

# APPARENT LONG SPACINGS FROM CLAY-WATER GELS, GLASSES, AND CRYSTALLINE MATERIALS DUE TO TOTAL REFLECTION OF X-RAYS

**Key Words**—Gel, Glass, Long spacings, Reflection, X-ray powder diffraction.

X-ray reflection or diffraction peaks were observed from sepiolite-water gels at  $2\theta$  angles of  $\sim 1^\circ$  which suggested inter-particle spacings of the order of 80 Å. The behavior of the peak as the gels dried and when modified experimental arrangements were used and eventually the observance of similar effects with other materials indicated that they arise from total (optical) reflection of X-rays rather than by diffraction. Inasmuch as long spacings are of considerable interest in clay mineralogy and because total reflection of X-rays has not been mentioned previously in relation to gels and clays, it is worth noting the conditions under which the effects were observed. These results are also relevant to measurements with interstratified clay minerals.

## EXPERIMENTAL METHODS AND OBSERVATIONS

### Calibration of the diffractometer for long-spacing measurements

Long-spacing alcohols,  $C_nH_{2n+1}OH$  with  $n = 14, 16, 18,$  and  $20$  were used as described previously (Brindley and Wan, 1974, 313–318; Brindley, 1981, 67–68). The very thin-layered samples previously prepared were still available to calibrate  $2\theta$  measurements in the range  $1$ – $5^\circ$ . A North American Philips diffractometer was used with  $CuK\alpha$  radiation operated at 40 kV, 10–15 ma, and fitted with a  $1/4^\circ$  slit system. The results, summarized in Table 1, show that  $2\theta$  measurements can be made reliably to  $0.01^\circ$  in the range studied.

### Observations with clay-water gels

The observations reported here arose in the course of studying sepiolite- and palygorskite-water gels. The

Table 1. Calibration of low-angle diffractometer readings using 001 reflections from alcohols,  $C_nH_{2n+1}OH$ .

n	l	$d(00l)^1$ (Å)	$2\theta$ (CuK $\alpha$ )	$2\theta$ (measured)	$\Delta$ ( $2\theta$ )
20	1	55.69	1.59	1.58	-0.01
18	1	49.86	1.77	1.76	-0.01
16	1	44.74	1.98	1.97	-0.01
14	1	39.63	2.23	2.24	0.01
20	2	27.84 (5)	3.17	3.16	-0.01
18	2	24.93	3.54	3.52	-0.02
16	2	22.37	3.95	3.95	0.00
14	2	19.81 (5)	4.46	4.45	-0.01

<sup>1</sup> After Brindley and Wan (1974).

gel samples were prevented from drying out by maintaining a humid atmosphere in the diffractometer sample chamber. Well-defined peaks were recorded at  $2\theta \sim 1^\circ$  corresponding to spacings of the order of 80 Å. When the samples were allowed to dry slowly, the spacing was expected to diminish and  $2\theta$  was expected to increase, but in fact  $2\theta$  decreased as the gels were dried. The gel smears were of the order of 0.5–1 mm thick. To improve the experimental arrangement, a glass slide was prepared with a cavity 4 cm  $\times$  0.5 cm and about 0.5 mm deep. The cavity was filled with the gel, and the gel surface was smoothed to be co-planar with the glass surface. This arrangement gave no gel diffraction peak.

It seemed possible that the diffraction peaks observed with smeared gel samples might be related to the displacement of the gel surface above that of the glass slide. This possibility was confirmed by displacing the cavity-mounted gel above the axis of the goniometer by inserting thin glass slides, about 0.2 mm thick, between the cavity holder and a base plate. Also the  $2\theta$  position of the peak was seen to be linearly related to the height,  $h$ , that the gel surface was raised above the axis of the goniometer.

Typical results are shown in Figure 1, where the observed peak position,  $2\theta$ , is plotted against  $h$ , in mm. The low-angle peak was recorded only when  $h$  was in the range 0.8–1.5 mm. When  $h < 0.8$  mm, the intense

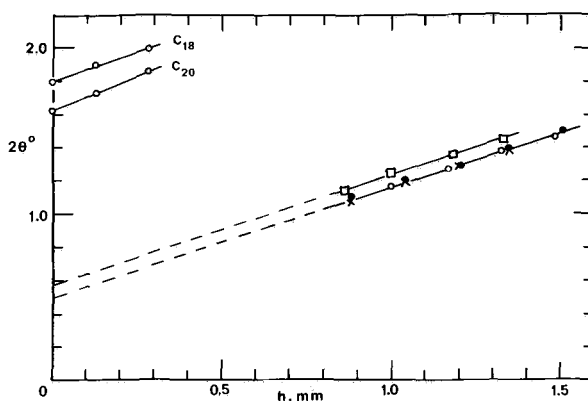


Figure 1. Values of  $2\theta$  recorded for low-angle reflections from gels, glasses, crystalline materials, and long-spacing alcohols displaced a distance  $h$  mm from axis of goniometer. ● = sepiolite-water gel with 15% sepiolite; ○ = glass slide; □ = mica; × = kaolinite; C18 and C20 = long-spacing alcohols.

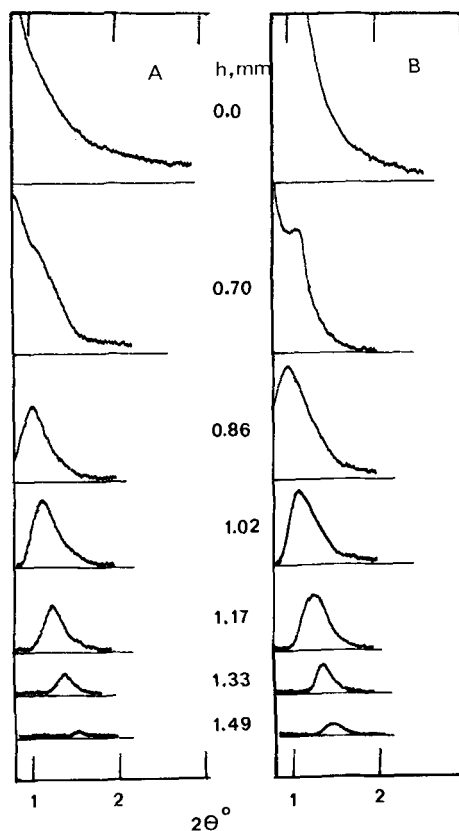


Figure 2. X-ray diffractometer patterns in the range  $1\text{--}2^\circ 2\theta$ ,  $\text{CuK}\alpha$  radiation, for (A) sepiolite-water gel in cavity holder, (B) glass slide, displaced distance  $h$  mm from axis of diffractometer.

incident X-ray beam entered the counter and no observations could be made; when  $h > 1.5$  mm, the sample surface was moved out of the X-ray beam. The range within which the observations were recorded corresponds to the sample surface lying within the peripheral part of the incident beam. The linear relation between  $2\theta$  and  $h$  suggests that the correct peak position may be obtained by linear extrapolation to  $h = 0$ . If the experiments had terminated at this point we could have reported inter-particle separations in the gels of the order of  $150 \text{ \AA}$ . Figure 2 shows the variation in the recorded peak as the sample was raised progressively above the axis of rotation of the goniometer.

#### Observations with glass, mica and kaolinite samples

The question was asked whether similar results to those obtained with gels could be obtained with other materials. Uncoated glass slides and thin plates of fused silica (Vycor) gave very similar results, namely no diffraction peak when inserted correctly in the diffractometer, but a similar peak when the sample was raised about 1 mm above the correct mounting. Still more

striking was the observation that 2-inch squares of high quality mica, and cavity holders filled with kaolinite gave similar results, which are plotted with appropriate symbols in Figure 1. The results clearly are not related to particular gels, glasses, or crystalline materials but are largely common to all of the materials examined. These data suggest that the results are related to the total reflection of X-rays at small angles rather than to diffraction effects by particular structures.

#### DISCUSSION

##### *Errors in long-spacing measurements of interstratified clay minerals due to displacement of sample surface*

The present observations may have an important bearing on the interpretation of long spacings of interstratified clay minerals which commonly occur in the range  $27\text{--}32 \text{ \AA}$ , and particularly in assessing the coefficient of variation (CV) of the individual basal spacings with respect to the mean basal spacing.

To determine if spacing measurements are significantly affected by sample displacements of the order of 0.1 mm, measurements were made with  $\text{C}_{20}$  and  $\text{C}_{18}$  alcohols displaced from the axis of the goniometer. The results for these alcohols are shown in Figure 1. The slopes of the lines are very similar to those found for the other materials and are of the order of  $0.07^\circ 2\theta$  for a sample displacement of 0.1 mm.

Consider now the effect of such an error on first-order spacings of  $30 \text{ \AA}$  and  $25 \text{ \AA}$ . A  $30\text{-\AA}$  spacing occurs at  $2\theta = 2.94^\circ$  with correct instrument adjustments, and would occur at  $2\theta = 3.01^\circ$  if the surface was displaced by 0.1 mm. This value would be recorded as a spacing of  $29.35 \text{ \AA}$  with an error of  $0.65 \text{ \AA}$ . A  $25\text{-\AA}$  spacing would appear as a spacing of  $24.54 \text{ \AA}$  with an error of  $0.46 \text{ \AA}$ . Normally, oriented clay samples are mounted with a thickness appreciably less than 0.1 mm. When ethylene glycol is added to cause swelling of smectite components, it is conceivable that a small excess of glycol may displace the surface of the sample appreciably and thereby cause a significant error in the measured spacing and in the CV determination for the material. The 001 reflection from interstratified minerals commonly contributes dominantly to the CV value for the sample and determines whether or not the mineral can be regarded as a *regular* interstratification of two layer types. Goniometer calibration and correct location of the sample surface are essential prerequisites for these determinations.

##### *Total reflection of X-rays*

Total reflection of light occurs when the glancing angle of incidence on an optically less dense material is less than the critical angle. The effect was demonstrated for X-rays by Compton in 1923 (see Compton and Allison, 1935) and was discussed at length by James (1948, p. 171 *et seq.*). The critical angle for X-rays for substances such as those considered here is of the order

of 10–15', which corresponds to a scattering angle  $2\theta$  of the order of 0.33–0.50°. The measured  $2\theta$  values of the present experiments when extrapolated to  $h = 0$  (i.e., assuming a *linear* extrapolation) are of the order of 0.50–0.60°. The results are of the right order of magnitude for total reflection of X-rays. An exact calculation of the optical relations involved is not easily made because the reflection effect is observed only when the sample surface is displaced from the axis of the goniometer and the counter tube is no longer directed exactly towards the center of the sample. However, the angle  $2\theta$  obtained graphically by extrapolating the observed peak positions to  $h = 0$ , and especially the similarity of the results for gels, glasses, and crystalline materials, strongly suggest that the observed effects are related to the total reflection of X-rays from surfaces.

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