Bayesian inference supersedes Rietveld technique in crystallographic structure refinement
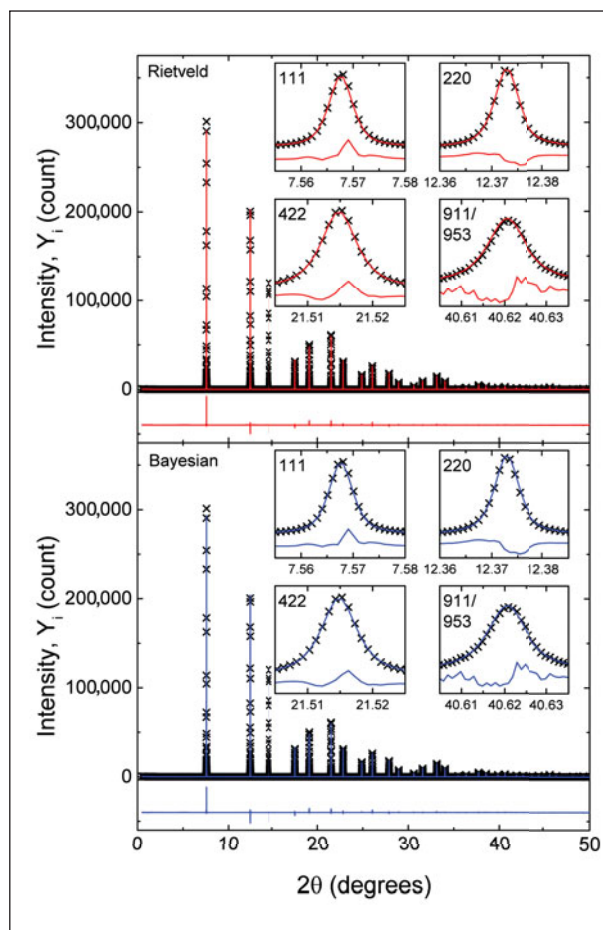
To know a crystal is to know its unit cell—the lengths of edges, angles, charges, and spins that align and misalign together to form a material. This paradigm has allowed crystallographers to catalog over 200,000 crystals with remarkable precision. For example, we know that the atoms in Si at 22.5°C are at an average separation of 5.43123 Angstroms. However, local chemical, defect, and strain states are not constant throughout a crystal lattice—which means that crystals are really heterogeneous and crystal parameters are rarely single-valued. A new *Nature Scientific Report* (doi:10.1038/srep31625) proposes a way to deal with this heterogeneity—by treating such values as probability distributions. By applying Bayesian inference to this paradigm, the researchers developed a new refinement algorithm for crystallographic diffraction data. This is considered an improvement over the currently popular Rietveld refinement technique, which has been used for over half a century. This work, which is a collaboration between the North Carolina State University (NCSU), National Institute of Standards and Technology, and Oak Ridge National Laboratory, was initiated by Jacob Jones and lead author Chris Fancher, both from NCSU.

X-ray diffraction (XRD) has been around for over a hundred years and has contributed to work that has resulted in 29 Nobel prizes. A crystal breaks an x-ray beam falling on it into a discrete set of spots that are marked by their angle and intensity. A spot from a single crystal corresponds to reflections from a single set of planes. In a polycrystalline sample, however, reflections from different planes in different grains can add together at a particular spot, which complicates the assignment of intensity, a crucial step in calculating cell parameters. The Rietveld method overcomes this by starting with a model of the crystal, comparing it with the observed distribution, and progressively refining the model until what is calculated matches what is observed.

The Bayesian approach samples not one but thousands of models with values selected by a Markov chain Monte Carlo algorithm that gives a distribution for each parameter. This is refined using experimental data until distribution is obtained not just for cell parameters, such as plane spacings, angles, and crystallite size distributions, but also instrumental parameters such as the x-ray wavelength, axial divergence, and peak fitting parameters. The researchers used this approach on a silicon standard, and observed that the wavelength and several other parameters were asymmetrically distributed about the mean—something the Rietveld technique cannot show. The researchers suggest determining the posterior distributions of instrumental parameters using a reference standard and then using this knowledge to solve the structures of complex materials.

Matthew Suchomel from CNRS, France, commented that "… information about the range and distribution of structural parameters afforded by this Bayesian approach could be very useful for important technological materials like Li-ion batteries and ferroelectrics, in which the real atomic structure parameters may not be homogenous—for example—because of stacking defects or domain boundary strains. In contrast, the traditional 'least squares' approach normally provides only a single value for each parameter with some uncertainty."

Mark Tschopp of the US Army Research Laboratory adds, "The significance of the article is that by using a Bayesian inference method, as opposed to the traditional Rietveld refinement method, they find that this method better estimates XRD model uncertainties and improves the model fit (i.e., reducing residuals), which can perhaps enable a more complete and quantitative picture of the underlying crystallographic structure." Both commentators were not associated with the original work.

Vineet Venugopal

Powder diffraction data of Si is compared with results of a Rietveld analysis and an average of the final 1000 Markov chain Monte Carlo samples (bottom). Insets of the reflections show that the Bayesian inference and Rietveld approaches achieve a similar fit to the observed diffraction data. Credit: *Nature Scientific Reports*.

Erratum: In *MRS Bulletin* **41** (9), 2016, p. 659, the units for the *y*-axis in the figure should be $/Wh.

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