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

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Abstract

The carbonation of ultramafic rocks, including tailings from ultramafic-hosted ore deposits, can be used to remove CO_2 from the atmosphere and store it safely within minerals over geologic timescales. Quantitative X-ray diffraction (XRD) using Rietveld refinements can be employed to estimate the amount of carbon sequestered by carbonate minerals that form as a result of weathering of ultramafic rocks. However, the presence of structurally disordered phases such as serpentine minerals, which are common in ultramafic ore bodies such as at the Woodsreef chrysotile mine (New South Wales, Australia), results in samples that cannot be analyzed using typical Rietveld refinement strategies. Previous investigations of carbon sequestration at Woodsreef and other ultramafic mine sites typically used modified Rietveld refinement methods that apply structureless pattern fitting for disordered phases; however, no detailed comparison of the accuracy (or precision) of these methods for carbon accounting has yet been attempted, making it difficult to determine the most appropriate analysis method. Such an analysis would need to test whether some methods more accurately quantify the abundances of certain minerals, such as pyroaurite [$Mg_6Fe^{3+}_2(CO_3)(OH)_{16}\cdot 4H_2O$] and other hydrotalcite group minerals, which suffer from severe preferred orientation and may play an important role in carbon sequestration at some mines. Here, we assess and compare the accuracy, and to a lesser extent the precision, of three different non-traditional Rietveld refinement methods for carbon accounting: (1) the PONKCS method, (2) the combined use of a Pawley fit for serpentine minerals and an internal standard (Pawley/internal standard method), and (3) the combined use of 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 the abundances of disordered phases in a sample and to obtain an estimate of the amorphous content and any unaccounted intensity in an XRD pattern. Eight artificial tailings samples with known mineralogical compositions were prepared to reflect the natural variation found within the tailings at the Woodsreef chrysotile mine. Rietveld refinement results for the three methods were compared with the known compositions of each sample to calculate absolute and relative error values and to evaluate the accuracy of the three methods, including whether they produce systematic under- or overestimates of mineral abundance. Estimated standard deviations were also calculated during refinements; these values, which are a measure of precision, were not strongly affected by the choice of refinement method. The abundance of serpentine minerals is, however, systematically overestimated when using the PONKCS and Pawley/internal standard methods, and the abundances of minor phases (<10 wt%) are systematically underestimated using all three methods. Refined abundances for pyroaurite were found to be increasingly susceptible to error with increasing abundance, with an underestimation of 6.6 wt% absolute (60.6% relative) for a sample containing 10.9 wt% pyroaurite. These significant errors are due to difficulties in mitigating preferred orientation of hydrotalcite minerals during sample preparation as well as modeling its effects on XRD patterns. The abundances of hydromagnesite [$Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$], another important host for atmospheric CO_2 during weathering of ultramafic rocks, was consistently underestimated by all three methods, with the highest underestimation being 3.7 wt% absolute (or 25.0% relative) for a sample containing 15.0 wt% hydromagnesite. Overall, the Pawley/internal standard method produced more accurate results than the PONKCS method, with an average bias per refinement of 6.7 wt%, compared with 10.3 wt% using PONKCS and 12.9 wt% for the combined PONKCS-Pawley/internal standard method. Furthermore, the values for the refined abundance of hydromagnesite obtained from refinements using the Pawley/internal standard method were significantly more accurate than those for refinements done with the PONKCS method, with relative errors typically <25% for hydromagnesite abundances between 5 and 15 wt%. 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; 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 hydromagnesite 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.

Keywords: Carbon accounting, X-ray diffraction, Rietveld analysis, PONKCS method, Pawley/internal standard method, serpentine, amorphous material, pyroaurite, hydromagnesite

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