \( (R1) \) of 2.0%, calculated for 794 unique observed reflections \((|F| \geq 4\sigma(|F|)) \) collected using MoKa radiation and a CCD-based area detector. The twin plane is \((001)\). Despite synthesis from a stoichiometric mixture, the population of copper in the \( A \) site refined to 0.88, in accord with prior results of 0.92 for natural metatorbernite [3]. An attempt was made to refine the structure in space group \( P4/nmm \) as previously reported [4], but this yielded unreasonable bond lengths and an agreement index \( (R1) \) of 8.2%.

The structure of synthetic trögerite, \( \text{H}_2\text{O}_2[(\text{UO}_2)\text{AsO}_4](\text{H}_2\text{O})_{6} \), \( Z = 2 \), tetragonal, \( a 7.1587(9), c 17.6293(31) \), space group \( P4/nmm \), was solved by direct methods and refined by full-matrix least-squares techniques to an agreement index \( (R1) \) of 2.0%, calculated for 399 unique observed reflections \((|F| \geq 4\sigma(|F|)) \) collected using MoKa radiation and a CCD-based area detector. The oxygen atoms associated with the \( \text{H}_2\text{O} \) and \( \text{H}_2\text{O}_2 \) groups were modeled as a split site and refined to occupancies of 0.75 and 0.25, respectively.

The structure of synthetic chernikovite, \( \text{H}_2\text{O}_2[(\text{UO}_2)\text{PO}_4](\text{H}_2\text{O})_{6} \), \( Z = 2 \), tetragonal, \( a 6.9962(4), c 17.4719(12) \), space group \( P4/ncc \), was solved by direct methods and refined by full-matrix least-squares techniques to an agreement index \( (R1) \) of 1.3%, calculated for 399 unique observed reflections \((|F| \geq 4\sigma(|F|)) \) collected using MoKa radiation and a CCD-based area detector. The oxygen atoms associated with the \( \text{H}_2\text{O} \) and \( \text{H}_2\text{O}_2 \) groups were modeled as a split site and refined to occupancies of 0.75 and 0.25, respectively. Chernikovite is a fast-proton solid conductor [5].