

of the wall rock. In this alteration of tremolite, magnesium and hydroxyl were liberated and converted either to phlogopite or to serpentine. The formation of scapolite appears to represent a localized type of metasomatism by the dike, for in general tremolite was altered directly to serpentine.

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## REFERENCES

- DANA, E. S. (1892), *A System of Mineralogy*, 6th. ed. John Wiley & Sons, New York.  
 LAMEY, C. A. (1934), Some metamorphic effects of the Republic granite. *Jour. Geol.* **42**, 248-263.  
 LARSEN, E. S. AND HARRY BERMAN (1934), The microscopic determination of the non-opaque minerals, *U. S. Geol. Survey, Bull.* **848**.

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QUANTITATIVE DETERMINATION OF KAOLINITE BY X-RAY  
 DIFFRACTION. A REPLY TO G. W. BRINDLEY AND  
 S. S. KURTOSSY *AM. MINERAL.* **46** (1962), 1205-1215

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In the above manuscript the authors came to the conclusion that the large spreading found in my experiments (1960) for the (001) reflections of various kaolinites was caused by preferential orientation.

The  $< 2 \mu$  separates dried 2 hours at  $110^{\circ}$  C. of 14 samples from pure well-known deposits of 6 different countries were investigated. They contained after x-ray and chemical analyses impurities to a maximum of 15% and their main particle size ranged after electron microscopy from 0.5-1.5  $\mu$  (Gabon) to 0.1-0.3  $\mu$  (Brokopondo). For the integrated intensities I (001,K)/I (020,B) was found = 1.9 to 0.85 = 200:100.

In the earlier experiments of Von Engelhardt (1955) 4 American kaolinites and 1 kaolinite from Provence (France) were investigated, which samples also occurred in my collection. The original kaolinites were in this case previously mixed with cork meal 100:100 volume %, and gave a spreading of 19.03:13.58 = 140:100 (American samples) and 19.03:11.31 = 177:100 (all samples). The finest kaolinite used in this investigation was after electron microscopy mainly of 0.05-0.30  $\mu$  and the coarsest of 0.08-1.34  $\mu$  size.

Both experiments, the variation in particle size of the samples being in the first experiment somewhat larger than in the second one, clearly

demonstrate a large spreading for the intensities of the (001) kaolinite reflection for samples from various origin. Therefore the indication accurate to minimal 5%, in quantitative determinations should be very doubtful.

The kaolinite samples used by Brindley and Kurtossy were of the same origin as those used by Murray and Lyons (1956) *e.g.* "a series of essentially pure kaolinites covering a range of particles size and degrees of crystal structure perfection." The well crystallized sample (s) in this case however consist, after the electron micrographs of the above authors, mainly of particles 0.5–2  $\mu$  and thus will be very sensitive to preferential orientation. The poorly crystallized sample was mainly of 0.2–0.5  $\mu$  size and therefore coarser than that of the finest sample used in the experiments of the two foregoing authors.

For the above series of kaolinites Brindley and Kurtossy found a spreading of 2.30 to 1.38 = 167:100 for I (001,K)/I(020,B). The organic cemented disorientated samples showed a spreading of 1.50 to 1.02 = 147:100 (without sample G = 1.38 to 1.02 = 135:100). Thus the gain by the cement treatment of the various kaolinite samples among which very coarse samples is 20%. But the relative spreading inherent to the samples is 47% (35%) which makes a quantitative analysis impossible. For the I (002,K)/(021,B) integrated intensities Brindley and Kurtossy found a spreading of 3.70–2.00 = 185:100. For the previously cemented samples was found: 2.40–1.35 = 178:100 (without sample G = 2.20–1.35 = 143:100). Also in this case there is a gain by the cement procedure but the spreading inherent to that existing in the various kaolinite samples is much larger. Analogous results are found for the I(001)/I(060) reflection of kaolinite (original = 9.15–4.10 = 233:100, cemented = 4.65–3.08 = 151:100) and the I(002)/I(060) reflection of kaolinite (original = 6.75–3.50 = 193:100 cemented = 3.70–2.35 = 157:100).

Brindley and Kurtossy recommend for analytical work a standard kaolinite giving a basal reflection of the same angular breadth as for the kaolinite sample to be estimated quantitatively. However, kaolinite particles in terra rossas and latosols may be even of particle size <0.1  $\mu$ . These particles are thereby covered by a "Beilby" layer of amorphous sesquihydroxides-silicic acid composition which not only hinder the  $x$ -rays to penetrate into the inner crystalline kernel, but thereby cause line broadening (Beutelspacher and Van der Marel, 1962).

The result is that when experimenting with the above soils, the intensities measured are only a fraction as compared to those of pure kaolinites including pure fine kaolinites with disordered structure; also considering the other components (amorphous matter, quartz etc.) by

which the kaolinite is accompanied (Van der Marel, 1962). Another difficulty is to isolate from these soils a pure kaolinite standard for quantitative purposes for a kaolinite-type in a quite different sample, having in common only its line breadth. For, the latter depends as well as on fineness of the sample as on the degree of structural disorder in the crystallites.

By use of the (060) kaolinite reflection which is less affected by preferential orientation, the spreading of the intensities of kaolinites from various origin remained large although there was a decrease of some 15% (Engelhardt, 1955).

At present it is generally accepted that minerals are covered by an amorphous (Beilby) layer. For quartz, which mineral was extensively investigated by several authors, a thickness of 0.03 to 0.15  $\mu$  was found (see literature). This amorphous layer should be the seat of cation exchange phenomenon in case of hydrolizable Al-silicate minerals (Hudig and Roborgh, 1936). As an average about 74  $\text{\AA}^2$  of the surface of these minerals (kaolinite, illite, expanded illite soil- and common montmorillonite) were found to be covered by one cation (Johnson and Lawrence, 1942; Mortland, 1954; Van der Marel, 1960, 1962). A thickness of the amorphous layer of only 0.003  $\mu$  on the surface of a kaolinite sample with a specific surface of 75  $\text{M}^2$  (specific surface of the samples investigated here ranged from 12–75  $\text{M}^2/\text{g}$ ), corresponds to a volume per cent of 22.5% and a weight per cent of 45.5% assuming its sp.w. = 2, such as for permutites. When the crystal is highest ordered there will only be a minimum of loss of  $x$ -rays which do not participate at a Bragg reflection as a result of atoms which are situated at regular distances from each other and also in planes parallel to each other.

Thus by the existence of a thin Beilby layer and a disorder in the crystal structure, the large variations found for the (001) reflection of kaolinites from various pure deposits, can easily be explained. The spreading in the intensities of the reflections of kaolinite as present in soils from various origin will be still larger. They are not only much finer but will also be more disordered because the conditions of formation are much poorer in this case. Moreover various minerals are found in soils representing an intermediate stage in the halloysite—kaolinite building up (Fieldes, 1955) or in the kaolinite-halloysite breakdown (hexagonal plates, rolled plates, tubes with hexagonal ends, tubes in all grades of perfection (see literature).

Also for halloysite various stages of crystal order and crystal size are known. Thus the  $x$ -ray spectrum of a halloysite may even be better developed than that of a kaolinite of the fire-clay mineral type (Beutels-

TABLE 1. INTEGRATED SURFACE OF MOST INTENSIVE REFLECTION OF MINERALS FROM VARIOUS ORIGIN RELATIVE TO THAT OF CERAHYDRATE (6.06 Å) AND OF QUARTZ (3.33 Å)

Sample	I mineral	Sample	I mineral
	I Cera		I Cera
<i>Hydrargillite</i> (4.35 Å) + 50% Cera:		<sup>1</sup> <i>Montmorillonite</i> (12.5–15.1 Å) + 10% Cera:	
A—artificial	0.90	312—Cameron, Ariz., U.S.A.	3.20
2—Surinam	0.95	240—Bantam, Java	3.47
232—Br. Guyana	1.10	304—Geisenheim, G.B.R.	3.65
985—Surinam	1.65	2—Jugoslavia	4.45
11—Minas Gerais, Brazil	15.70	67—Javapai, Calif., U.S.A.	4.79
		318—Montmorillon, France	5.10
<i>Boehmite</i> (6.06 Å) + 50% quartz:		343—Amory, Miss., U.S.A.	5.04
C—Artificial (Cerahydrate)	2.03	344—Bayard, New Mexico, U.S.A.	6.24
148—Hungary	3.34	331—Selina, Ark. U.S.A.	9.65
		<sup>1</sup> <i>Nontronite</i> (13.8–14.8 Å) + 10% Cera:	
<i>Goethite</i> (4.19 Å) + 5% Cera:		269—Garfield, Wash., U.S.A.	9.21
87—Cornwall	19.5	349—Andreasberg (G.B.R.)	10.66
C—Conakry	8.75		
		<i>Muscovite</i> (10.0 Å) + 10% Cera:	
<i>Limonite</i> (4.18 Å) + 5% Cera:		945—Sweden	9.83
956—Cook's Islands	3.06	465—Georgia, U.S.A.	12.01
607—Netherlands	5.75		
84—U.S.A.	6.55	<i>Sericite</i> (10.0 Å) + 10% Cera:	
		823—Calif., U.S.A.	13.04
<i>Hematite</i> (2.69 Å) + 20% Cera:		<sup>1</sup> <i>Illite</i> (10.0 Å) + 10% Cera:	
155—artificial 150° C.	1.42	556—Belgium	0.80
572—artificial 700° C.	1.96	619—Australia	1.38
612—Minnesota	2.10	461—Illinois (purified, Ward)	1.57
1093—Arizona	2.93	949—Luxembourg	1.75
		298—Illinois	2.15
		289—Goose Lake	2.53

<sup>1</sup> Separate <2μ (montmorillonite and nontronite = pure; illite = nearly pure).

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pacher and Van der Marel, 1962). Lastly many stages exist between allophane and halloysite (see literature).

But not only platy kaolinite, which mineral has a very variable particle size, also fine platy minerals like illite and montmorillonite which will not easily give a preferential orientation effect when the sample is dried before it is packed in the sample holder, show a wide variation in the intensity of their x-ray reflections. The same holds for non-platy minerals like boehmite, goethite, limonite, hematite (Table 1).

The result is that also for these minerals a quantitative estimate, the adjective meant in the sense of an accuracy of minimal 5%, will be wholly impossible. Only in case of well-defined samples also otherwise checked on impurities and of which also identical standard material is available for checking, reliable quantitative analyses can be made.

## REFERENCES

- BEUTELSPACHER, H. AND H. W. VAN DER MAREL (1961), Kennzeichen zur Identifizierung von Kaolinit "Fireclay," Mineral und Halloysit, ihre Verbreitung und Bildung. *Tonindustrie Zeit.* **85**, 517-525, 570-582.
- (1962), Der elektronen-optische Nachweis von amorphem Material als störender Faktor bei der quantitativen Analyse von Tonmineralen in Böden. *Acta Univ. Carolinae, Prague, Geol. Suppl. I*; *Proc. 2nd. Internat. Congr. Clay Minerals* (in press).
- BRINDLEY, G. W. AND S. S. KURTOSSY (1961), Quantitative determination of kaolinite by x-ray diffraction. *Am. Mineral.* **46**, 1205-1215.
- ENGELHARDT, W. VON (1955), Über die Möglichkeit der quantitativen Phasenanalyse von Tonen mit Röntgenstrahlen. *Zeit. Kristall.* **106**, 430-459.
- FIELDES, M. (1955), Allophane and related mineral colloids. *New Zealand Jour. Sci. Techn.* **37**, 336-350.
- HUDIG, J. AND R. H. J. ROBORGH (1936), On the uniform behaviour of the Dutch clays for their exchange capacity. *Landbouwk. Tijds.* **48**, 33-39.
- JOHNSON, A. L. AND W. G. LAWRENCE (1942), Surface area and its effect on exchange capacity of kaolinite. *Jour. Am. Ceram. Soc.* **25**, 344-346.
- MORTLAND, M. M. (1954), Specific surface and its relationships to some physical and chemical properties of soil. *Soil Sci.* **78**, 343-347.
- MURRAY, H. H. AND S. C. LYONS (1956), Correlation of papercoating quality with degree of crystal perfection of kaolinite. *Proc. 14th Natl. Conf. Clay Minerals. Natl. Acad. Sci. N.R.C. Publ.* **456**, 31-40.
- VAN DER MAREL, H. W. (1960), Quantitative analysis of kaolinite. *Silicates Industriels*, **25**, 23-31, 76-80.
- (1962), The quantitative determination of minerals in clays. *Acta Univ. Carolinae, Prague, Geol. Suppl. I*; *Proc. 2nd Internat. Congr. Clay Minerals* (in press).

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

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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