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Editorial

Editorial for the Special Issue "The Rietveld Method in Geomaterials Characterisation"

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The raw materials obtained from the Earth's crust (Geomaterials) are of fundamental importance for a wide range of industries. Two of their characteristics make the study of these materials especially challenging: they are almost always polyphase and, in most cases, fine-grained (powdery). Both these features leave powder diffraction (of X-rays or neutron beams) techniques as the only effective approach to study in sufficient detail the quantitative phase compositions of these materials as well as the crystal structures of their components. Moreover, the quantification of phase composition, even for coarse-grained geomaterials, is best performed by grinding them into powders, providing statistically representative phase distribution results.

Fortunately, the Rietveld method provides an accurate and effective pathway for solving the above problems. It employs a least squares approach to refine a theoretical line profile (calculated from a known or postulated crystal structure) until it matches the measured profile. Introduced in 1969 by the famous Dutch crystallographer Hugo Rietveld, today the method is the 'de facto' standard for whole pattern (full profile) refinement of powder diffraction data. The method has been so successful that nowadays the structure of powdery materials is routinely being determined nearly as accurately as the results obtained by single crystal diffraction techniques.

In the current Special Issue, a good example of the above is Kostov-Kytin et al. [1]. It demonstrates the accuracy and capabilities of the Rietveld procedure to track the structural transformations and framework flexibility of crystal structures via the example of the naturally water-containing zirconosilicate elpidite, subjected to thermal treatment from room temperature to 300 °C. The obtained results are in accordance with previously reported data from in situ single crystal X-ray diffraction studies on heated samples of the same mineral. More light has been drawn on the temperature interval in which the non-reconstructive topotactic phase transition occurs upon partial dehydration. The framework flexibility, observed as a response to the water loss and subsequent thermal expansion, was evaluated in terms of an intentionally introduced set of geometric parameters characterizing the spatial orientation of symmetrically related zirconium octahedra in the structure, the coordination polyhedral volumes, their distortion indices, and bond angle variances.

In another study [2] Rietveld structure refinement provided detailed data for the dynamics of cation exchange in natural clinoptilolite. Partial and almost complete barium exchange on clinoptilolite is performed and structurally studied for different durations (2 h, 24 h, 72 h, 168 h, 12 d, 22 d) at room temperature and 90 °C of the ion exchange process. Continuing ion exchange up to the 22nd day is proved by EDS analyses data and powder XRD (intensity changes of 020 and 200 peaks). Rietveld structure refinement was first performed on the maximum Ba exchanged clinoptilolite at 90 °C for 22 days (3.04 atoms per unit cell). Four barium and nine H_2O sites were refined. The split positions Ba2 and Ba(K) (around the *M*3 site in channel C) were found to be mostly occupied by 2.23 atoms per unit cell. The rest of refined samples showed different occupations of the positions of incoming Ba^{2+} and outgoing cations (Na^+, Ca^{2+}, K^+, Mg^{2+}) during ion exchange, describing extra-framework cationic movements, which are released easily without preferable directions. The exchanges at 90 °C and room temperature were found to

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proceed similarly up to the 2nd hour, but then at room temperature the process is slowed and at 22nd day 1.64 barium atoms per unit cell are structurally refined.

In a similar study of a synthetic perovskite type compound $BiFeO_3$ [3], the Rietveld refinement of the crystal structure, based on powder X-ray diffraction patterns, was applied to study the influence of the partial substitution of Bi by rare-earth (RE) elements with different ionic radii on the structural and morphological properties of the ferrite phase. Substitution by large RE ions was found to preserve the rhombohedral symmetry of $BiFeO_3$, whereas substitution by smaller RE ions led to the coexistence of two polymorphic perovskite phases with rhombohedral *R3c* and orthorhombic *Pnma* symmetries. The unit cell parameters, as well as the interatomic distances and angles, not only around the A cation but also around the iron ions, were influenced by the substitution. The mean crystallite and particle size decreased with the decrease in the ionic radius of the substituting RE ion.

Today, the Rietveld method is not only being used for structure refinement, but it is also a key analytical method for quantitative phase analysis using powder diffraction techniques. Powered by the capabilities of the Rietveld method, the geological community today has the chance not only to better characterize geomaterials of current industrial interest, but also to revisit the quantitative characteristics of geological matter and widen our knowledge about generic natural processes.

A brilliant example of the latter is the Quantitative Phase Analysis of Skarn Rocks [4] where the Rietveld method, using X-ray powder diffraction data, was applied to selected skarn samples. The traditional methods for quantitative analysis (point-counting and norm calculations) are not applicable for such inhomogeneous samples, containing minerals with highly variable chemical compositions. Up to eight individual mineral phases have been measured in each sample. To obtain the mineral quantities in the skarn rocks, preliminary optical microscopy and chemical investigation by electron probe microanalysis (EPMA) were performed for the identification of some starting components for the Rietveld analysis and to make comparisons with the Rietveld X-ray powder diffraction results. A good correlation between the refined mineral compositions and the data of the EPMA measurements was achieved.

Another example of a solution provided by the Rietveld method, where traditional methods had previously "hit the wall", is the study of maghemite in Brazilian iron ores [5]. Maghemite (γ-Fe_2O_3) is an intermediate metastable phase, formed during magnetite oxidation at low temperatures, on its route to hematite. It has magnetic susceptibility and a crystal structure close to magnetite, with which it forms a solid solution, while compositionally it is same as hematite. Maghemite is thus easily misidentified as magnetite by X-ray diffraction and/or as hematite by spot chemical analysis in iron ore characterization routines. The correct quantification of maghemite is of crucial importance for the effective processing of iron ores and soils. This was achieved in samples of Brazilian soils and iron ores by the Rietveld method using a constrained refinement of the X-ray patterns. The results were confirmed by reflected light microscopy and Raman spectroscopy, thus qualitatively validating the method. X-ray diffraction with the refinement of the isomorphic substitution of Fe^{2+} by Fe^{3+} along the magnetite–maghemite solid solution could help to suitably characterize maghemite in iron ores.

Finally, it should be mentioned that in some research branches, such as cement studies, where the precise quantification of a numerous phases in powdery material is of crucial importance [6], the Rietveld method has long been the accepted quantification standard.

All the above examples show that the field of applications of the Rietveld method is constantly growing because of its capability to extract detailed crystallographic data from polyphase powdery samples, which are easy to handle and study. It was recently demonstrated [7–9] that in combination with the pair distribution function (PDF) method even the Anisotropic Atomic Displacement Parameters (ADPs) of atoms can be precisely determined.

I hope that the examples in this Special Issue provide a wider view of the capabilities of the Rietveld method and will inspire researchers with new ideas of how to solve otherwise inextricable problems.

Conflicts of Interest: The authors declare no conflict of interest.

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