

Comparison of Rietveld-compatible structureless fitting analysis methods for accurate quantification of carbon dioxide fixation in ultramafic mine tailings

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The carbonation of ultramafic rocks, including tailings from ultramafic-hosted ore deposits, can be used to sequester CO₂ from the atmosphere and store it safely within minerals over geologic time scales.^{1, 2} Quantitative X-ray diffraction (XRD) using Rietveld refinements can be used to estimate the amount of carbon sequestered by carbonate minerals that form as a result of weathering of ultramafic rocks.^{1, 2} However, the presence of structurally disordered phases such as serpentine minerals, which are common in ultramafic ore bodies, means that such samples cannot be analysed using typical Rietveld refinement strategies.² Previous investigations of carbon sequestration at Woodsreef and other ultramafic mine sites have used modified Rietveld refinement methods that apply structureless pattern fitting for disordered phases;² however, no detailed comparison of the accuracy of these methods for carbon accounting has yet been done, making it difficult to determine the most appropriate analysis method. A comparison of these methods is needed, and should consider the accuracy of quantitative results on a mineral-by-mineral bases, with particular importance placed on minerals that sequester carbon, such as Mg-carbonate minerals and hydrotalcite group minerals, which suffer from severe preferred orientation.

Here, we assess and compare the accuracy of three different non-traditional Rietveld refinement methods for carbon accounting: (1) the PONKCS method,³ (2) the combined use of a Pawley fit for serpentine minerals and an internal standard (Pawley/internal standard method)¹ and (3) the combined use of the PONKCS and Pawley/internal standard methods. We examine which of these approaches represents the most accurate way to quantify the abundances of serpentine, pyroaurite and other carbonate-bearing phases in a given sample. We demonstrate that by combining the PONKCS and Pawley/internal standard methods it is possible to quantify disordered phases in a sample, and to also get an estimate of the amorphous content and any unaccounted for intensity in an XRD pattern. Eight artificial tailings samples with known compositions were made to reflect the natural variation found within the tailings at the Woodsreef chrysotile mine (NSW, Australia). Rietveld refinement results for the three methods were compared to the known compositions of each sample to calculate absolute and relative error values and evaluate the accuracy of the three methods, including whether they produce systematic under- or overestimates of mineral abundance.

Overall, the Pawley/internal standard method produced more accurate results compared to the PONKCS method, with an average bias per refinement of 6.7 wt%, compared to 10.3 wt% using PONKCS and 12.9 wt% for the combined PONKCS-Pawley/internal standard method. The simpler and faster sample preparation makes the PONKCS method well-suited for rapid carbon accounting, for instance in the field using a portable XRD;² however, the superior accuracy gained when using an internal standard make the Pawley/internal standard method the preferable means of undertaking a detailed laboratory-based study. As all three methods displayed an underestimation of carbonate phases, applying these methods to natural samples will likely produce an underestimate of Mg-carbonate and hydrotalcite group mineral abundances. As such, crystallographic accounting strategies that use modified Rietveld refinement methods produce a conservative estimate of the carbon sequestered in minerals.

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2. Turvey, C. C.; Wilson, S. A.; Hamilton, J. L.; Southam, G., Field-based accounting of CO₂ sequestration in ultramafic mine wastes using portable X-ray diffraction. *American Mineralogist* **2017**.
3. Scarlett, N. V. Y.; Madsen, I. C., Quantification of phases with partial or no known crystal structures. *Powder Diffraction* **2006**, *21*, (4), 278-284.