12.5-5 RIETVELD REFINEMENT AND DIFFERENCE FOURIER ANALYSIS OF THE TODOROKITE STRUCTURE USING POWDER X-RAY DATA. By J.E. Post, Dept. of Mineral Sciences, Smithsonian Institution, Washington, D.C., and D.L. Bish, Los Alamos Natl. Laboratory, Los Alamos, NM.

Todorokite [$(Na,Ca,K)_{.6}(Mn,Mg)_6O_{12}\cdot 3.2H_2O$] is thought to be one of the major Mn oxide phases in ocean Mn nodules, and is also of interest because it exhibits zeolite-like cation exchange behavior. Todorokite typically occurs as poorly crystalline masses, therefore it has not been possible to study its structure with single crystal diffraction methods. TEM studies by Turner (1982) show todorokite to have a tunnel structure similar to romanechite, but reveal no structural details including tunnel cation and water positions. We have completed Rietveld refinements on todorokite samples from South Africa and Cuba, using powder x-ray data. The starting model for the Mn,O framework was determined by distance-least-squares refinement, using romanechite Mn-O distances. Only the profile parameters were allowed to vary in the initial cycles of Rietveld refinement. Then, Fourier difference maps were calculated from the observed Bragg intensities determined by the refinement. The maps show the largest peaks for both samples to be in the tunnels at about (.37,0,.37), and smaller peaks at (.70,.5,.40) and (.65,0,.34). Structure energy calculations on todorokite using the program WMIN (Busing, 1981), with modified electron gas repulsive terms, yield minimum energy water positions that correspond closely to the first two peaks on the difference map, and minimum energy Na/Ca positions near the third peak. Continued Rietveld refinements varying atom positions and tunnel site occupancies yield Rwp values of 0.125 and 0.13 for the Cuban and S. African samples, respectively.

12.5-6 THE STRUCTURE DETERMINATION OF α-$CrPO_4$ AND $MnPO_4.H_2O$ BY POWDER SYNCHROTRON X-RAY DIFFRACTION. By J.P. Attfield, A.K. Cheetham, P. Lightfoot and A.W. Sleight, University of Oxford, Department of Chemical Crystallography, 9 Parks Rd., Oxford OX1 3PD, U.K. and E.I. Du Pont de Nemours & Co, Experimental Station, Wilmington, Delaware 19898, U.S.A.

Recent advances in both the experimental and computational aspects of powder diffraction have brought the technique to the point where the *ab initio* determination of crystal structures from powder data is becoming routine. The general approach, involving indexing of the pattern, assignment of space group, and solution of the structure by Patterson or direct methods, has been described by Christensen *et al.* (Aust. J. Phys., 1985, 38,497-505), and the feasibility has been demonstrated using ultra high resolution neutron and synchrotron X-ray data (Cheetham *et al.*, Nature, 1986, 320, 46-48; Attfield *et al.*, Nature, 1986, 322, 620-622).
The results of two synchrotron X-ray studies will be presented. The structure determination of α-$CrPO_4$ (Imma; a=10.406, b=12.899, c=6.299 Å) will be described and the results will be compared with a refinement of powder neutron diffraction data collected on the same sample. The structure consists of an infinite network of linked CrO_6 octahedra and PO_4 tetrahedra,. An interesting feature is the sharing of a common edge between CrO_6 and PO_4 units, both of which are distorted, resulting in a short non-bonding Cr-P distance of 2.68Å and an O-O contact of 2.33Å. The solution of the structure of a new phase, $MnPO_4.H_2O$ (C2/c; a=6.912, b=7.470, c=7.357 Å, β=112.3°) will also be discussed, including the location of the hydrogen atoms. The structure comprises a network of vertex-sharing MnO_6 octahedra and PO_4 tetrahedra, the former distorted by the Jahn-Teller mechanism. The water molecules are located in small channels running parallel to the c axis.

12.5-7 APPLICATION OF X-RAY WHOLE-POWDER-PATTERN FITTING TECHNIQUE TO THE CHARACTERIZATION OF MULTICOMPONENT CERAMIC MATERIALS. By H. Toraya, Ceramic Engineering Research Laboratory, Nagoya Institute of Technology, Asahigaoka, Tajimi 507 Japan.

The procedure of whole-powder-pattern fitting (WPPF) without reference to a structural model, first proposed by Pawley for use with neutron powder data [J. Appl. Cryst. (1981), 14, 357-361] and then applied to X-ray powder diffractometer data [H. Toraya, J. Appl. Cryst.(1986), 19, 440-447], has further been extended to the characterization of multicomponent ceramic materials. For this purpose, the procedure is improved in some respects: 1) automatic peak shift correction in refining unit cell parameters of the sample containing an internal standard material, 2) remodeling of angular dependent peak asymmetry and intensity decaying rate of the diffraction profile in order to avoid the parameter divergence in the LS, 3) introduction of the overall scale factors, which can be refined instead of individaul integrated intensities. Refined unit cell parameters are accurate to about 10^{-3}- 10^{-4} Å. The WPPF technique can extract the maximum information from the whole powder data, and can obtain a much higher accuracy compared to the conventional profile fitting technique, particularly to analyze a minor phase in the mixture. The WPPF is carried out for the quantitative analysis and unit cell measurement of Y_2O_3 stabilized ZrO_2 polymorphs, of which analyses have hitherto been abandoned due to the complexity of the pattern. Other examples will also be presented.

12.5-8 INFLUENCE OF PARTICLE SIZE DISTRIBUTION ON RIETVELD PROFILE ANALYSIS PARAMETERS FOR LOW-QUARTZ. By A.S. Zydek and B.H. O'Connor, Department of Applied Physics, Curtin University of Technology, Perth, Western Australia.

O'Connor and Chang (1986) have described the pronounced systematic errors which occur in conventional quantitative assays of powders by the Klug and Alexander method when the milling procedure used to prepare the powder produces a sub-optimum particle size distribution. In view of this and other sources of systematic error which bias conventional quantitative procedures, O'Connor and Raven (1987) have promoted Rietveld profile analysis of mixtures as a superior technique for quantitative analysis.

In the present study, the authors have employed a suite of specimens similar to that used by O'Connor and Chang. Micronizing mill specimens were produced for a range of milling times under wet- and dry-grinding conditions. Milling times ranged from one to twenty minutes, and particle size distributions were measured for material produced in each trial.

The data have been used to study the dependence of various Rietveld parameters on milling procedure-profile widths, gamma parameter (mix of Lorentzian/Gaussian character), integrated intensity estimates. The results show that quantitative analysis by Rietveld profiling is less prone to systematic error than conventional methods.

REFERENCES:

O'Connor, B.H. and Chang, W-J. (1986). "X-ray Spectrometry", 15, 267-270.
O'Connor, B.H. and Raven, M.D. "Powder Diffraction", (submitted).