

The Monte Carlo method for finding missing atoms in solving crystal structures from powder diffraction data without applying a rigid-body approximation

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The Monte Carlo method is applied to finding missing atoms in solving inorganic crystal structures without applying a rigid-body approximation. Whole powder patterns of α -SiO₂ and Mg₂SiO₄ were used for testing a procedure. Four atoms among the six in the asymmetric unit of Mg₂SiO₄ could be found in the present analysis. The use of well-refined profile parameters enhanced the frequency of correct structure configurations in the Monte Carlo search. Utilizing structural information available for constructing a trial configuration is also considered to be important for efficiently searching the structure solution. A procedure for assignment of equivalent positions to respective atoms is presented. The method can be used as a powerful tool for finding missing atoms in a partially solved structure. A histogram of weighted reliability index in Monte Carlo calculations is very informative for evaluating the performance of the method. © 2001 International Centre for Diffraction Data. [DOI: 10.1154/1.1351155]

I. INTRODUCTION

Ab initio structure determination from powder diffraction data is currently of great interest in crystallography and materials science. A number of crystal structures have been solved, and direct methods, modified for treating powder diffraction data, have been used as a major tool for phasing (Giacovazzo, 1996; Altomare *et al.*, 1994). However, solving crystal structures using diffraction data of a reciprocal lattice compressed into one dimension is not straightforward, and the structure solution is often incomplete and accompanied by missing atoms and/or ghosts. Obtaining a complete structure solution becomes more difficult as the number of severely overlapping reflections increases in a powder diffraction pattern.

So-called direct-space methods have been proposed as new approaches for structure solution, and the Monte Carlo method, the simulated annealing method, and the genetic algorithm are included in this category [see, for example, a review by Harris and Tremayne (1996)]. These methods directly fit a calculated diffraction pattern to the observed pattern, and thus they do not require the pattern decomposition process for extracting integrated intensities. To solve structures having a large number of unknown parameters is, however, practically impossible without utilizing data other than those of diffraction intensities (Putz *et al.*, 1999), and a rigid-body approximation is introduced to reduce the number of variables. The rigid-body (or flexible rigid-body) approximation can be effectively used when a crystal contains rigid molecules, and these methods have been successful in solving organic crystal structures (Tremayne *et al.*, 1999; Schmidt and Dinnebier, 1999). It is, however, not simple to introduce the rigid-body approximation into modeling inorganic crystals.

In the present study, the Monte Carlo method is applied to finding missing atoms when solving inorganic crystal

structures without applying the rigid-body approximation. Factors that influence the frequency of correct structure configurations are analyzed. A problem of choosing equivalent positions for respective atoms is discussed.

II. PROCEDURE

A. Monte Carlo calculation

The Monte Carlo method, used in the present study, follows the procedure described by Harris *et al.* (1994), using the Metropolis importance sampling algorithm (Metropolis *et al.*, 1953). The objective function is the weighted reliability index R_{wp} given by

$$R_{wp} = 100 \times \left(\frac{\sum w_i (Y_{oi} - Y_{ci})^2}{\sum w_i Y_{oi}^2} \right)^{1/2},$$

where Y_{oi} and Y_{ci} are the observed and calculated profile intensities at the i th step, respectively, and w_i is the weight given by $w_i = Y_{oi}^{-1}$.

A Monte Carlo calculation is started from an initial configuration $\{x_j^0\}$ ($j = 1$ to M_p , and M_p is the number of variables). In the n th Monte Carlo move, a trial configuration is generated by $x_j^n = x_j^{n-1} + d_{\max} \times r_j$, where r_j ($-1 \leq r_j \leq 1$) is a random number and d_{\max} is the maximum displacement of x_j^n . An overall scale factor S for adjusting the Y_{ci} to the Y_{oi} is least-squares fitted, and the objective function is evaluated for $\{x_j^n\}$. To decide whether the n th configuration should be accepted or rejected follows the Metropolis importance sampling algorithm (Harris *et al.*, 1994). The $n+1$ th Monte Carlo move is started from the $\{x_j^n\}$ or the $\{x_j^{n-1}\}$ according to whether the $\{x_j^n\}$ is accepted or rejected after the n th Monte Carlo move.

In the present procedure, the x_j^n 's are fractional coordinates of atoms to be found, and the configuration $\{x_j^n\}$ represents a trial structural model. No constraint was applied to relative positions of x_j^n 's.

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TABLE I. Experimental conditions for intensity data collection of α -SiO₂ and Mg₂SiO₄ samples.

	α -SiO ₂	Mg ₂ SiO ₄	
Source	CuK α	CuK α	Synchrotron radiation
Wavelength (Å)	1.540 562 1.544 390	1.540 562 1.544 390	1.210
Diffractometer	Rigaku RAD-IIA	Rigaku RAD-IIA	MDS ^a
Monochromator	Graphite	Graphite	Si(111)
Analyzer			Ge(111)
Divergence slit (°)	1	1	
Receiving slit (mm)	0.3	0.3	
Specimen	Flat	Flat	Flat
Scan mode	θ - 2θ step scan	θ - 2θ step scan	2θ step scan
Scan range ($2\theta^\circ$)	15–145	15–145	7–129.9
Step interval ($2\theta^\circ$)	0.02	0.02	0.005
Counting time (s)	6	12	1

^aMDS: Synchrotron radiation powder diffractometer with multiple-detector system.

B. Criterion of structure solution

In testing the procedure, we need to decide whether the configuration $\{x_j^n\}$ is a correct structure solution or not. The symbol $\{x_j^{\text{conv}}\}$ represents a set of structural parameters at convergence, which may be obtained by Rietveld refinement (Rietveld, 1969) after deriving the correct structural model, and Δd_k represents the distance between the k th atom at $\{x_j^n\}$ and the corresponding atom at $\{x_j^{\text{conv}}\}$ in Ångströms. The symbol Δ represents an average value of Δd_k ($k=1$ to M_a), and M_a is the number of atoms to be found).

In a recent study on Rietveld refinement of Mg₂SiO₄ using laboratory X-ray data, Yamamoto (2000) demonstrated that positional parameters of atoms could be converged to final parameter values in the least-squares fitting when $\Delta < 0.25$ – 0.3 Å. Therefore, if Δ , calculated for $\{x_j^n\}$, is less than a preset value, for example 0.25 Å, then the configuration $\{x_j^n\}$ is counted as one structure solution.

C. Computer program

The computer program MCS (Version 1.00) for Monte Carlo calculation was written using FORTRAN 77. Most subroutines used for calculating profile intensities in PFLS (Version 5.00) for Rietveld refinement (Toraya, 1998) were embedded into MCS to calculate the profile intensities for the trial configuration $\{x_j^n\}$. Input data are (1) observed profile intensities, (2) unit-cell and profile parameters, (3) symmetry operations for an assigned space group, (4) atomic scattering factor tables, and (5) atomic parameters for initial configuration. Calculation of structure amplitude $|F(hkl)|$ is carried out only for the asymmetric unit in the unit cell. Any atom in the structure can be chosen as a missing atom.

III. EXPERIMENTAL

A. Test samples

Samples of α -SiO₂ and Mg₂SiO₄ powders were used for obtaining test diffraction patterns: preparation of these samples is described by Toraya (1998). α -SiO₂ belongs to the trigonal system (space group: $P3_221$) and it has a simple structure consisting of two atoms in the asymmetric unit.

Mg₂SiO₄, a natural product of which is known as “forsterite,” has the olivine structure. It belongs to the orthorhombic system ($Pbnm$), and the structure consists of six atoms in the asymmetric unit. Crystal data and atomic parameters of these materials will be found elsewhere (Kihara 1990; Lager *et al.*, 1981).

B. Intensity data collection

The powdered samples were packed separately into flat glass specimen holders. Profile intensities of α -SiO₂ and Mg₂SiO₄ were measured with Cu K α radiation and a focusing powder diffractometer (Rigaku, RAD II-A). Profile intensities of Mg₂SiO₄ were also measured with synchrotron radiation (wavelength = 1.21 Å) and a powder diffractometer with a multiple-detector system (MDS) (Toraya *et al.*, 1996) at the beam line BL-4B₂ at the Photon Factory in Tsukuba, Japan. These intensity data sets are designated LAB and SR, respectively, according to their X-ray sources. Experimental details are given in Table I.

IV. DATA ANALYSIS

A. Preparation of profile parameters

In each Monte Carlo move, only the overall scale factor is refined, and the other profile parameters such as those of the unit-cell, U , V and W in the Caglioti *et al.* formula (1958), etc., are fixed. Therefore, values of profile parameters before starting the Monte Carlo calculation should be close to those, which would be obtained by Rietveld refinement at the final stage of analysis. In the present study, the profile parameters were obtained by the computer program WPPF (Version 3.00) (Toraya, 1986) for the whole-powder-pattern decomposition method based on the Pawley algorithm (Pawley, 1981). Refined parameters were those in the fifth-degree polynomial background function, the 2θ -zero correction, the unit-cell parameters, the U , V and W parameters, profile width asymmetry, and the η parameters in the low- and high-angle sides of the split-type pseudo-Voigt function.

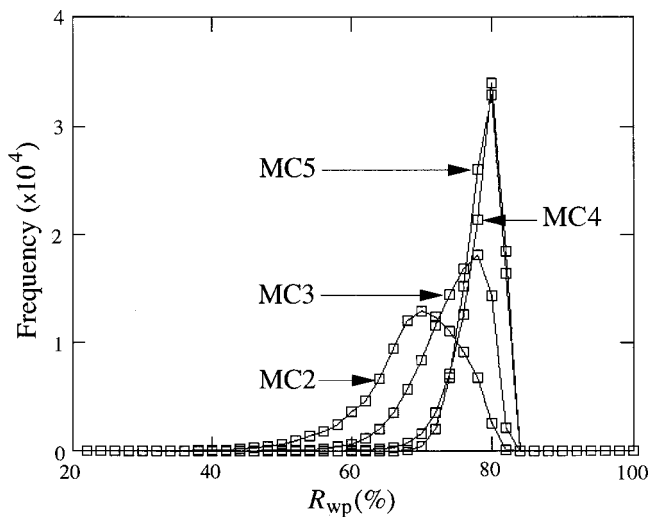


Figure 1. Histograms of R_{wp} values for Mg_2SiO_4 . Four distribution curves were obtained by varying the number of missing atoms from 2 to 5 (MC2–MC5).

B. Monte Carlo calculation

In the case of α - SiO_2 , the Si (the number of equivalent positions and Wyckoff notation: $3b$) and O ($6c$) atoms were all treated as missing atoms and searched by MCS. In the case of Mg_2SiO_4 , O2 ($4c$) and O3 ($8d$) atoms were first treated as missing atoms. Then, the number of missing atoms was increased from two to five by adding, one by one, O1 ($4c$), Si ($4c$), and Mg2 ($4c$). These Monte Carlo calculations are designated MC2, MC3, MC4 and MC5, according to the number of missing atoms.

In starting the Monte Carlo calculation, we set $x_j^0 = 0$ for the missing atoms, and the positional parameters of the remaining atoms and the displacement parameters of all atoms were fixed at the literature values (Lager *et al.*, 1981). In Mg_2SiO_4 , two sets of profile parameters, designated PA and PB, were used: PA was obtained by refining the profile parameters using WPPF, and PB was obtained by Rietveld refinement using the final atomic parameters.

The 2θ -ranges of LAB used by MCS were 15° – 145° for both α - SiO_2 and Mg_2SiO_4 . The 2θ -range of SR was set to 7° – 97° so as to give the same $\sin \theta/\lambda$ range (0.619 \AA^{-1}) as that of LAB. In each Monte Carlo calculation, 100 000 Monte Carlo moves were carried out. The d_{\max} was set at 1.0 \AA , and a threshold value for controlling the rate of acceptance was set so as to give an overall rate of acceptance at $\sim 40\%$. Atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography*, Vol. IV (1974).

V. RESULTS AND DISCUSSION

A. Maximum numbers of atoms found in Mg_2SiO_4

A histogram of R_{wp} values in a Monte Carlo calculation is much more informative than a plot of the R_{wp} values for individual Monte Carlo moves against Monte Carlo move numbers. Figure 1 shows histograms of R_{wp} for MC2–MC5 using LAB and PA. Tables II and III give the numbers of structure solutions and minimum and maximum R_{wp} values, respectively, for corresponding Δ ranges.

TABLE II. Number of structure solutions for Mg_2SiO_4 in various Δ ranges.

		Δ (Å)	MC2	MC3	MC4	MC5
LAB	PA	0–0.05	0	0	0	0
		0.05–0.1	3	0	0	0
		0.1–0.15	29	2	0	0
		0.15–0.2	96	6	0	0
		0.2–0.25	230	15	1	0
		0.25–0.3	426	29	0	0
	Total		784	52	1	0
	PB	0–0.05	0	0	0	0
		0.05–0.1	4	0	0	0
		0.1–0.15	28	7	0	0
		0.15–0.2	68	20	1	0
		0.2–0.25	181	110	0	0
		0.25–0.3	348	222	3	0
	Total		629	359	4	0
SR	PB	0–0.05	0	0	0	0
		0.05–0.1	9	0	0	0
		0.1–0.15	80	10	0	0
		0.15–0.2	213	40	0	0
		0.2–0.25	563	157	0	0
		0.25–0.3	1020	338	0	0
	Total		1885	545	0	0

The increase of the number of missing atoms induces (1) an increase of the minimum R_{wp} value; (2) a shift of the center of gravity of the distribution curve from $R_{wp} \sim 70\%$ to 80% ; (3) a sharpening of the shape of the distribution curve; (4) an increase of the maximum frequency; and (5) a decrease in the number of structure solutions. Upper limits of R_{wp} values for the configurations $\{x_j^n\}$, which satisfy the criterion of $\Delta < 0.25 \text{ \AA}$, are in the range of 45% – 58% in MC2 and MC3. In MC4, just one structure solution could be found in each case of LAB, and an R_{wp} value for the structure solution is very close to the upper limit of R_{wp} . Therefore, to find four missing atoms among the six atoms in Mg_2SiO_4 is considered to be a very critical test of the present Monte Carlo calculations.

B. Factors influencing the number of structure solutions

1. The total number of Monte Carlo moves

Although it is not efficient, increasing the total number of Monte Carlo moves will proportionately increase the number of structure solutions. In the present calculation, ten structure solutions would be obtained for MC4 if we executed one million Monte Carlo moves. Recently, Miura and Kikuchi (1999) reported that five atoms, which were treated as missing in Mg_2SiO_4 , could be found after 30 million Monte Carlo moves in their two-step search.

2. Well-refined profile parameters and high-resolution data

In Table III, minimum R_{wp} values for PB in MC2 and MC3 of LAB are lower by 8% – 13% than those for PA, and the number of structure solutions for PB is three to eight

TABLE III. R_{wp} values for Mg_2SiO_4 in respective Δ ranges.

		Δ (Å)	MC2	MC3	MC4	MC5
LAB	PA	0–0.05	—	—	—	—
		0.05–0.1	35.6–37.7	—	—	—
		0.1–0.15	35.5–41.0	36.7–37.8	—	—
		0.15–0.2	36.8–46.8	39.4–46.9	—	—
		0.2–0.25	37.9–53.0	41.4–50.4	53.3	—
		0.25–0.3	40.2–55.8	44.3–55.7	—	—
	Full range		35.5–80.5	36.7–81.3	49.4–81.5	62.3–81.5
	PB	0–0.05	—	—	—	—
		0.05–0.1	22.2–23.7	—	—	—
		0.1–0.15	22.2–30.9	24.2–50.5	—	—
		0.15–0.2	24.6–36.9	31.3–46.5	52.0	—
		0.2–0.25	26.6–45.0	29.8–57.0	—	—
		0.25–0.3	29.6–51.3	34.5–57.5	48.8–54.7	—
	Full range		22.2–79.9	24.2–81.2	48.8–81.5	51.8–81.5
SR	PB	0–0.05	—	—	—	—
		0.05–0.1	16.7–23.6	—	—	—
		0.1–0.15	18.1–28.2	21.2–32.5	—	—
		0.15–0.2	20.6–38.6	25.3–40.1	—	—
		0.2–0.25	25.3–49.0	29.2–50.3	—	—
		0.25–0.3	29.8–54.7	32.0–57.8	—	—
	Full range		16.7–77.6	21.2–78.0	44.4–78.2	61.2–78.2

times greater than those for PA in MC3. Using a set of well-refined profile parameters is effective at increasing the number of structure solutions. High-resolution diffraction data of SR, of which the full-width at half-maximum is about a quarter of that for LAB in the low-angle region, is also effective at increasing the number of structure solutions.

3. Shift of the center of gravity of the distribution curve

If we set an upper limit on the R_{wp} value, for example 50%, below which the structure solutions are obtained, the number of solutions is equal to the area under the tail of the distribution curve in the range $R_{wp} < 50\%$. Therefore, the number of structure solutions can be increased if the center of gravity of the distribution curve is shifted towards the low R_{wp} . In Figure 1, the distribution curve for MC4 is similar to that for MC5 with no structure solution, and most of trial configurations under these two curves in the R_{wp} range of 70%–82% may have a completely or nearly completely random structure. In the case of MC3, three atoms among the six atoms were moved at random while the remaining three atoms, which were fixed at the correct positions, would contribute to the calculated intensities for lowering the R_{wp} value. The center of gravity of the distribution curve is, therefore, shifted towards the low R_{wp} side. In the case of MC2, more atoms at the correct positions than those in the case of MC3 contribute to a further shift of the center of gravity. These observations indicate that inclusion of structural information, even of a partially solved structure, into the intensity calculation is effective to increase the number of structure solutions. They are also in accordance with successful applications of the rigid-body approximation in solving organic crystal structures.

C. Assignment of equivalent positions

It is usually unnecessary to assign equivalent positions to respective atoms when solving organic crystal structures using a rigid-body approximation. As will be shown in the following two cases, however, the assignment of equivalent positions is routinely required in solving inorganic structures without applying a rigid-body approximation. Numbers of equivalent positions, Wyckoff notations and point symmetry for the space groups $P3_221$ (α - SiO_2) and $Pbnm$ (Mg_2SiO_4), used in the following discussion, will be found in *International Tables for Crystallography*, Vol. A (1983).

1. α - SiO_2

Total numbers of Si and O atoms in a unit cell can be easily derived from the knowledge of the chemical formula (SiO_2) and the number of chemical formula units ($Z=3$). There are two possible ways of distributing three Si atoms at either of the two special equivalent positions a or b . On the other hand, six oxygen atoms can be uniquely distributed at the general equivalent position c . An alternative way of distributing the six oxygen atoms at the two special equivalent positions can be rejected because all Si and oxygen atoms lying on the (100) and (110) planes cannot form SiO_4 tetrahedra. Therefore, only two models A and B are to be considered: (A) Si atoms at the position a + oxygen atoms at c and (B) Si atoms at b + oxygen atoms at c . These two models are, however, identical: one model can be derived from the other by exchanging the a -axis with the b -axis and a subsequent translation of the structure by $1/2$ along the c -axis.

MCS was applied to LAB for finding four positional parameters (x coordinate of the Si atom and x , y , z coordinates of the oxygen atom) by using the two models A and B.

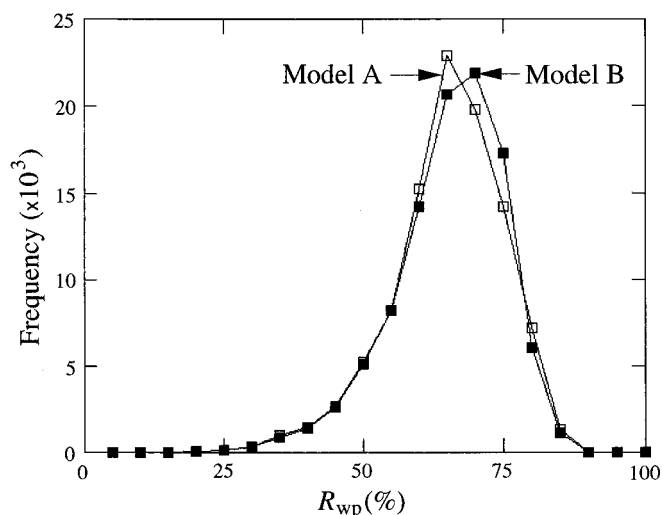


Figure 2. Histograms of R_{wp} values for α - SiO_2 . Two distribution curves were obtained by using models A and B.

Figure 2 shows histograms of R_{wp} . As expected, the two distribution curves have shapes similar to each other, indicating that structure solutions for the two models were obtained at a nearly equal probability.

2. Mg_2SiO_4

The total numbers of Mg, Si and oxygen atoms are 8, 4 and 16, respectively, in the unit cell of Mg_2SiO_4 . Since an SiO_4 tetrahedron does not have a center of symmetry, the Si atoms can be uniquely assigned to the special equivalent position c . Possibilities of distributing the eight Mg atoms at either a general equivalent position d or two special equivalent positions $a+b$ can be excluded, because the short a - and c -axis lengths result in too short Mg–Mg distances. Moreover, it is hard to consider a model in which all Si and Mg atoms are on the planes at $z = \frac{1}{4}$ and $\frac{3}{4}$, so the possibility of distributing the Mg atoms at two special equivalent positions c can be excluded. The remaining possible ways are to distribute Mg atoms at two special equivalent positions in either a combination of $a+c$ or a combination of $b+c$. These two ways are, however, also identical to each other: one coincides with the other when the origin of the unit cell is shifted by $(\frac{1}{2}, 0, 0)$. Therefore, the Mg atoms are uniquely distributed at special equivalent positions a and c .

Regarding the distribution of oxygen atoms, the position a is occupied by Mg atoms. The distribution of oxygen atoms at position b will result in a bond length of $\sim 2.38 \text{ \AA}$ for Mg–O, and this bond length is too long compared to the literature value of $\sim 2.0 \text{ \AA}$. Therefore, the following two models C and D are possible for distributing the sixteen oxygen atoms: model C, the oxygen atoms at $d+d$, and model D, the oxygen atoms at $d+c+c$. A third model, distributing all oxygen atoms at $c+c+c+c$, was rejected because this model distributes all oxygen atoms on the planes at $z = \frac{1}{4}$ and $\frac{3}{4}$.

Results obtained by assuming model D are described in Sects. V A and B. Monte Carlo calculations using model C for finding three oxygen atoms O1 to O3 (MC3) gave minimum R_{wp} factors of 50.9% and 46.1% for LAB using PA and PB, respectively, and model D was found to be the correct model.

In the present analysis, the difference in the R_{wp} factor between models C and D in Monte Carlo calculation was more than 10%. In other cases, however, it will sometimes occur that the difference is too small to distinguish a correct model from wrong ones. Further refinements of the models by the Rietveld method will be able to choose the correct model.

D. Applications to real problems

We have applied the present procedure to solve real problems as described briefly below.

1. Determination of positions of zeolitic Ca and H_2O in tobermorite

Tobermorite, $\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 5\text{H}_2\text{O}$, is one of the cement minerals. Its framework structure $[\text{Ca}_4\text{Si}_6\text{O}_{17} \cdot 2\text{H}_2\text{O}]$ has been analyzed by single crystal methods (Merlino *et al.*, 1999). However, positions of the zeolitic Ca atom and three water molecules in the channel of the framework were unclear. Their positions could be found by the present procedure (Yamazaki and Toraya, 2001).

2. Structure determination of 2,2-dihydroxymethylbutanoic acid ($\text{C}_6\text{H}_{12}\text{O}_4$)

The crystal structure of 2,2-dihydroxymethylbutanoic acid ($\text{C}_6\text{H}_{12}\text{O}_4$) in monoclinic form was determined *ab initio* from synchrotron radiation powder diffraction data. Two oxygen and five carbon atoms among the ten nonhydrogen atoms were first derived by the direct method. The missing two oxygen and one carbon atoms were found by the present procedure without applying constraints to their relative positions (Tanahashi *et al.*, 2001).

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