The Impact of the Rietveld Method in Mineralogy and Geology: The Impossible is now Possible

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Some of the earliest applications of X-ray diffraction methods were in the geological and mineralogical fields, and many of the first structures solved by the Braggs were of minerals (NaCl, ZnS, and diamond). The book *Atomic Structure of Minerals*, based on W. L. Bragg's lectures in 1934 at Cornell University, was published in 1937, giving a summary of our knowledge of mineral structures eighty years ago (only 22 years after the discovery of X-ray diffraction!). It is remarkable that much of our current knowledge of structures is only a *refinement* of the data provided almost a century ago. For its first 50 years, X-ray powder diffraction (XRPD) was a method generally used for phase identification, semi-quantitative (at best) analysis of phase abundances, and determination of low-precision unit-cell parameter information. Several important improvements in X-ray diffraction occurred over the past half century, including the development of readily available (so-called) Bragg-Brentano powder diffractometers in the late 1940's and the general availability of automated powder diffractometers in the late 1970's. These two paved the way for the application of the Rietveld method, making XRPD a powerful method capable of providing accurate quantitative multicomponent analyses, with high-precision (and accurate) unit-cell information on non-trace phases, with detection limits easily below 1%. The first decade after the development of the Rietveld method saw few applications, and Rietveld refinements were then restricted to single phases and were done primarily for their originally intended purpose, to refine crystal structures for materials that were unavailable in single-crystal form. Developments in the late 1980's paved the way for the now-common applications of the Rietveld method in quantitatively using *all* of the data in an XRPD pattern.

The Rietveld method is now part of virtually every XRPD application, including laboratory, synchrotron, on-line, *in situ* field, and even extraterrestrial uses. Several key areas have seen extraordinary benefits in mineralogy, and analysts now routinely exploit peak positions, intensities, *and* profiles to solve previously intractable quantitative problems with multicomponent mixtures. Perhaps the most common application is in quantitative multicomponent analysis, and the Rietveld method has provided unprecedented insight into the makeup of rocks and mixtures. This information can be obtained rapidly, even on-line or in the field, and it facilitates quantitative coupling with other types of data such as chemical compositions. For example, such data for rocks at Yucca Mountain, Nevada, coupled with total chemical data, allowed determination of past chemical fluxes due to alteration by groundwater. Use of the Rietveld method with data from a calibrated diffractometer allows determination not only of precise unit-cell (uc) parameters but highly *accurate* values, as the important systematic errors affecting peak positions can be easily modeled. Before the advent of full-pattern fitting methods like the Rietveld method, single-crystal methods were usually preferred for determination of uc parameters, but XRPD uc values are now superior and preferred. These accurate data can be used in making detailed geological inferences, e.g., for evaluating different generations of coexisting micas or amphiboles in metamorphic rocks. Modern XRPD instruments have sufficient resolution to distinguish between compositionally similar minerals, which can be very powerful in Ar-Ar or K-Ar dating of rocks with multiple generations of K-bearing minerals. Finally, the Rietveld method facilitates extraction of information on the nature of peak broadening, something that was (and often still is) largely ignored. This information on crystallite size and strain provides considerable insight into many geological materials that are only partially ordered. For example, studies of natural dolomite- and calcite-bearing carbonate rocks reveal that many of these contain partially disordered and cation-substituted carbonate phases, further showing that many rocks contain dolomite that is not "ideal."

These approaches can all be applied during field studies (e.g., with *in situ* analyses at field or mine sites), during industrial on-line analyses, with environmental control (T, P, humidity, time, etc.), and even remotely on another planet such as Mars. And all of these types of studies can thus profit simultaneously from all of the above strengths of the Rietveld method, with a *single* XRPD dataset providing phase amounts (often down to the sub-percent level), accurate uc parameters for all non-trace phases, and information on crystallite size and strain for major phases. Ongoing enhancements of the method include applications to disordered materials such as clay minerals.