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APPLICATION OF RIETVELD REFINEMENT TECHNIQUES TO A DISORDERED II*b* Mg-CHAMOSITE

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Abstract—The structure of a disordered II*b* Mg-chamosite was studied using Rietveld refinement techniques and powder X-ray diffraction (CuKα, 18–120° 2θ in 0.02° 2θ increments). The refinement in space group $C\bar{1}$ yielded high precision lattice parameters (a = 5.36982(5)Å, b = 9.3031(9)Å, c = 14.2610(6)Å, α = 90.315(5)°, β = 97.234(7)°, γ = 90.022(9)°) and atomic coordinates very similar to previous studies. However, the presence of semi-random stacking in this specimen created a situation in which not all atoms could be precisely located: the positions of the octahedral cations and anions which repeat at intervals of $\pm b/3$ could be uniquely determined in three dimensions whereas only the *z* parameter of the other atoms could be refined. The reasonable appearance of the final model, despite the fact that many of the atom positions could be located in only one dimension, may have resulted because all of the atoms in this structure except O(5) repeat at intervals which are very nearly $\pm b/3$.

Key Words—Chlorite, Disorder, Rietveld refinement.

INTRODUCTION

The Rietveld method (Rietveld, 1967; 1969) is a technique for refining crystal structures from X-ray and neutron powder diffraction data. The ability to derive detailed information about a crystal structure from powder diffraction data is especially important in studies of materials such as the clay minerals which occur exclusively in a finely crystalline state (see Post and Bish, 1989). The general structures of clay minerals can be deduced by analogy with macrocrystalline minerals amenable to single-crystal studies (e.g., Bailey, 1984), however, the details must be worked out through careful crystal structure studies using techniques such as Rietveld refinement. To date, a limited number of clay mineral structures have been studied using the Rietveld method: kaolinite (Adams, 1983; Suitch and Young, 1983; Young and Hewat, 1988; Bish and Von Dreele, 1989; Bish and Von Dreele, 1990); nacrite (Toraya *et al.*, 1980); dickite (Adams and Hewat, 1982; Bish, 1991); chamosite (Walker and Bish, 1989); clinochlore (Rakovan and Guggenheim, 1991); and sepiolite (Bish and Post, 1987).

An important limitation on the refinement of clay mineral structures is the ubiquitous presence of disorder. In chlorites, a common type of disorder is semi-random stacking which necessarily limits the amount of information present in the diffraction data to that related to those atoms unaffected by the disorder. In semi-random stacking, the 2:1 layers above and below the interlayer maintain hydrogen bond contact by adopting positions related by $\pm b/3$. At each interface above and below the interlayer sheet, three positions are available, and the layers on either side of the interface adopt one of these positions randomly. Because the layers "choose" randomly from among a limited number of choices, the resulting structures are termed "semi-random." The layer shifts are all related by $\pm b/3$ irrespective of which position is chosen. Thus, reflections with indices in which $k = 3n$ are not affected by semi-random stacking whereas those with indices in which $k \neq 3n$ will be streaked, producing a two-dimensional diffraction band.

Refinement of the crystal structure of a II*b* Mg-chamosite has been attempted using Rietveld methods. The sample exhibits semi-random stacking, limiting the amount of information to be extracted from the diffraction data. The purpose of this paper is to discuss the information which can and cannot be obtained through refinement of the structure of a mineral with this type of disorder.

EXPERIMENTAL TECHNIQUES AND RESULTS

The sample was scraped from an outcrop of the Lebanon Granite on the west side of NH Route 120 about 2 miles north of Lebanon, New Hampshire (USA) where fine-grained chlorite occurs with fluorite cubes in a mat covering exposed fracture faces. Chemical analysis of the mineral by X-ray fluorescence (Table 1) may be resolved to the following structural formula (normalized to 56 negative charges):

$$(Mg_{3.54}Al_{2.66}Fe^{2+}{}_{5.44}Mn_{0.16}\square_{0.2})\text{-}(Si_{5.70}Al_{2.29}Ti_{0.01})O_{20}(OH)_{16}.$$

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Table 1. Chemical analysis of sample.[1]

		Cations (28 oxygens)	
SiO_2	27.30	Si	5.70
TiO_2	0.10	Ti	0.01
Al_2O_3	21.14	Al	4.96
MgO	11.40	Mg	3.54
MnO	0.88	Mn	0.16
FeO	31.12	Fe^{2+}	5.44
H_2O	9.11[2]		
Total	100.05		

[1] Analysis by X-ray fluorescence.
[2] Weight loss upon ignition.

The chemical analysis indicates that the chlorite is a Mg-chamosite (Martin *et al.*, 1991).

The <400 mesh (<38 μm) size fraction of the sample was obtained by dry sieving with a sonic sifter, and the resulting powder was backloaded into an aluminum mount and analyzed with CuKα radiation. The analytical run was divided into two parts: between 18 and 70° 2θ the count rate was 4 seconds per 0.02° 2θ step, and between 70 and 120° 2θ the count rate was 20 seconds per 0.02° 2θ step. X-ray data were analyzed with the Generalized Structure Analysis System (GSAS) refinement package (Larson and Von Dreele, 1990). The starting model used was a triclinic II*b*-4 chlorite structure (Joswig and Fuess, 1990).

After analysis in space group $C\bar{1}$, a χ^2 of 8.4 and a Rwp of 16.3% were obtained from 2724 reflections. Lattice parameters were: a = 5.36982(5) Å, b = 9.3031(9) Å, c = 14.2610(6) Å, α = 90.315(5)°, β = 97.234(7)°, γ = 90.022(9)° with a resulting cell volume of 706.729(64) Å^3. In addition to lattice parameters, a four-coefficient background function, a pseudo-Voight profile function (Larson and von Dreele, 1990), and a preferred orientation function using [001] as the anisotropic broadening axis were also refined. Soft constraints were used, as suggested by Walker and Bish (1989), to constrain cation-oxygen bond distances. In all, 42 soft constraints were used contributing 1.1% to the total minimization function, $M = \Sigma\ W_i(y_o - y_i)^2$, in which W_i is the weight of the observation, y_o is the observed intensity, and y_i is the calculated intensity.

Values for site occupancies, atom positions, isotropic temperature factors, and average refined metal-oxygen bond distances are given in Table 2. For the octahedral cations and anions, the *x*, *y*, and *z* values are refined coordinates. For all other atoms only the *z* values are refined coordinates; *x* and *y* coordinates are the results of the refinement but do not represent actual atomic positions due to the presence of structural disorder as discussed in the next section. Final profile parameters are very close to instrumental values, indicating that diffracting domain size and crystallite strain contribute little to broadening of X-ray peaks. Thus crystallite domains are relatively large, in accord with the results of Walker *et al.* (1990), who reported that domain sizes in transmission electron microscope images of this sample were greater than 1000 Å in the *a*-*b* plane and greater than 350 Å along *z*. The results of this analysis are very similar to those of Joswig and Fuess (1990); lattice parameters in the studies are within 1% and calculated atomic coordinates (even for atoms reported without standard deviations in Table 2) are within 2%.

Table 2. Atomic occupancies, positional and thermal parameters, and selected average bond lengths.

Site	Atom	Fraction	x[1]	y[1]	z[1]	U_{iso}	Average M-O[2]
M(1a)	Mg	0.538	0	0	0	0.002	2.065
M(1b)	Fe	0.462	0	0	0	0.002	
M(2a)	Mg	0.496	0.0141 (9)	0.3348 (6)	0.0027 (3)	0.002	2.104
M(2b)	Fe	0.504	0.0141 (9)	0.3348 (6)	0.0027 (3)	0.002	
M(3a)	Mg	0.494	0.0032 (3)	0.1683 (5)	0.5004 (3)	0.002	2.055
M(3b)	Fe	0.506	0.0032 (3)	0.1683 (5)	0.5004 (3)	0.002	
M(4)	Al	1.362	0	0.5	0.5	0.003	2.030
T(1)	Si,Al	1.0	0.24	0.170	0.1941 (3)	0.001	1.657
T(2)	Si,Al	1.0	0.73	0.998	0.1945 (3)	0.001	1.668
O(1)	O	1.0	0.191 (1)	0.1635 (6)	0.0789 (4)	0.011	
O(2)	O	1.0	0.705 (6)	0.998 (2)	0.0756 (4)	0.011	
O(3)	O	1.0	0.231	0.336	0.2374 (9)	0.011	
O(4)	O	1.0	0.528	0.118	0.2302 (9)	0.011	
O(5)	OH	1.0	0.018	0.061	0.2306 (10)	0.011	
O(6)	OH	1.0	0.689 (1)	0.3312 (6)	0.0742 (4)	0.011	
O(7)	OH	1.0	0.144 (1)	0.9990 (7)	0.4300 (5)	0.011	
O(8)	OH	1.0	0.143 (1)	0.3361 (7)	0.4286 (5)	0.011	
O(9)	OH	1.0	0.643 (1)	0.1627 (7)	0.4311 (5)	0.011	

[1] Values in parentheses are standard deviations of refined coordinate in the last decimal place. For all atoms except the octahedral cations and anions, only the *z* values are refined coordinates; *x* and *y* coordinates reported without standard deviations (except for M(1) and M(4) which are on special positions) are the results of the refinement but do not represent actual atomic positions due to the presence of structural disorder. These values are included for discussion purposes only (see text).
[2] Average metal-anion bond distances.

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In addition, the average observed cation-oxygen bond lengths are very similar.

Semi-random stacking is very common in chlorites but is often difficult to detect because of the weakness of the $k \neq 3n$ reflections in powder patterns. Two portions of the experimental pattern are reproduced in Figure 1: 19–24° 2θ (1a) and 33–40° 2θ (1b). The indices of the reflections contributing to each peak are labeled. Differences between the two figures are striking. Whereas in Figure 1a only one peak is present (020, 110, $\bar{1}10$) and six peaks are calculated, six peaks are present in Figure 1b and six are calculated. The diffraction phenomenon in Figure 1a is that of a two-dimensional diffraction band (02;11) involving reflections for which $k \neq 3n$, indicating semi-random stacking of the chlorite layers (Bailey and Brown, 1962). In Figure 1b no band is evident because all of the peaks have indices in which $k = 3n$. Streaking of the $k \neq 3n$ rows in selected area electron diffraction patterns was also reported by Walker *et al.* (1990), further evidence of semi-random stacking.

DISCUSSION

The values reported in Table 2, both real and those affected by disorder, agree well with those of Joswig and Fuess (1990); therefore, the results appear reasonable for a chlorite of this composition. However, one must consider the limitations in the data when attempting to draw conclusions from the results.

Cell parameters obtained in this analysis are of higher precision than those of Joswig and Fuess (1990). Such high-precision cell parameters, characteristic of Rietveld refinements, were possible because data to 120° 2θ were included and because the cell parameters were derived from a calculated pattern which was fit to the observed pattern on a point by point basis, instead of from the locations of discrete reflections.

Although the results of this study appear to be reasonable for a chlorite of this composition, the presence of semi-random stacking limits the amount of information present in the diffraction data. Therefore, some of the atom positions and bond lengths have not been uniquely determined (see footnote 1 to Table 2). The ultimate result of semi-random stacking is that the diffraction data only contain information on the composition of planes of atoms repeating along z, as well as information on atoms within those planes which repeat at intervals of $\pm b/3$; three-dimensional aspects of all other atomic positions are disordered by the nature of the stacking repeat and are not refinable. The only atoms which repeat at $\pm b/3$ in the chlorite structure are the octahedral cations and anions (Bailey, 1991), and these are the only atoms in Table 2 for which standard deviations are given for the x, y, and z coordinates; all other atoms do not repeat at $\pm b/3$ and, therefore, only the z coordinates are refinable. The excess of atoms reported in the M(4) octahedral position

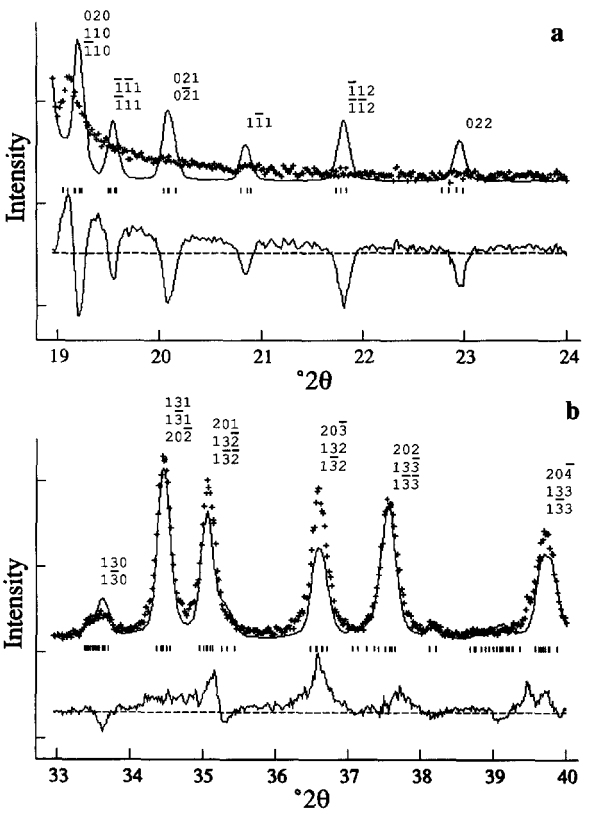


Figure 1. Selected portions of the diffraction pattern of the sample showing experimental data (crosses), calculated diffraction profile (solid curve through the crosses), difference curve between experimental and calculated values (solid curve at the bottom of each figure), and the calculated positions of α_1 and α_2 reflections (small bars above difference curve). (a) Diffraction pattern between 19 and 24° 2θ; (b) diffraction pattern between 33 and 40° 2θ (CuKα radiation).

is probably due to the results being averages of the M(3) and M(4) sites which are indistinguishable because of the semi-random stacking, and because M(4) was constrained to be all Al.

Given the limitations of the diffraction data, it is noteworthy that a reasonable result was obtained. It is possible that the use of soft constraints in this refinement forced the model into a reasonable fit despite the limitations of the data. The small contribution of the soft constraints to the minimization function, however, indicates that the soft constraints did little to affect the results. Closer inspection of the results of Joswig and Fuess (1990; Table 1), however, indicates that all atoms except O(5) repeat at intervals of approximately $\pm b/3$, suggesting that the good fit may be related to the fact that most of the information about the positions of these atoms is contained in the relatively strong $k = 3n$ reflections which are in the experimental pattern.

The result reported here illustrates the dangers of applying techniques such as Rietveld refinement to disordered minerals without being cognizant of the in-

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formation which is and is not present; it is possible to obtain results which appear reasonable when, in fact, the results may not be supported by the data. This possibility is especially important to consider when attempting to refine aspects of the structures of highly disordered minerals, such as those with turbostratic stacking, where the diffraction data contain only one-dimensional information analogous to a projection of all atoms onto *z*.

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REFERENCES

Adams, J. M. (1983) Hydrogen atom positions in kaolinite by neutron profile refinement: *Clays & Clay Minerals* **31,** 352–356.

Adams, J. M. and Hewat, A. W. (1982) Hydrogen atom positions in dickite: *Clays & Clay Minerals* **29,** 316–356.

Bailey, S. W. (1984) Structures of layer silicates: in *Crystal Structures of Clay Minerals and their X-ray Identification,* G. W. Brindley and G. Brown, eds., Mineralogical Society of London, 1–123.

Bailey, S. W. (1991) Practical notes concerning the indexing of X-ray powder diffraction patterns of clay minerals: *Clays & Clay Minerals* **39,** 184–190.

Bailey, S. W. and Brown, B. E. (1962) Chlorite polytypism. I. Regular and semi-random one-layer structures: *Amer. Mineral.* **47,** 819–850.

Bish, D. L. (1991) Rietveld refinement of the dickite structure at 12K: *Programs and Abstracts,* 28th Annual Meeting, The Clay Minerals Society, Houston, Texas, 15.

Bish, D. L. and Post, J. E. (1987) Refinement of the sepiolite structure and location of tunnel water molecules using the Rietveld method: *Programs and Abstracts,* 24th Annual Meeting, The Clay Minerals Society, Socorro, New Mexico, 33.

Bish, D. L. and Von Dreele, R. B. (1989) Rietveld refinement of non-hydrogen atomic positions in kaolinite: *Clays & Clay Minerals* **37,** 289–296.

Bish, D. L. and Von Dreele, R. B. (1990) The crystal structure of kaolinite including hydrogen atoms: *Programs and Abstracts,* 27th Annual Meeting, The Clay Minerals Society, Columbia, Missouri, 25.

Joswig, W. and Fuess, H. (1990) Refinement of a one-layer triclinic chlorite: *Clays & Clay Minerals* **38,** 216–218.

Larson, A. C. and Von Dreele, R. B. (1990) *GSAS Generalized Structure Analysis System.* LAUR 86-748. Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

Martin, R. T., Bailey, S. W., Eberl, D. D., Fanning, D. S., Guggenheim, S., Kodama, H., Pevear, D. R., Srodon, J., and Wicks, F. J. (1991) Report of the Clay Minerals Society Nomenclature Committee: Revised classification of clay minerals: *Clays & Clay Minerals* **39,** 333–335.

Post, J. E. and Bish, D. L. (1989) Rietveld refinement of crystal structures using powder X-ray diffraction data: in *Modern Powder Diffraction,* D. L. Bish and J. E. Post, eds., *Reviews in Mineralogy* **20,** Mineralogical Society of America, Washington, D.C., 277–308.

Rakovan, J. and Guggenheim, S. (1991) Rietveld refinement of a II*b* clinochlore: *Programs and Abstracts,* 28th Annual Meeting, The Clay Minerals Society, Houston, Texas, 132.

Rietveld, H. M. (1967) Line profiles of neutron powder-diffraction peaks for structure refinement: *Acta Cryst.* **22,** 151–152.

Rietveld, H. M. (1969) A profile refinement method for nuclear and magnetic structures: *J. Appl. Crystallog.* **2,** 65–71.

Suitch, P. R. and Young, R. A. (1983) Atom positions in highly ordered kaolinite: *Clays & Clay Minerals* **31,** 357–366.

Toraya, H., Iwai, S., and Marumo, F. (1980) The structural investigation of a kaolinite mineral by X-ray powder pattern-fitting: *Mineral. J. (Japan)* **10,** 168–180.

Young, R. A and Hewat, A. W. (1988) Verification of the triclinic crystal structure of kaolinite: *Clays and Clay Minerals* **36,** 225–232.

Walker, J. R. and Bish, D. L. (1989) Rietveld refinement of II*b* chlorite: *Programs and Abstracts,* 26th Annual Meeting, The Clay Minerals Society, Sacramento, California, 73.

Walker, J. R., Bish, D. L., and Veblen, D. R. (1990) Comparison of coherent diffracting domain size as estimated from powder X-ray diffraction data and as measured in TEM images: *Programs and Abstracts,* 27th Annual Meeting, The Clay Minerals Society, Columbia, Missouri, 125.

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