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X-RAY POWDER DIFFRACTION OF MINERALOGICAL SAMPLES BY X-RAY GOEBEL MIRRORS

V. PERDIKATSIS[1], V. PSYCHARIS[2]

ABSTRACT

Comparative studies are presented on a series of standard and mineralogical samples with X-ray powder diffraction methods, which have been made with a diffractometer possessing the traditional Bragg-Brentano geometry and a second one equipped with a parabolic Goebel mirror (parallel optics). The diffractometers with the Bragg-Brentano geometry are used extensively for the analysis of polycrystalline samples, the main drawback of which is the high expertise needed by the user in order to maintain an instrument in perfect alignment and the careful preparation of the studied samples. Samples measured with a Goebel mirror in parallel optics are free from displacement errors caused by the displacement of the surface or by the surface roughness of the samples. The advantages of the parallel optics are valuable in the case of study of mineralogical samples with the same structure and variable chemical composition (feldspars, amphiboles, pyroxenes, clays etc.) or samples with irregular shapes. Another advantage of Goebel mirrors is the high intensity.

KEY WORDS: X-ray powder diffraction, Goebel mirror, Parallel x-ray beam diffractometer, Quartz, Montmorillonite.

1.INTRODUCTION

X-ray Diffraction is one of the most common tools in determinative Mineralogy. The design of modern X-ray powder Diffractometers is based on Bragg-Brentano parafocusing geometry (Fig.1a. This was the basic geometry of the most popular diffractometers used in geology and material science and contributed to the invention and development of new materials. Because of the importance of x-ray powder diffraction in the study of materials, many changes have been made in the different components that compose a powder diffractometer (x-ray sources, detectors, monochromators etc.) The origin for these changes is new applications or improve-

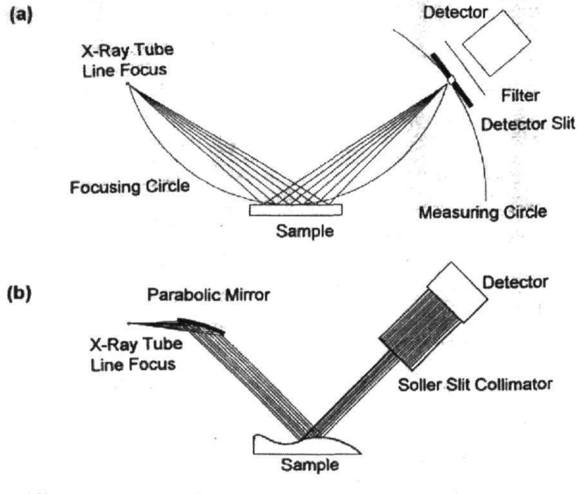

Figure 1. Diffractometers with a) Bragg-Brentano parafocusing geometry and b) with parabolic Goebel mirror (parallel optics).

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[1] Insitute of Geology and Mineral Exploration, Messogion 70, 115 27 Athens
[2] Institute of Materials Science, NCSR « Demokritos», 15310 Ag. Paraskevi Attiki, Greece

ments in order to overcome disadvantages caused by the parafocusing geometry. For this diffractometer one of the main sources of errors in the measured 2Θ angles of Bragg reflections is the displacement of the sample surface from the center of the measuring circle (Figure 1) and the roughness of the sample surface. In recent years X-ray mirrors (Goebel mirrors) have been designed which produce a parallel X-ray beam (Fig.-1b). Using a diffractometer with such a parallel X-ray beam optic (fig.1b), the measurements are free from displacement errors and errors due to surface roughness. One important point concerning these mirrors is that they are very easily adapted to the Bragg-Brentano diffractometer.

Most mineral-groups consist of mixed crystal phases, due to cation replacement. Such mineral groups are the feldspars $(Ca,Na)Si_2(Si,Al)O_8)$, pyroxenes $((Ca,Mg,Fe^{2+},Al)Si(Al)O_3)$, amphiboles $((Ca,Na)_2(Fe^{2+},Mg)_4Al(Si_7(Si,Al)O_{22}(OH,F)_2)$, garnets $((Ca,Mg,Fe^{2+},Mn^{2+})_3(Al,Fe^{3+})_2Si_3O_{12})$, micas $((K,Na)_2(R^{3+})_2(R^{2+})_2(Si_6(Si,Al)_2)O_{20}(OH)_4)$, where R^{3+} is Al or Fe^{3+} and R^{2+} is Mg or Fe^{2+}, clay minerals etc.

In the above minerals the d values of the X-ray patterns depend on the chemical composition. This fact occurs in diffractograms as a shift in 2θ positions, which could also be produced by displacement and surface errors.

It is evident that the parallel beam optic in X-ray powder diffraction, which is free of displacement and surface errors, can offer measurements of high quality in everyday routine mineralogical analysis, especially in minerals with high d values, such as mica and clay minerals.

In this work, an international mica standard of the National Bureau of Standards and a quartz sample are measured and compared with both diffractometer arrangements. To check the sensitivity of the Parallel Beam Instrument to detect chemically substituted elements at specific crystallographic sites, a montmorillonite sample, Na and Ca saturated, with and without glycerol was measured with both techniques.

2.EXPERIMENTAL

Measurements with diffractometers with Bragg-Brentano parafocusing geometry.

The 2Θ angle of a Bragg peak measured with a well-aligned Bragg-Brentano diffractometer, depends mainly on the relative position of the sample surface with respect to the center of the measuring circle of the diffractometer [Figure 1a]. For the measurement of an X-ray powder diffraction diagram special sample holders are used and if the studied samples are prepared with care, these types of errors are usually avoided. In cases of samples of small amount these types of errors do exist, because the powders are positioned in modified holders or are spread on glass surfaces and then positioned in the proper place for measurement. In the case of organic samples (small X-ray absorption) even a well prepared sample could present a displacement error because of its transparency to X-rays. Finally, irregularly shaped samples are impossible to measured with these diffractometers.

A displacement (S) of the sample surface from the center of the diffractometer causes an error $\Delta 2\Theta$ given by the relation (Bish et al.,1989):

$$\Delta 2\theta = 2 \cdot S \cdot \cos \Theta / r$$

Where θ is the diffraction angle and r (205mm) the distance from the X-ray source to the center of the diffractometer (or the radius of the measuring circle). For positive S values the Bragg peaks move to higher angles and for negative to smaller angles. The above relation has been plotted for different values of S as a function of the diffraction angle in Figure 2. In Figure 3 the error in d values is plotted as a function of $\Delta 2\Theta$ error. From fig.-2 it is concluded that a displacement in the order of 100μ causes an error in 2Θ in the order of 0.060°. In turn this error at small angles (<10°) causes an error in the first decimal place of the d values (E) (Figure 3). An error of this order of magnitude could be very crucial for phase characterization, for example of clay minerals with lattice plane spacing >10 Å ($2\Theta_B=$ for CuK_α radiation) for a poorly prepared sample.

Parabolic Goebel Mirrors-Parallel beam optics

Goebel Mirrors are one dimensional artificial diffraction gratings that have recently been developed and have been given different focusing schemes, parabolic for the production of a parallel beam of X-rays and elliptic for the production of a focusing beam. The applications discussed in this paper concern the parabolic shaped mirrors (Fig.-4).

These focusing devices have been developed by a German researcher named Herbert Goebel, (Goebel 1995, Shuster and Goebel 1995) of Siemens Group and are widely used in X-ray powder diffraction applications, named after him in honor of his contribution.

Goebel mirrors are periodic multilayers, consisting of 20 to 100 bilayers made from W/Si or W/B_4C with a

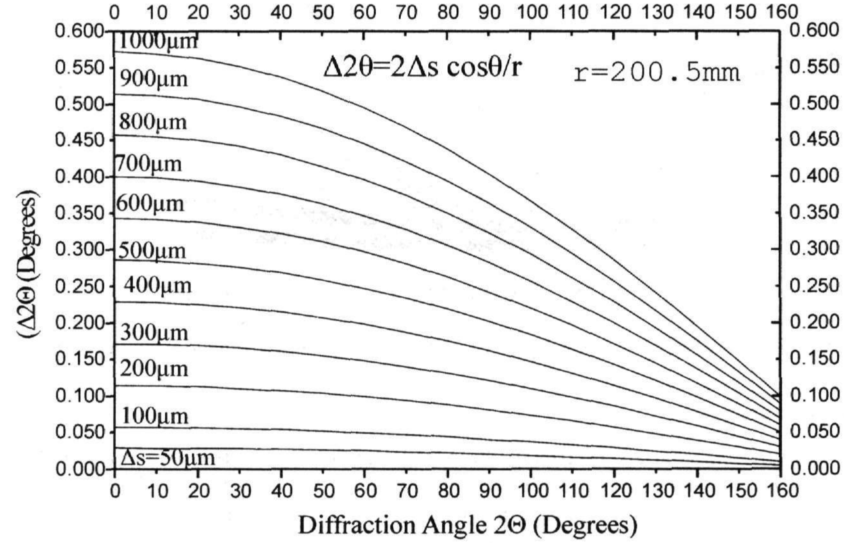

Figure 2. Variation of Δ2Θ as a function of diffraction angle Θ for different values of the displacement error.

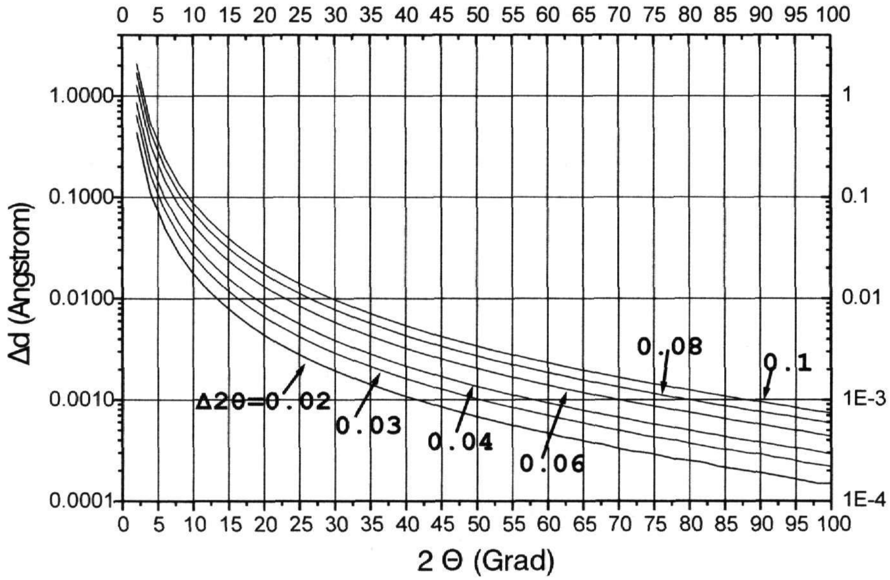

Figure 3. Error (Δd) in lattice spacing values d as a function of the diffraction angle for different error values Δ2Θ.

bilayer thickness in the range of 30-50Å (Figure 4). The focusing property of the parabolic mirrors is based on the appropriate curvature of their shape which have and on the fact that the d spacing (the bilayer thickness)is graded (Figure 4). These two factors define the focusing properties to the mirrors and a high intensity flux (>70% of the primary beam intensity).

As one can clearly see in Figure 1b, when a parabolic mirror is placed between the source and the sample a parallel beam of rays is produced which fall on the sample and as a result the rays reflected by the sample are parallel. The parallel optics of the x-rays result in the suppression of the displacement errors. Lattice spacing greater than 10E could be measured with accuracy greater than 0.01Å .

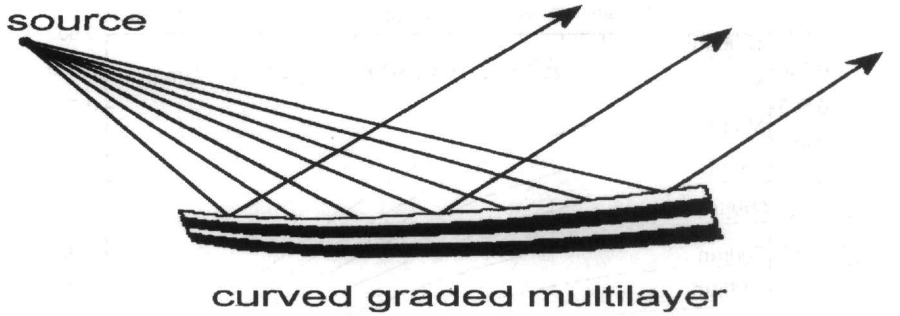

Figure 4. Parabolic Goebel mirror with bilayers of W/Si or W/B_4C and graded d spacing (parallel optics).

Experimental measurements

In order to verify the possible advantages of the parallel optics against the parafocusing Bragg-Brentano geometry, a series of measurements was performed using diffractometers with both focusing geometries. The Bragg-Brentano diffractometer (BB-instrument) is a D500 Siemens instrument and the diffractometer with the parallel optics is a D500 Siemens instrument supplied with a parabolic Goebel mirror (P-instrument). For the measurements CuKα radiation was used. For the measurements with the Bragg-Brentano diffractometer a secondary graphite monochromator was used and the scattered and diffraction slits were 1^0.

Bragg-Brentano type diffractometers are located at the Institute of Materials Science of "Democritos" and at IGME. The later was supplied with a parabolic Goebel mirror with a soller slit of 0.16° aperture.

The samples were prepared once and they were measured with both instruments.

The data evaluation were done using DIFFRAC Plus from BRUKER AXS and SOCABIM.

3.RESULTS AND DISCUSSION

In order to investigate the influence of displacement errors on the X-ray diffraction diagrams, with Bragg-Brentano and Parallel beam instruments, three samples were measured: Phlogopite, Quartz and Montmorillonite.

Phlogopite standard: *($KMg_3Si_3AlO_{10}(F,OH)_2$, National Bureau of Standards Report, Hubbard (1982), Standard No 675).*

The Phlogopite standard was selected as a low 2Θ angle standard. The X-ray pattern of Phlogopite have a very intense peak at 2Θ angle of ≈ 9.0° for CuKα radiation, Figure 5. The surface of the sample prepared for this standard was placed at ≈ 250μm above the ideal position. Figure 5 shows the diffraction patterns recorded with both instruments from the same sample.

The expected 2Θ angle for the (001) peak is 8.86°. The peak recorded with the BB-instrument is at 9.0°. The error $\Delta 2\Theta=0.14^\circ$ is close to the value expected from the diagrams given in [Figure 2] for S=250μm. The corresponding d-spacing values are 9.98 Å (standard value) and 9.81 Å (BB-instrument). The corresponding peak recorded with the P-instrument was at $2\Theta=8.85^\circ$ (d-spacing 9.98 Å). From the direct comparison of these values with those of the standard, it is clearly concluded that the displacement of the sample has no influence on the 2Θ values recorded by the P-instrument. (Table 1).

Quartz standard (SiO_2): The other standard studied was natural Quartz in the form of powder with a grain size of less than 20μm. This material is very stable and pure and very rare chemical substitution at Silicon sites is observed. These properties make quartz a very useful material as a standard in X-ray powder diffraction experiments with very stable structural parameters (unit cell dimensions etc., independent of its origin.

The measured sample with the P-instrument was prepared with no special care. The derived d-spacing values are very close to the theoretical ones. The error in Δ2Θ is less than 0.01 °, which gives an accuracy less than ±0.001E in the values of unit cell dimensions derived by the Rietveld method (Bish and Howard 1988).

The corresponding measurements with the BB-instrument give an average error in the order of $\Delta 2\theta \sim 0.02^0$, which corresponds to a surface displacement of ~50μm. The unit cell dimensions derived from this measurement are the same as the previous one (P-instrument case) but with a higher error (±0.002Å).

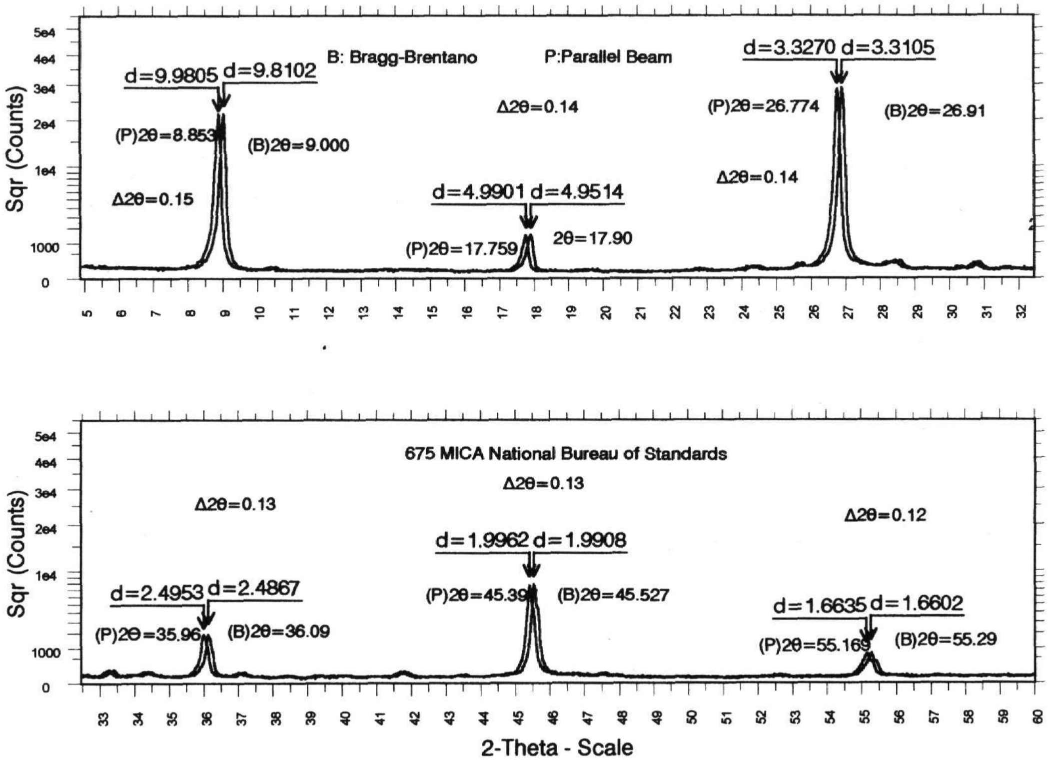

Figure 5. X-ray diffraction diagrams for the Mica 675 Standard, recorded with the diffractometer with the Bragg-Brentano parafocusing Geometry and with the Parobolic Goebel Mirror.

Table 1. Comparative measurements for Bragg-Brentano and Parallel Beam Optic diffractometer of Standard Reference Material 675, Phlogopite (National Bureau of Standards).

	hkl	**(001)**	**(002)**	**(003)**	**(004)**	**(005)**	**(006)**
Bragg-Brentano	**2θ°**	**9.00**	**17.90**	**26.91**	**36.09**	**45.527**	**55.29**
	d. Å	9.8102	4.9514	3.3105	2.4867	1.9908	1.6602
Parallel beam optic	**2θ°**	**8.853**	**17.759**	**26.774**	**35.962**	**45.397**	**55.169**
	d. Å	9.9805	4.9901	3.3270	2.4953	1.9962	1.6635
Differences	Δ2θ°	0.15	0.14	0.14	0.13	0.13	0.12
	Δd Å	0.17	0.039	0.016	0.008	0.005	0.003
Expected 2θ (National Bureau of Standards)	**2θ°**	**8.853**	**17.759**	**26.774**	**35.962**	**45.397**	**55.169**
	d. Å	9.9805	4.9901	3.3270	2.4953	1.9962	1.6635

Montmorillonite:

Normally for x-ray powder diffraction of clays a <2μm grain size is taken. The most widely used method is to pipette a clay-water suspension onto a glass slide, as a sample holder. The method is easy, quick and produces a good orientation of the basal reflections. The sedimentation of the clay gives a layer thickness of 20-100 μm, which cannot be exactly controlled and therefore displacement errors can occur very easily in Bragg-Brentano geometry. This problem can be more serious in treatment of the clay with glycerol.

For this comparative study a pure Montmorillonite sample from Melos island was used. The sample was studied after saturation with Ca^{++}- and Na^{+}- ions. The measurements were performed in 50%RH, with and without glycerol treatment. No special care was taken for the sample surface regarding surface smoothness and specimen displacement, regarding the theoretical position on the diffractometer axis.

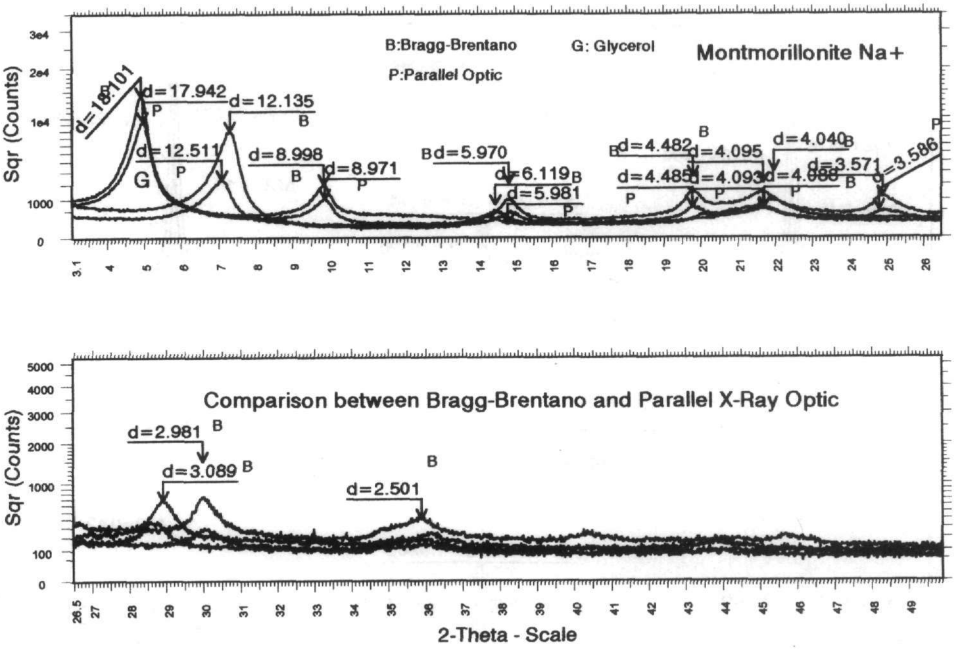

Figure 6. X-ray diffraction diagrams for Montmorillonite Na$^+$, recorded with diffractometer with the Bragg-Brentano parafocusing Geometry and with the Parobolic Goebel Mirror.

In figures 6 and 7 the corresponding diffractograms are represented and in tables 2 and 3 the corresponding d values.

Table 2. Comparative measurements for Bragg-Brentano and Parallel Beam Optic diffractometer of Montmorillonite Na$^+$ saturated.

		Air (50% RH)		**Glycerol**			
Bragg-Brentano	**2Θ°**	7.28	14.46	4.90	9.82	14.83	19.79
	D Å	12.14	6.12	18.10	8.99	5.97	4.482
Parallel beam optic	**2Θ°**	7.06	14.15	4.92	9.85	14.80	19.80
	D Å	12.51	6.255	17.94	8.971	5.981	4.485
Differences	Δ2Θ°	0.22	0.31	0.02	.003	0.03	0.01
	Δd Å	0.37	0.14	0.16	0.02	0.01	0.003

Taking in to account the exact diffractometer adjustment at 2θ=0°, the differences between Bragg-Brentano and parallel beam optic are due to specimem surface displacement and surface roughness. The consequence is a shift in 2θ position in the Bragg-Brentano geometry.

The d-values measured by the parallel beam optic are the correct ones and comparable with those in literature (Wilson 1987, Brindley 1980).

4.CONCLUSIONS

The measurements of X-ray powder diffraction patterns of a series of mineral samples have shown that the measurements made with the parallel beam optics diffractometer are of higher precision than these made with the Bragg-Brentano parafocusing geometry diffractometer. The measurements made on montmorillonite is an example of how useful the parallel beam optic in X-ray powder diffraction can be. Since free from displacement and surface errors, it can offer measurements of high quality in everyday routine mineralogical analysis, especially in minerals with high d values, such as mica and clay minerals or in mineral groups with cation replacement as in the case of fepdspars $(Ca,Na)Si_2(Si,Al)O_8$), pyroxenes $((Ca,Mg,Fe^{2+},Al)Si(Al)O_3)$, amphiboles

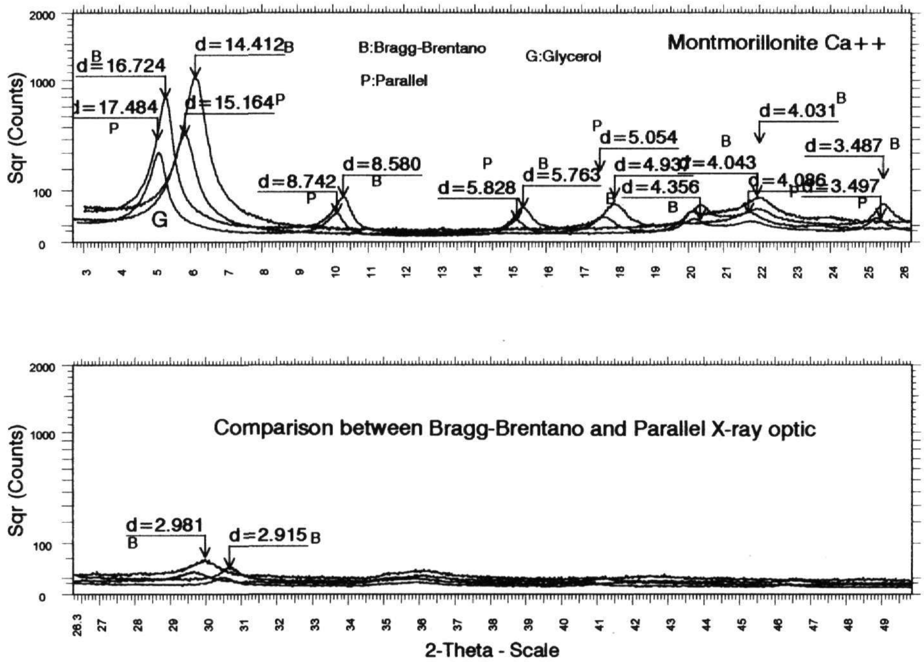

Figure 7. X-ray diffraction diagrams for Montmorillonite Ca^{++}, recorded with diffractometer with the Bragg-Brentano parafocusing Geometry and with the Parobolic Goebel Mirror.

Table 3. Comparative measurements for Bragg-Brentano and Parallel Beam Optic diffractometer of Montmorillonite Ca^{++} saturated.

		Air (50% RH)		Glycerol		
Bragg-Brentano	2Θ°	6.13	17.95	5.28	10.30	15.36
	D Å	14.41	4.937	16.72	8.58	5.776
Parallel beam optic	2Θ°	5.82	17.53	5.05	10.11	15.19
	D Å	15.16	5.054	17.48	8.742	5.828
Differences	Δ2Θ°	0.31	0.42	0.23	0.19	0.17
	Δd Å	0.75	0.12	0.23	0.16	0.05

$((Ca,Na)_2(Fe^{2+},Mg)_4,Al(Si_7(Si,Al)O_{22}(OH,F)_2)$,garnets $((Ca,Mg,Fe^{2+},Mn^{2+})_3$ $(Al,Fe^{3+})_2Si_3O_{12})$, micas$((K,Na)_2(R^{3+})_2(R^{2+})_2$ $(Si_6(Si,Al)_2)O_{20}(OH)_4)$, where R^{3+} is Al or Fe^{3+} and R^{2+} is Mg or Fe^{2+}, clay minerals etc.

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