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VARIATION IN DIFFRACTOMETER PROFILES OF POWDER WITH A GAUSSIAN DISPERSION OF THE CHEMICAL COMPOSITION

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ABSTRACT

The effect of the dispersion of the chemical composition of the grains on the peak, centroid, and median of a diffractometer profile, as well as on its shape, is calculated. For this purpose, the reflection (130) of olivines ($2\theta \approx 32°$) was chosen. It was observed that as the dispersion of the chemical composition is increased, so the peak of the profile tends to move towards value of 2θ higher than the theoretical value. The median, on the other hand, tends to move towards values of 2θ lower than the theoretical value while the centroid remains pratically unchanged. The profile widens and becomes symmetric.

INTRODUCTION

Gottardi (1967) pointed out that, in the rock-forming minerals, the gaussian dispersion of the chemical composition of the grains can cause a shift of the lines of a powder pattern and therefore a false valuation of the chemical composition of the mineral itself.

The purpose of this work is to establish to what extent the gaussian dispersion of the chemical composition of the grains of minerals influences the position of the peak of a diffractometer profile, its centroid, and its median, as well as the shape of the profile itself. Here the "peak" is the point of greatest intensity of the profile, the "centroid" is the centre of gravity of the profile and the "median" is the central point at half height.

The results have been obtained bearing in mind the following three points. The intensity of a reflection varies with the chemical composition of the reflecting crystal, since its structure factor varies. Therefore each crystal of a powder reflects with an intensity generally different from that of the other crystals, and, as a result, it "weighs" in a different way on the resulting diffractometer profile. The absorption coefficient μ of the X-ray beam also depends on the chemical composition of the crossed grain. Therefore the reflected intensity is a function not only of the length of the X-ray path in the substance, but also of the chemical composition of the reflecting grain and of the other crossed grains. The spectrum of the incident X-ray beam using a suitable filter (without a monochromator) is not strictly monochromatic, nor is it symmetrical with regard to the wavelength λ of the maximum integrated intensity for α_1 and α_2. Now, as every grain reflects the X rays with a value 2θ of the peak which is a function of its chemical composition, the shape of the resulting profile will be equal to that one of a single grain only if all reflecting grains have strictly the same chemical composition.

In order to estimate quantitatively the effects mentioned, the reflection (130) of olivines was chosen. This choice has several advantages for our purposes. First, olivines have only two chemical variables, (Mg and Fe); moreover, both the absorption coefficient μ and the structure factor F vary greatly from forsterite to fayalite. Second, the reflection (130) is among the most intense, and the value of the reflection angle 2θ, about 32°, is high enough to show the asymmetry of the profile but not high enough to radically uncouple the radiations α_1 and α_2.

DESCRIPTION OF COMPUTING METHOD

The following method was used: First the experimental diffractometric profile of the line (130) of the pure synthetic forsterite without Fe radiation was measured with CuKα. The incident X-ray beam was filtered with a Ni filter with pulse-height discrimination, because these are the conditions frequently used in X-ray powder diffractometry. Henceforth this profile will simply be called "theoretical profile." It is assumed that the shape of this profile does not vary in the interval $\Delta 2\theta \approx 44'$ corresponding to the difference between the reflection angle $2\theta_1$ of forsterite and the reflection angle $2\theta_2$ of fayalite. Moreover, it was assumed that the dispersion of the chemical composition of the grains was gaussian, a hypothesis which seems to be correct at least for average chemical compositions not very near extreme terms. The standard deviation of the dispersion of the chemical composition, which henceforth shall be called σ_{cc}, can be set arbitrarily. Let us suppose the grains are spherical, and their dimensions are according to a normal logarithmic gaussian. As will be shown later, the choice of the shape and of the distributions of the grains does not make an appreciable difference to the results.

The calculation is performed as follows:

1) Let us assume that an X-ray beam reaches a very small volume Δv of a grain with random chemical composition, dimension, and distance from the surface of the sample (see Fig. 1). The volume, Δv will reflect the X-ray beam with an intensity proportional to the square of its structure factor F, which is a function of the chemical composition of the grain. Now, since the atomic parameters of forsterite and fayalite differ very slightly (Birle, *et al.*, 1968), we can assume, with a fair degree of confidence, that F varies linearly from 67.5 for forsterite to 141.35 for fayalite.

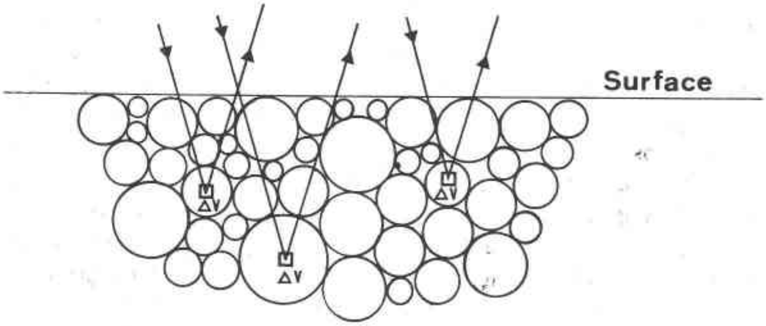

FIG. 1. X-ray reflection from very small volumes, Δv, with random chemical composition and distance from the surface of the sample.

We have therefore:

$$F_{\Delta v} = 73.85x + 67.5,$$

where x is the mole fraction of fayalite molecules in the grains.

2) The X-ray beam will be partially absorbed by both the grain containing the volume Δv and other grains crossed by the beam (also chosen with random dimensions and chemical composition). The transmission coefficient is therefore $T = \exp(-\Sigma_i \mu_i l_i)$ where Σ_i is the sum over all grains crossed by the X-ray beam. Since μ varies linearly from 107.5 for the forsterite to 796.4 for the fayalite, we have

$$\mu_i = 688.9x + 107.5,$$

where x is, as usual, the percent of fayalite molecules in the grains.

3) It is now possible to determine the intensity of radiation reflected by the volume Δv in terms of θ. It will be

$$I_\theta = I_0 \cdot F^2 \cdot \exp\left(- \sum_i \mu_i l_i\right)$$

where I_0 is the intensity of the theoretical profile.

The peak of profile will coincide with the 2θ value that it is obtained from

$$2d_{130} \sin \theta = \lambda_{\alpha_1}$$

where d_{130} is a function of the chemical composition of volume Δv and λ_{α_1} is the wavelength of the α_1 component of the X-ray beam. The value of d_{130} is obtained from the cell dimensions of forsterite and fayalite given by Louisnathan and Smith (1968). Obviously, all the sources of

TABLE 1. VARIATION OF 2θ, IN RESPECT TO THE THEORETICAL VALUE, OF THE PEAK AT DIFFERENT σ_{cc} VALUES, AS THE MOLE PERCENT OF FAYALITE COMPONENT VARIES

Mole percent fayalite	Theoretical value of 2θ ($\sigma_{cc}=0\%$)	$\sigma_{cc}=3\%$	$\sigma_{cc}=5\%$	$\sigma_{cc}=7\%$
		±3″	±3″	±3″
18	32°12′ 9″	32°12′12″	32°12′23″	
26	32° 8′33″	32° 8′36″	32° 8′54″	32° 8′55″
34	32° 4′58″	32° 5′ 0″	32° 5′14″	32° 5′23″
42	32° 1′24″	32° 1′30″	32° 1′44″	32° 1′53″
50	31°57′51″	31°57′54″	31″58′10″	31°58′19″
58	31°54′19″	31°54′23″	31°54′36″	31°54′47″
66	31°50′47″	31°50′48″	31°51′ 4″	31°51′15″
74	31°47′16″	31°47′16″	31°47′33″	31°47′47″
82	31°43′46″	31°43′48″	31°44′ 6″	

error connected with the measure of the angular value of the peak of the "theoretical profile" are without influence on the results.

4) Repeating the steps 1), 2), 3), a number of times, and adding the profiles obtained for the volumes Δv until the required degree of precision is reached, there will be obtained the "calculated" diffractometer profile of the reflection (130) of olivines for a sample in which the value of σ_{cc} has been prefixed.

Following this method a Fortran II program has been written for the IBM 7090 computer.

The "calculated" profiles for nine different ratios Fe/(Mg+Fe) and for three different values of σ_{cc} ($\sigma_{cc}=3\%$, $\sigma_{cc}=5\%$, $\sigma_{cc}=7\%$) have been obtained. In this calculation it is assumed that the mean dimension of grains is 8 μm and that the standard deviation of dimensions is 2.3 μm. These values have been chosen because we consider that they are nearer to the mean dimension and to its standard deviation of crystals of a powder obtained by grinding.

The incident radiation used is CuKα.

The standard error of all calculated 2θ values is $3'' \approx 0.114$ percent of variation of chemical composition of the sample.

DISCUSSION

The conclusions are based on the comparison between the profile of olivine, with various Mg/Fe ratios and equal chemical composition for all grains, and the profiles "calculated" with the same Mg/Fe ratios but with variable chemical composition of the grains.

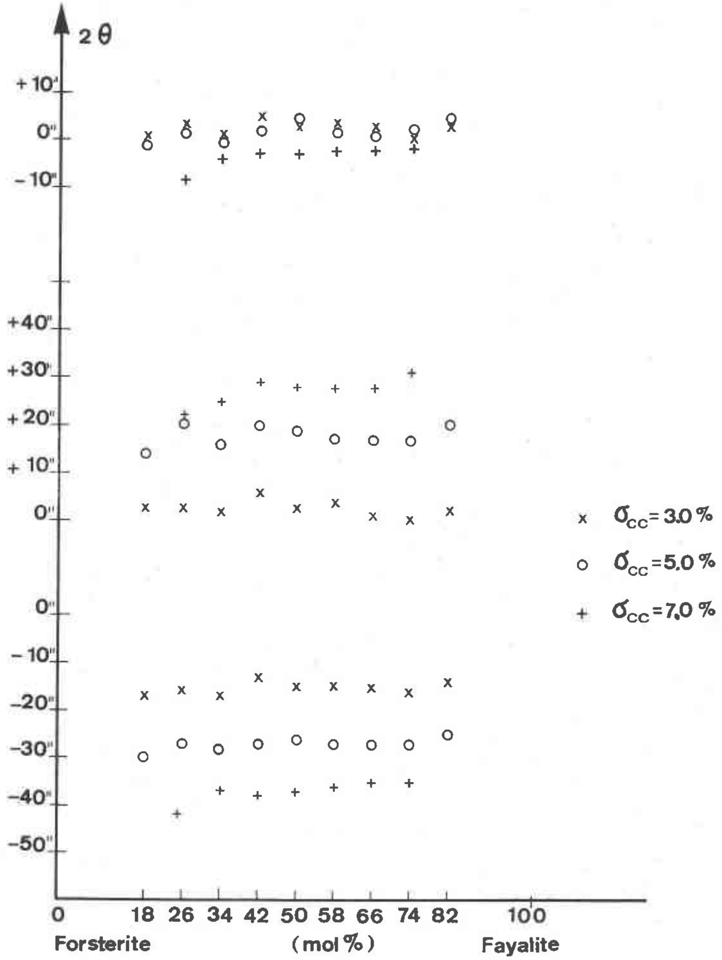

Fig. 2. Variation of 2θ, with respect to the theoretical value, of the centroid of the calculated profile (at the top), of the peak (at the center), and of the median (at the bottom), at different σ_{cc} values, as the percent of fayalite molecules varies.

From this comparison it may be seen that the peak of the "calculated" profile is shifted from the theoretical values of 2θ (see Table 1 and Fig. 2) This shift is practically inconsequential for samples with a fairly low σ_{cc} ($\sigma_{cc} \leq 3\%$), but increases as σ_{cc} increases, to reach appreciable values (about 15″–20″ for σ_{cc} of the order of 5%).

This shift has two fundamental causes.

The first and most important is given by the asymmetry of the theoretical profile due to the presence of CuKα_2 component in the X-ray

TABLE 2. VARIATION OF 2*θ*, WITH RESPECT TO THE THEORETICAL VALUE, OF THE MEDIAN AT DIFFERENT σ_{cc} VALUES, AS THE MOLE PERCENT OF FAYALITE COMPONENT VARIES

Mole percent fayalite	Theoretical value of $2\theta(\sigma_{cc}=0\%)$	$\sigma_{cc}=3\%$	$\sigma_{cc}=5\%$	$\sigma_{cc}=7\%$	2θ value for $\mathrm{CuK}_{\alpha}^{-}$
		±3″	±3″	±3″	
18	32″13′28″	32°13′11″	32°12′58″		32°13′48″
26	32° 9′52″	32° 9′36″	32° 9′25″	32° 9′10″	32°10′12″
34	32° 6′17″	32° 6′ 0″	32° 5′49″	32° 5′40″	32° 6′36″
42	32° 2′43″	32° 2′30″	32° 2′16″	32° 2′ 5″	32° 3′ 2″
50	31°59′10″	31°58′55″	31°58′44″	31°58′33″	31°59′28″
58	31°55′38″	31°55′23″	31°55′11″	31°55′ 2″	31°55′56″
66	31°52′ 6″	31°51′51″	31°51′39″	31°51′31″	31°52′24″
74	31°48′35″	31°48′19″	31°48′ 8″	31°48′ 0″	31°48′52″
82	31°45′ 5″	31°44′51″	31°44′40″		31°45′22″

beam. The asymmetry causes a shift of the peak, proportional to σ_{cc}, towards increasing 2*θ*, thus provoking an over-estimation of Mg content of the sample. This shift does seem independent of the Mg/Fe ratio, for σ_{cc} that are not very high.

The second cause is a consequence of the bigger diffracting power of crystals richer in Fe. These crystals "weigh" more on the calculated profile, giving a shift of the peak towards lower 2*θ*.

The two opposite effects tend to compensate at low values of σ_{cc},

TABLE 3. VARIATION OF 2*θ*, WITH RESPECT TO THE THEORETICAL VALUE, OF THE CENTROID AT DIFFERENT σ_{cc} VALUES, AS THE MOLE PERCENT OF FAYALITE COMPONENT VARIES

Mole percent fayalite	Theoretical value of $2\theta(\sigma_{cc}=0\%)$	$\sigma_{cc}=3\%$	$\sigma_{cc}=5\%$	$\sigma_{cc}=7\%$
		±3″	±3″	±3″
18	32°12′45″	32°12′46″	32°12′44″	
26	32° 9′ 9″	32° 9′12″	32° 9′11″	32° 9′ 1″
34	32° 5′34″	32° 5′35″	32° 5′34″	32° 5′30″
42	32° 2′ 0″	32° 2′ 5″	32° 2′ 2″	32° 1′57″
50	31°58′27″	31°58′30″	31°58′31″	31°58′24″
58	31°54′55″	31°54′58″	31°54′57″	31°54′53″
66	31°51′23″	31°51′26″	31°51′24″	31°51′21″
74	31°47′52″	31°47′53″	31°47′54″	31°47′51″
82	31°44′22″	31°44′25″	31°44′26″	

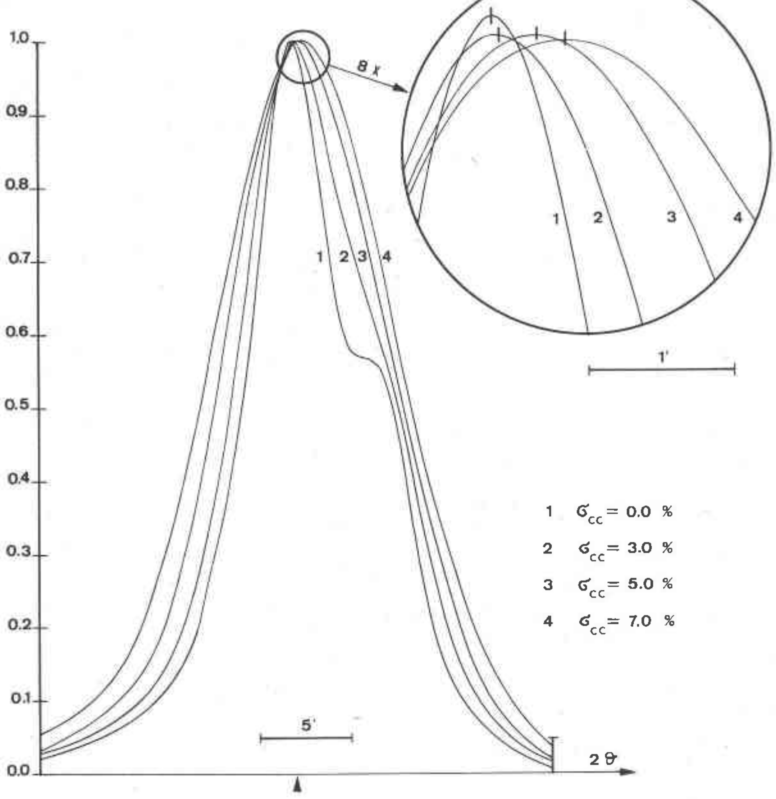

FIG. 3. Variation of the shape of the profile as σ_{cc} varies

but at very high values of the standard error ($\sigma_{cc} \geq 3\%$) the first effect is definitely prevalent ($\Delta 2\theta \approx 18''$ for $\sigma_{cc} = 5\%$).

By the comparison of two profiles, obtained by considering the grains as absorbing and as not absorbing we have seen that the effect of absorption is practically inconsequential both as concerns the shape of the profile and the position of the peak. This means that both the choice of the distribution curve of the dimensions of the grains and the average dimension of grains itself is irrelevant to the results.

If we now examine the 2θ value of the median (Table 2 and Fig. 2), a shift of this value may be seen towards decreasing 2θ, that is proportional to σ_{cc} (about $5''$–$6''$ for every percent of σ_{cc}). This shift is therefore greater than the shift of the peak.

On the other hand, the 2θ value of the centroid of the calculated profile remains practically unchanged (see Table 3 and Fig. 2) as the dispersion of the chemical composition changes; this holds good even for very high σ_{cc} values ($\sigma_{cc} > 5\%$).

We can conclude that an increase in the dispersion of the chemical composition of the grains in a crystalline powder widens the diffractometer profile and removes the asymmetry of the profile itself (see Fig. 3). This makes the difference between the 2θ value of the peak and the 2θ value of the median, which is 1′20″ in samples having a constant chemical composition of the olivine grains, tend to decrease with increasing σ_{cc}. Therefore, the two angular values are displaced towards the centroid which, as stated above, does not perceptibly shift with varying σ_{cc}.

CONCLUSIONS

Assuming that, in the rock-forming minerals, the σ_{cc} value is of the order of 3–5 percent, the shift of the peak for the (130) reflection of olivine is about 10″ towards higher 2θ. Moreover, at least in the field from 15 up to 85 percent of fayalite molecules, it is practically independent of the Mg/Fe ratio. All this leads to an error in the valuation of Mg/Fe ratio, the Mg being overestimated by about 0.5 percent.

The shift of the median is more evident; this shift, independent of the Mg/Fe ratio, is of the order of 20″ for the same standard deviation. As stated above this shift is towards lower 2θ, giving a 1 percent overestimate of the Fe amount.

Finally, it must be pointed out that the shape of the profile undergoes a notable deformation as σ_{cc} increases. This could give a rough valuation of the dispersion of the chemical composition of the sample.

The procedure, in this case applied to the reflection (130) of olivine, can obviously be applied to any isomorphic system characterized by only two variant elements.

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