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
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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$_2$O BY POWDER SYNCHROTRON X-RAY DIFFRACTION. By
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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$_2$O (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 CHARACTERIZA-
TION OF MULTICOMPONENT CERAMIC MATERIALS.
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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 diffrac-
tometer 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$_2$O$_3$ 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 quantit-
ative 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 Spec-
    trometry", 15, 267-270.
O'Connor, B.H. and Raven, M.D. "Powder Diffraction",
    (submitted).