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QUANTITATIVE DETERMINATION OF KAOLINITE BY *X*-RAY DIFFRACTION. A REPLY TO H. W. VAN DER MAREL

G. W. BRINDLEY AND SARI S. KURTOSSY, *The Pennsylvania State University, University Park, Pennsylvania*

Preferential orientation of the platy crystals of kaolinite can have a considerable effect on the intensities of the basal reflections. In an investigation, such as that of Dr. v. d. Marel (1960), where variations of basal intensities are under consideration, one would expect to see some discussion of how this aspect of the problem was treated. The only statement by Dr. v. d. Marel was the following: "The samples were first dried at 105° C. for some hours (to prevent preferential orientation) and afterwards run with a Philips . . . diffraction spectrometer . . . " . No further information is given in his subsequent note. We also dried our specimens in a similar way and additionally we used a 1″ diameter rotating holder specially constructed so that it could be filled from the back, a procedure

which is often thought to reduce orientation. The method was described in our paper (Brindley and Kurtossy, 1961, p. 1209). We also (probably for the first time) defined an orientation index which can be used nearly quantitatively to assess if there is preferential orientation. Despite the care taken, our samples which gave the sharper x-ray reflections showed very appreciable orientation. Admittedly, our kaolinites (particle sizes of the order $0.5-2\mu$) were coarser than those used by Dr. v.d. Marel (sizes about $0.2-1\mu$) and therefore probably more prone to preferential orientation, but nevertheless we think the onus is on Dr. v. d. Marel to provide evidence that his results were *not* affected by orientation. His present note adds nothing on this point beyond a reference to experiments by von Engelhardt in which cork meal was added to kaolinite, but this only raises a further question of the efficacy of the cork meal.

A second point raised by Dr. v. d. Marel is that the method we employed of using an organic cement to prevent orientation does not bring the reflected intensities from different kaolinites fully into agreement. This is true. However, one has to distinguish between (a) what may be a random scatter of the results, and (b) a trend of the intensities to decrease with increasing angular breadth of the reflections. These will be considered separately.

At any one angular breadth, for example $B = 0.3°$ which is an average value over the range we studied, the intensities in relative units are I (001) $= 1.23 \pm 0.06$ (see Fig. 3 of our paper) and I (002) $= 2.05 \pm 0.15$ (see Fig. 4). These limits correspond to the dashed lines in our figures, which encompass 13 out of the 15 kaolinites studied. We made no attempt to bring the two errant clays into line, considering that the overall picture was satisfactory. The accuracy attainable in quantitative work will turn on whether this spread of intensities, about $\pm 5-7\%$, represents real variations among kaolinites or experimental errors which might be reduced by more careful experimentation. We made three totally independent determinations for each reported value; Dr. v. d. Marel made 15 diffractometer runs per sample. We considered it more important to re-mix and re-pack samples than only to repeat diffractometer runs which we find reasonably reproducible with the rotating holder.

The tendency of the intensities to decrease as B increases is noted in our paper and is probably associated with an increasing disorder, since our kaolinites ranged from very well crystallized to strongly disordered materials. However, the change of intensity is still not enormous. From $B = 0.2°$ (the least recorded) to $B = 0.4°$ (which is exceeded by only one sample) I (001) ranges from an average value about 1.32 to an average of 1.15, and I (002) from about 2.20 to 1.90. The decrease over this

range is about 15% and it was for this reason that we wrote (p. 1214) that "it is advisable when selecting a standard kaolinite to choose one with about the same angular reflection breadth as the kaolinite to be measured." Dr. v. d. Marel seems to have about the same range of angular widths, from 1.26–2.58 in his units for twelve kaolinites and one fire clay, with integrated x-ray intensities from high values around 1.8 (actually 1.74, 1.88) to low values around 0.90 (actually 0.87, 0.89, 0.96). We find it very difficult to think that a substantial part of this large variation does not arise from preferential orientation.

In conclusion, we would say that we think this discussion has value beyond a mere dispute between two investigators, in that it emphasises the difficulties of quantitative work in this field. Still better ways of eliminating the orientation problem are required, and the special problems which arise when exceedingly small particles are measured must be kept in mind.

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