

## QUANTITATIVE ANALYSIS OF THE CLAY SEPARATE OF SOILS

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## SUMMARY

Quantitative analysis of soil clay minerals after X-ray, differential thermal, infrared, cation exchange and chemical analysis is treated.

Particle size, crystallite size, the grade of structural ordering in the minerals, and the surface being covered by an amorphous (Beilby) layer, have large influence on the results. Examples are given.

Difficulties in quantitative analysis are furthermore increased because usually different clay minerals are found to occur together in the clay separate of soils. A coincidence of X-ray reflections, infrared absorption bands and d. t. a. heat reactions is the result. Examples are given.

Crusts of amorphous sesquihydroxide, silicic acid, allophane, etc. and organic matter covering the inner crystalline particle kernel, are another obstacle in quantitative analysis. They scatter the X-rays and hinder the flow of heat in the sample when it is investigated after the d. t. a. method.

At last the various minerals which are formed in nature by the transformation of one clay mineral into the other by weathering, are another source of great errors in quantitative analysis. An example is given for the dioctahedral mica minerals.

## Acknowledgement

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## INTRODUCTION

There is an increasing interest in Agricultural and Soil Mechanics laboratories with respect to the different kinds of clay minerals in soils and their quantitative estimation; especially for soils from countries of which practical experience on land reclamation, construction of dikes, roads etc., is not yet available. Also, pedologists are interested in the kind and amount of clay minerals in soils because of the study and characterisation of their profiles f. i. in podzol- and pseudo-gley soils great differences in clay mineral composition



and morphology exist for short distances in the profile. Sediment petrologists are interested in the composition of clay minerals for stratigraphical purposes.

At the identification of clay minerals in soils many difficulties exist thus; f. i. at the expansion of the closed mica (10 Å) minerals (the most widespread clay mineral in soils) many stages are formed. As this expansion is accompanied by a decrease in the amount of the interlayered K-ions and an increase of specific surface, expanded illite or expanded glauconite may swell just like montmorillonite.

Many authors have pointed to the above processes to occur in nature — R. H. Bray 1937, M. L. Jackson et al 1948, J. L. White 1951, H. Hamdi and W. Epprecht 1954, Ch. E. Weaver 1957, H. W. van der Marel 1959.

Loss of interlayer charge during this transformation may be caused by re-silification of the tetraeders. — M. L. Jackson et al. 1948. Such because the bond force constant for Si-O is larger as that for Al-O' = 5.85 and  $5.06 \times 10^5$  dynes/cm. respectively.

Of course this process should proceed under conditions with an excess of silicic acid such as prevail in regions where the end member of this kind of illite with swelling properties are usually found-black regur (India), Gumbo — (U. S. A.), tir noirs (Marocco), margalite — (Java), badob — (Sudan) and black turf soils (S. Africa, Rhodesia).

Contraction and opening of the layers depends primarily on the charge density. This is greatest for vermiculite (Si-Al substitutions in the tetraeders and low specific surface) and the smallest for montmorillonite (Al-Mg substitutions in the deeper situated octaeders and large specific surface). Other factors are Coulomb attraction and polarisation attraction. The latter because in this case of holes of definite size, short distance London — Van der Waals forces resulting from interaction of continuously varying dipoles in opposite atoms or ions (exaggerated by the orbital movement of the electrons) have a selective effect on the contraction of the layers - H. W. van der Marel (1954).<sup>1</sup>

Thus interlayered Li, Na, Ca, Mg do not contract the layers of vermiculite,

<sup>1</sup>) E- Coulomb =  $-\mathcal{N} \frac{e_1 e_2 z_1 z_2}{r}$  kcal/mole;  $e_1$  and  $e_2$  = charge and  $z_1$  and  $z_2$  = valence of ions,  $r$  = distance

E-London-Van der Waals =  $-\frac{3}{2} \mathcal{N} \frac{\alpha_1 \alpha_2}{r^6} \frac{I_1 I_2}{I_1 + I_2}$  in which  $\alpha$  = polarizability (Å<sup>3</sup>) (Li<sup>+</sup> = 0.02, Na<sup>+</sup> = 0.21, K<sup>+</sup> = 0.97, NH<sub>4</sub><sup>+</sup> = 1.60, Mg<sup>++</sup> = 0.2, Ca<sup>++</sup> = 0.2, Ba<sup>++</sup> = 1.63 Å<sup>3</sup>);  $I$  = ionization energy of electron in lowest energy level (Li = 124, Na = 118, K = 100, NH<sub>4</sub> = ca. 87, Mg = 176, Ca = 141, Ba = 134 kcal/atom — see literature);  $\mathcal{N}$  = Avogadro's number;  $r$  = shortest distance between two particles. An exact mathematical calculation of the ultimate effect for the several ions is impossible because of their partial covalent character, the unequal distribution of the field strength on the surface of the layers and because the ions are not bound to a free surface but are enclosed between two layers. Moreover, repulsive interaction of opposite Stern-Gouy double layers and the precise value for the dielectric constant ( $\epsilon$ ) of molecules which are directly bound to the surface or very near to this surface increases complicated nature of this matter — see E. J. W. Verwey and J. Th. G. Overbeek (1948), H. van Olphen (1954).



expanded illite and montmorillonite, when wetted or dried with a concentrated solution of their salts. Interlayered Ba only contract the layers of highly charged vermiculite. However, K,  $\text{NH}_4$ , Rb and Cs contract the layers of vermiculite and expanded illite and also those of montmorillonite when the layers have been brought before together by artificial drying. Hydrogen ions do not contract the layers as they are strongly bound to the negatively charged inter-layer surfaces by strong electrostatic (Coulomb) attraction because of their small size. Another natural process in soils is that under certain conditions brucite-like layers of sesquihydroxide composition are interleaved in 2 : 1 expanded minerals — G. Brown 1954, C. J. Rich and S. S. Obenshain 1955, M. G. Klages and J. L. White 1957, B. L. Sawhney 1958, C. J. Rich 1960.

Or, that a primary (magmatic) chlorite by weathering has loosened its interleaved brucite layer in several degrees of tightness. Therefore also in this case many stages may result among which swelling minerals, but of chlorite — origin. A serious obstacle in quantitative clay mineral analysis is the particle size effect — see for the X-ray method: J. Ch. L. Favejée, 1939, G. W. Brindley, 1945, Z. W. Wilchinsky, 1951, L. Alexander et al. 1948, G. Nagelschmidt et al. 1952, R. L. Gordon et al., 1952, W. von Engelhardt, 1955, R. L. Gordon and G. W. Harris, 1955, C. Legrand and J. Nicolas, 1958, G. W. Brindley and S. Udagawa, 1959; for the d. t. a. method: G. J. van Nieuwenburg and H. A. J. Pieters, 1929, P. L. Arens, 1951, F. H. Norton, 1940, R. Norin, 1941, S. Speil et al., 1945, W. D. Laws and J. B. Page, 1946, R. E. Grim, 1947, F. Lippmann, 1952, R. T. Martin and M. B. Russell, 1952, L. Bramao et al. 1952, R. H. S. Robertson et al. 1954, A. R. Carthew, 1955, H. W. van der Marel, 1960; for the infra-red method: A. H. Pfund, 1934, G. Duyckaerts, 1959, H. W. van der Marel, 1960; for the cation exchange method: R. E. Grim and R. H. Bray, 1936, R. E. Grim, 1939, C. G. Harman and F. Fraulini, 1940, A. L. Johnson and W. G. Lawrence, 1942, M. M. Mortland, 1954, H. W. van der Marel, 1960.

The particle size effect is caused by entrapment of the X-rays between too coarse particles, reflection and scattering, hindered escape of vapour and decrease of conductivity at the d. t. a. The particle size effect may furthermore be caused by the occurrence of an amorphous layer-Beilby layer (1921) on the surface of the clay minerals. After the experiments of P. B. Dempster (1951), D. W. Clelland et al. 1952, D. W. Clelland and P. D. Ritchie, 1952, P. B. Dempster and P. D. Ritchie, 1952, G. Nagelschmidt et al. 1952, J. G. Gibb et al. 1953, its thickness should be about 0.03 to 0.15  $\mu$  for quartz. When calculated on a specific surface of 200  $\text{m}^2/\text{g}$  (fine expanded illite) and 500  $\text{m}^2/\text{g}$  (montmorillonite) thereby assuming a sp. w. of the amorphous matter to be about 2 as in permutites and the thickness of the layer to be only about 10 Å, the clay particles should contain 40 % and 100 % amorphous matter.

If the particles are too small or if the crystallites have crystal defects (mosaic



structure) there is increased scattering of the X-rays — J. Despujols 1957, or the I. R. rays — A. H. Pfund 1934. Another disturbing factor in quantitative analysis is the grade of order in the crystallites.

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.

Also in a highly ordered crystal there will be a maximum of resonance absorption of I. R. rays for a certain vibration of two atoms (or of an atom and an atom group etc.). For, the deviations in the distances between these atoms (or atoms and atom groups etc) are the smallest and their surroundings (atoms and atomgroups) are in this case also the most constant as compared with that of a badly ordered crystal.

The heat of reaction ( $\Delta H$ ), the free energy ( $\Delta F$ ) and the activation energy ( $\Delta E^*$ ) for a certain mineral as calculated from integrated peak area calibrated against standard minerals of well known  $\Delta H$ , volumetric  $\log \Delta p/T$  ( $p$  = gas volume), and  $\log \Delta k/T$  ( $k$  = reaction constant), measurements, is neither constant. It will be the largest in the best ordered state. Amorphous inorganic and organic matter covering the surface of the clay minerals as common in the clay separate of soils is a further disturbing factor—see for details H. Beutelspacher and H. W. van der Marel — this Journal.

Non uniformity in the identification and nomenclature for a certain clay mineral by the clay mineralogists in the various countries have also increased the difficulties in clay mineral analysis of soils. Literature on clay minerals is overflowed at present by new names for one and the same mineral but identified and classified after different methods.

Quantitative analysis of clay minerals in soils is furthermore complicated by the simultaneously occurrence of several clay minerals in the same soil sample. Among them are wide spread minerals which up to now have not been found to occur as monominerals. Thus standard material is lacking here. Moreover the X-ray, D. t. a., I. R. and C. E. C. characteristics of various of these minerals overlap each other.

## I. Methods

### 1) Samples

The various soils were suspended in Atterberg cylinders with 0.01 N NaOH and the separate  $< 2 \mu$  was siphoned off. After concentration of the fine particles on a waterbath, the suspension was filtered under suction and washed out with pure water.

The samples were then dried, powdered and sieved through a  $50 \mu$  sieve. The



samples  $< 2 \mu$  investigated here contained only maximal 5 to 10 % of organic matter.

## 2) Method of analysis

**Specifigue surface.** The R. S. Dyal and S. B. Hendricks (1950) ethylene glycol procedure was followed which in this case is to be preferred to the B. E. T. method (1938) because the highly polarizable ethylen glycol molecules can better move apart the dried aggregated clay particles than the inert nitrogen molecules. To avoid temperature effects the exsicator with the weighing flasks ( $1 \times 1$  cm) were placed in a thermostated bath at  $27,5^{\circ}\text{C}$  — see also G. E. Wilkinson and F. Gray 1954.

**Chemical analyses (Bausch analyses).** The clay (2 to 4 g) was dissolved by  $\text{HF-H}_2\text{SO}_4$ ;  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  were determined by flame photometry,  $\text{CaO}$  by  $\text{KMnO}_4$  titration,  $\text{MgO}$  by separation with 8-hydroxyquinoline sulfate,  $\text{Mn}_3\text{O}_4$  by the colorimetric  $(\text{NH}_4)_2 \text{S}_2\text{O}_8$  oxidation method,  $\text{Fe}_2\text{O}_3$  by stannochloride-reduction followed by  $\text{KMnO}_4$  titration,  $\text{P}_2\text{O}_5$  by the ammonium molybdate (Lorenz) precipitation method,  $\text{TiO}_2$  by colorimetric  $\text{H}_2\text{O}_2$  oxidation,  $\text{Al}_2\text{O}_3$  by the difference method ( $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{P}_2\text{O}_2 + \text{TiO}_2 - \text{Fe}_2\text{O}_3 + \text{P}_2\text{O}_5 + \text{TiO}_2$ ).  $\text{SiO}_2$  was determined separately by first dissolving the sample in  $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ , precipitation of  $\text{SiO}_2$  by  $\text{HCl}$  and the  $\text{HF} - \text{H}_2\text{SO}_4$  difference method.

**Cation exchange capacity. (C.E.C.)** The dried clay (2 to 4 g) was first mixed with 80 cc pure quartz sand. Than the mixture was percolated in a glass tube (drawn out at the lower end) first with 300 cc of 0.5 N Na-acetate of  $\text{pH} = 8.2$ . This slight alkaline solution is used to remove strongly adsorbed H-ions. The excess of salt is washed out with 300 cc 80 % ethylalcohol and the sample-quartz mixture is than percolated with 250 cc 0.5 N  $\text{NH}_4\text{Cl}$  ( $\text{pH} = \text{ca } 5.6$ ). In the percolate Na is determined quantitatively by flame photometry = adsorbed Na from Na-acetate ( $\text{pH} = 8.2$ ) — H. W. van der Marel (1950). Na-acetate was used because salt solutions of divalent cations give insoluble basic hydroxides when washing out the excess of salt with water or dilute alcohol (80 %). Also basic cations of less valency —  $\text{Mg}(\text{OH})^+$ ,  $\text{Zn}(\text{OH})^+$  — are adsorbed instead of the divalent cations — H. W. van der Marel 1935, C. A. Bower and E. Truog 1941, H. Jenny and M. M. Engabaly 1943.

Solutions of  $\text{NH}_4$ -salts ( $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4$ -acetate) are neither suited because  $\text{NH}_4^+$ -ions are fixed by K-fixating clay minerals (expanded illite) from which results a decrease in C. E. C. — L. Kolodny 1938, J. D. Peterson and D. S. Jannings 1938, E. Truog and R. J. Jones 1938, J. S. Joffe and L. Kolodny 1939, J. S. Joffe and A. K. Levine 1940, A. K. Levine 1941, H. W. van der Marel 1954, Sawhney et al. 1959.

**X-ray diffraction.** The samples were dried at  $105^{\circ}\text{C}$  for some hours (to



prevent preferential orientation) and afterwards investigated with a Philips Xenon filled proportional counter-diffraction spectrometer, Co-radiation ( $K \alpha_1 \alpha_2 = 1.787 \text{ \AA}$ ) with rotating sample holder and registration of the Bragg reflections, which first have passed a discriminator, by a recorder. As packing density and tube radiation are not constant, the intensity of a selected reflection of the sample is compared with that of a standard mineral, with which the sample is previously mixed. In this case the O. G. Griffin (1954) Cerahydrate standard (artificial  $\gamma \text{ AlOOH}$ ) was used which is to be preferred to the commonly used  $\text{MgO}$ ,  $\text{CaF}_2$  or cholesterol standards because its mass absorption coefficient ( $\mu/\rho = 44 \text{ cm}^2/\text{g}$ ) is of the same order as that of most common clay minerals (kaolinite = 47, quartz = 55, mica = 66). The goniometer was run  $4 \times$  repeatedly over the specified  $2 \theta$  range and an average value was calculated from the countings. The registered intensities were corrected for base line (background). The latter depends on optical conditions of the instrument (surface of the focus, intensity of the current, thickness of the Fe-filter, slit width, discriminator). Moreover on properties inherent to the sample (particle size, amorphous matter).

**Differential thermal analysis. (d.t.a.)** The dried samples were run in a C. M. A. De Bruyn apparatus (1954) which has Pt-Pt/Rh thermocouples, their potentials being amplified before they are registered by a Brown recorder. Three samples can be investigated simultaneously. To prevent exothermal oxidation reactions which mask the thermal reactions inherent to the sample investigated, nitrogen was flushed through the oven (at a pressure of 0.1 m. m. Hg). To prevent errors in quantitative analyses caused by differences in the heat capacity of the samples, these and also the standard calibration powder ( $\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$ ) were previously diluted with the  $\alpha \text{ Al}_2\text{O}_3$  reference material at a rate of 150 to 250 mg and then the mixture was equally packed in the sample holder — R. W. Grimshaw and A. L. Roberts 1953.

Moreover all the samples were analysed with the same thermocouple in the same ovenhole. Also an oven with the thermocouples outside the sample instead of inside — S. L. Boersma principe (1955) was used.

**Infra-red analysis.** The transparent KBr disc technique of U. Schiedt and H. Rheinwein (1952) and M. M. Stimson and M. J. O'Donnell (1952) was followed. In this case 2.3 mg (0.5 mg) of the sample was first mixed and ground with 400 mg KBr in a vibratory grinder. Thereafter the mixture was pressed to transparent pellets under vacuum suction. The samples were run in the double beam Perkin Elmer Model N 13 and the Leitz Model 129 infra-red Spectrophotometer of the Analytical Institute T. N. O., Delft (Netherlands) and the Institute for Biochemistry Braunschweig (Germany) respectively.\*

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The extinction  $(E) = -\log \frac{I}{I_0}$  ( $I$  = intensity transmitted and  $I_0$  = intensity incident radiation) at its maximum absorption were determined after the base-line method of N. Wright (1941) and J. J. Heigl et al (1947) which corrects for background scattering.

Integrated absorption intensities can be calculated in the same way but is very tedious. I. R. instruments exist e. g. Perkin Elmer model 21 provided with an absolute intensity integrator attachment.

**X-ray diffraction.** In the Goniometer diffraction procedure, X-rays of intensity  $I_0$  fall on the mineral sample in form of a powder lightly pressed to a flat block. In this case for a certain mineral the following function exists for the intensity ( $I$ ) of a certain Bragg-reflection

$$I = K f (F, A)$$

$K$  = constant depending on slit widths, current density, wave length, polarisation factor, Lorentz factor, multiplicity factor.

$A$  = absorption factor.

$F$  = structure factor.

**Absorption factor** For a powder sample consisting of several minerals of weight fraction  $x_1, x_2 \dots$  etc. having a density of  $\rho_1, \rho_2 \dots \rho_i$  etc. and a linear absorption coefficient of  $\mu_1 \mu_2 \dots \mu_i$  the following relation exists—see L. Alexander and H. P. Klug (1948)

$$A = \frac{x_1}{\rho [\mu_1^* - \mu_M^*] + \mu_M^*}$$

mass absorption coefficient matrix =

$$\mu_M^* = \mu_2^* x_2 + \mu_3^* x_3 + \dots = \frac{\sum_2^n \mu_i^* x_i}{1 - x_1}$$

$\rho$  = apparent density sample  $x_1 \quad \mu_1^* = \frac{\mu_1}{\rho_1} ; \mu_2^* = \frac{\mu_2}{\rho_2}$  etc.

Tables of mass absorption coefficient, of various elements including scattering (nearly constant = ca. 0.2) for various radiation (see Internationale Tabellen zur Bestimmung von Kristallstrukturen, Gebr. Borntraeger, Berlin 1945, vol. 2, pp 577—578) permits calculation of absorption coefficients of clay minerals from their chemical composition.

Thus for the used Co-radiation: kaolinite = 46, montmorillonite = 40, quartz = 53, muscovite = 65, calcite = 115, cellulose = 12 cm<sup>2</sup>/g. From the above follows that especially the clay separate of soils with large amounts of calcite (marl soils) or of organic matter (marsh soils) will give trouble at quantitative analyses, because they also contain minerals which absorb the X-rays to a quite different grade.



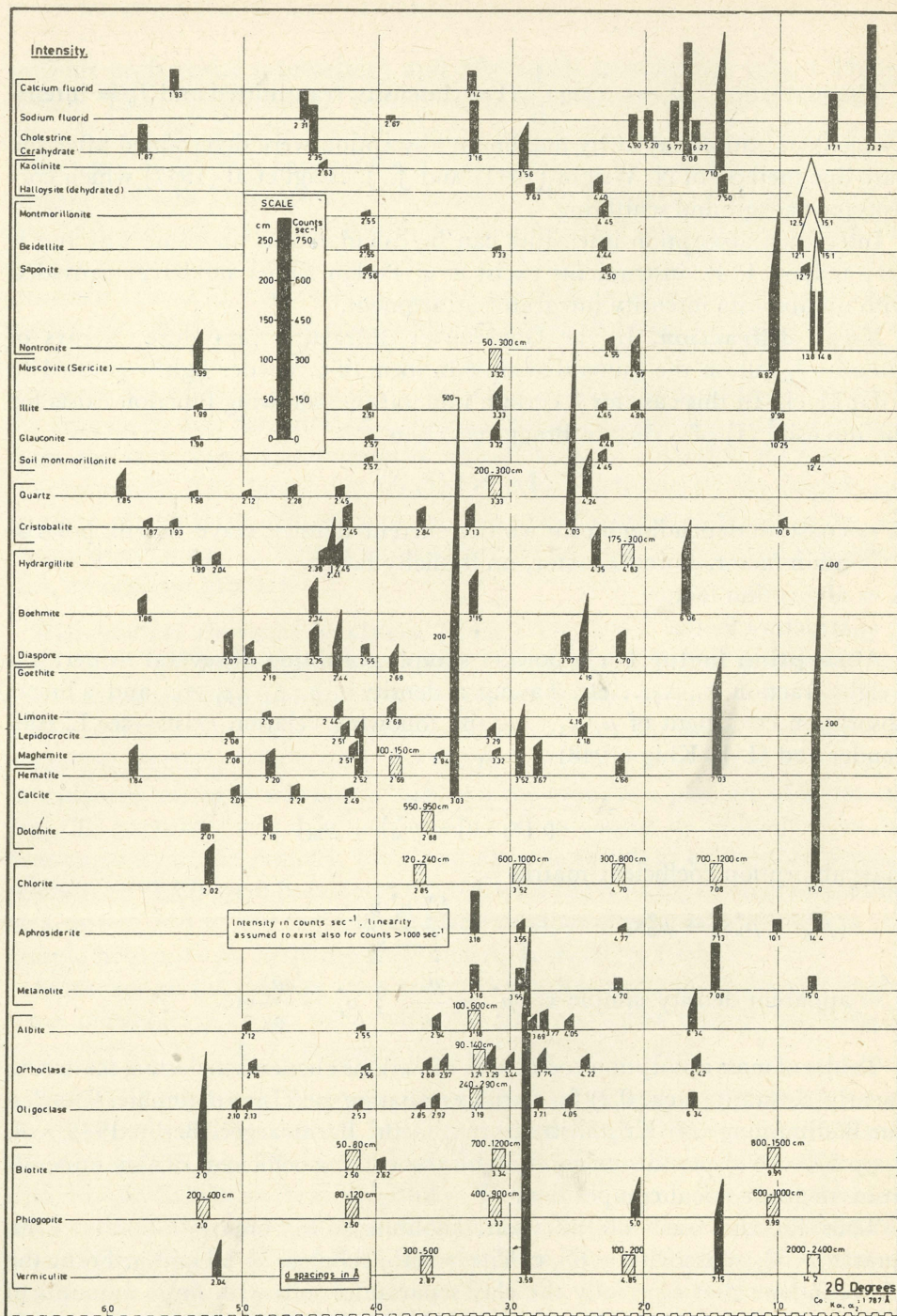


Figure 1: X-ray spectra of most common minerals in the clay separate ( $< 2 \mu$ ) of soils and some related minerals.



The only remedy is to dilute the samples with gum arabic (W. A. Mitchell, 1960) or with the standard mineral which is used for comparison in case the intensity will not become too weak. For quantitative determinations of clay minerals the Cerahydrate (artificial  $\gamma$  AlOOH) standard of O. G. Griffin (1954) was chosen. It has a  $\mu/\rho$  of 44 and its most intensive reflection  $d = 6.06 \text{ \AA}$  (020), is situated just the most near to that of the basal spacings of the various clay minerals figure 1. The latter are the most suited for quantitative determinations because they are the less overlapped. Other recommended standards like NaF,  $\text{CaF}_2$  and cholesterine are less suited because their  $\mu/\rho$  is quite different ( $\text{CaF}_2 = 145$ , cholesterine = 6) or their reflections are too far from those of the characteristic spacings of the clay minerals ( $\text{NaF}$  and  $\text{CaF}_2$ ). Isomorphous substitutions of atoms in the structure of clay minerals, which vary largely in their mass absorption, will also give large differences in the intensity of the reflected rays. Isomorphous substitutions of Fe/Mg and Al/Fe in the basic structure are very common in the illite, montmorillonite and chlorite-group of clay minerals. Appreciable differences in the absorption coefficient of a mineral result also from isomorphous substitutions of exchangeable  $\text{Ca}^{++}$  or  $\text{Mg}^{++}$  for  $\text{H}^+$  in clay minerals with a high cation exchange capacity (Montmorillonite, soil montmorillonite, expanded illite). Interlayering of  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})^{++}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})^{++}$  between expanded layers of illite and soil montmorillonite, will also change the intensities of the reflections appreciably, because the minerals which are found in nature are neither of constant composition.

**Structure factor (F).** The scattering power per unit cell (structure factor) depends in first instance on the atomic scattering power (F) i. e. the intensity of scattering of a single atom relative to that of a single electron placed at the nucleus. Tables of this ratio (which depends on  $\sin \theta/\lambda$ ) for several atoms (and ions) but not corrected for temperature, are given in Internationale Tabellen zur Bestimmung von Kristallstruktur, Gebrüder Borntraeger, Berlin, Vol. 2, pages 571—573. Thus f. i. for small angles ( $\sin \theta/\lambda = 0.1$ ) is found (for atoms at rest at absolute zero): Li = 2.2, Na = 9.6, K = 16.5, Ca = 17.5, Mg = 10.5, Fe = 23.1, Rb = 33.5, Ba = 51.7, O = 7.1, Fe = 23.1, Al = 11, Si = 11.3, C = 5.2. Therefore also in this case the above substitutions of atoms (ions) or the interlayering of atom groups, will produce appreciable differences in the intensity of the observed Bragg reflections. The effect however will be just the reverse as that for absorption.

Table 1 shows the intensities of the basal spacings of expanded illite, montmorillonite and vermiculite when saturated with several kations. Large differences exist—see also I. Barshad 1950.

The structure factor further depends on the arrangement and distance between the atom (ions) in the crystal planes of the unit cell. In an ideal lattice



TABLE 1

Integrated surface of (001) spacing of vermiculite, expanden illite and montmorillonite relative to (020)-spacing of Cerahydrate (6.06 Å).

Exchangeable cation	Mass absorption coefficient $\mu/\rho$	Scattering factor $\text{Sin}\Theta/\lambda \cdot 10^{-8}$ ( $\Theta = \text{ca. } 5^\circ$ )	Surface (001) spacing of mineral relative to (020) spacing of Cerahydrate		
			713 Tetuan Vermiculite 80 % C. H.	592-Netherl. expanded illite 5 % C. H.	63-England Montmorillonit 10 % C. H.
Li	1.8	1.98	3.4	3.8	5.7
Mg	65	9.85	0.9	1.2	9.5
K	220	17.5	0.3	2.3	3.0
Ca	260	17.6	0.6	2.5	10.7
Rb	160	35.4	1.7	0.9	2.5
Ba	500	51.0	0.4	1.8	5.3
	Original sample		1.2	6.3	8.0

identical atoms occupy equivalent sites. Therefore slight differences in the arrangement of these elements (ions) caused by disorder or strain, will broaden the Bragg reflections especially at the higher angles. If the amount of these deviations are sufficient large, there is no loss of intensity because the effect can be measured by integration. In the other case there is a decrease in intensity because the effect cannot be discerned from background radiation.

The scattering intensity of an unit cell which consists of different atoms (ions) can be represented by the equation-see Internationale Tabellen 1935.

$$F = \sum f_0 \exp 2 \pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \text{ or:}$$

$$F = \sum f_0 \cos 2 \pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) + \sum f_0 \sin 2 \pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)$$

see for values of  $\cos 2 \pi (\dots)$  and  $\sin 2 \pi (\dots)$  for various space groups the "Structure factor Tables" of K. Lonsdale 1936.

In the ideal case of a perfect crystal (diamond)  $F$  stands in the intensity equation as  $F$ , but as  $F^2$  in case of an ideal imperfect = mosaic crystal. The latter consists of crystals each consisting of an aggregate of independently scattering ideal crystals. Most crystals however are of imperfect structure. Even for rock salt (M. Renninger, 1934) and quartz (J. Despujols 1957) wide variations are found in the intensity of their (200) reflections from one individual to another. Therefore slight differences in the order of perfection of the crystals will give large deviations in the intensity of the observed reflections.

Coarse crystallites lose diffracted radiation by secondary extinction (interaction of the incident and the reflected rays, entrapment of the rays in crevices, radiation prevented to reach lower crystals which are just in the position to give



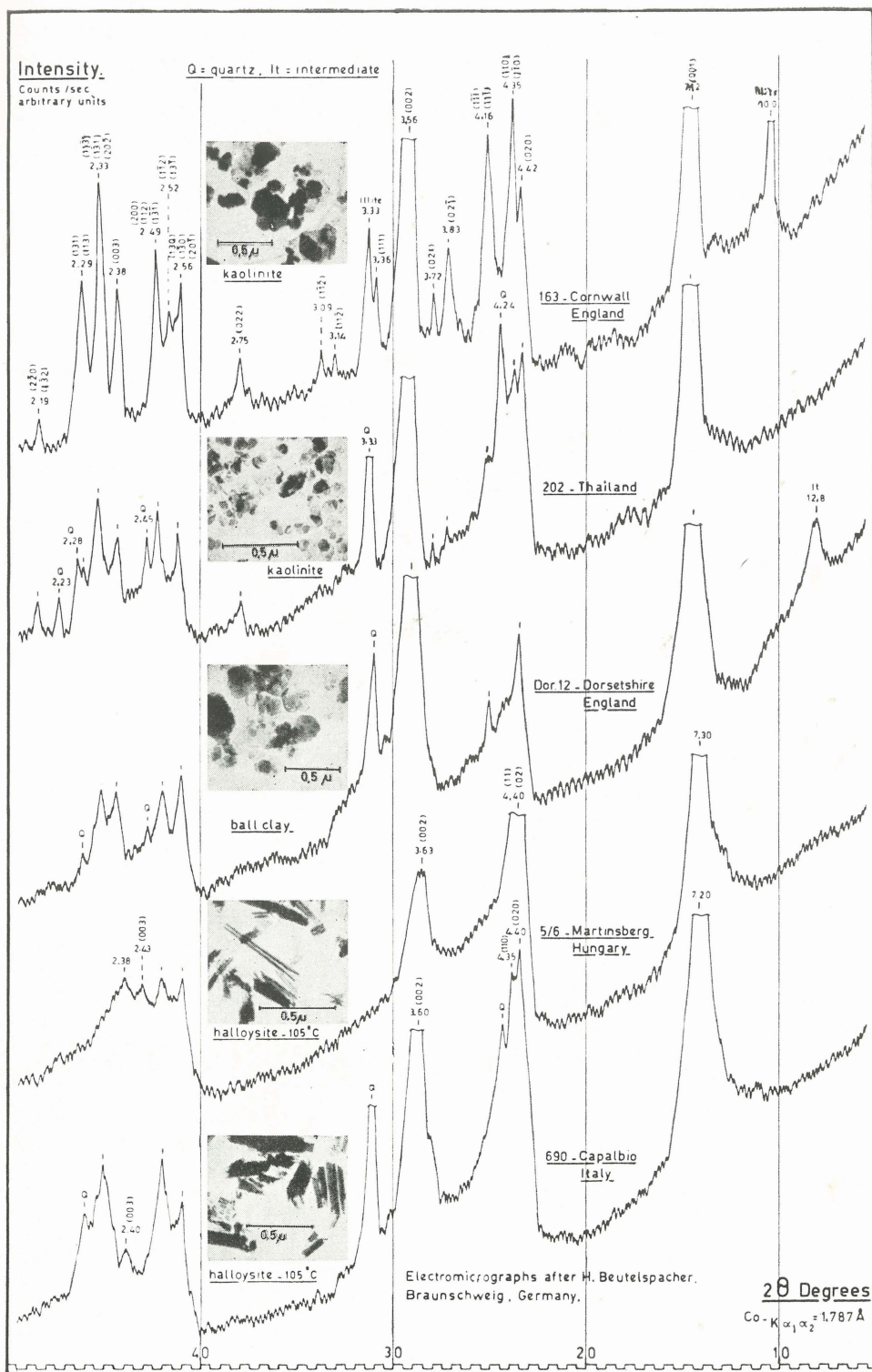


Figure 3: X-ray diffraction spectra of pure kaolinite, ball clay and halloysite (105 °C)—  
d spacings in Å.



a Bragg reflection by absorption in upper crystals). Rotating the samples gives only a slight improvement. Equations have been suggested to determine from the loss of intensity, the size of the particles — see literature.

If the crystallite size decreases below  $10^{-1}$  to  $10^{-3} \mu$  depending on absorption coefficient, crystallite size and shape, grade of distortion of the lattices, the Bragg reflections are broadened. This effect (which is directly related to  $1/\cos \theta$ , is caused by small deviations from the path of the mean diffracted X-ray direction, which are not ruled out or intensified by accumulation in successive underlying planes. Many theories and equations have been suggested to determine from the broadening of the reflections, the crystallite size of the sample—see literature. Line broadening means loss of intensity because too weak intensities cannot be measured and thus are identified as background.

TABLE 2

Integrated surface of most intensive reflection of powdered - and of clay minerals from various origin relative to that of Cerahydrate (6.06 Å) and of quartz (3.33 Å).

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



In table 2 is demonstrated the large differences which exist in the intensity of the Bragg reflections of several minerals among which also clay minerals. G. W. Brindley and S. Udagawa (1959) recommend to ground quartz power of 200 mesh,  $\frac{1}{2}$  to 1 hour in a mill before it can be used for quantitative analyses. After R. L. Gordon and G.W. Harris (1955), quartz particles of 3- to 30  $\mu$  give maximum intensity. If they are larger or smaller there is a decrease. However the intensities of the quartz reflections are not constant. They depend on particle size which is partly an extinction and partly an amorphous Beilby layer effect — G. Nagelschmidt et al. (1952), R. L. Gordon et al. (1952), S. S. Pollack et al. (1954), W. von Engelhardt (1955), C. Legrand and J. Nicolas (1958). The non uniformity of peak intensity and peak area of two pure quartz samples is also demonstrated in figure 2.

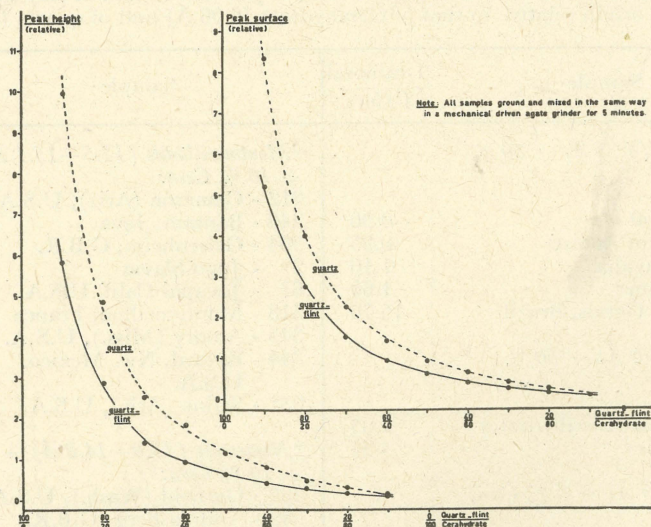


Figure 2: Peak height and peak surface of 4.24 Å reflection of pure quartz and of pure quartz-flint (white), relative to ditto of 2.34 Å reflection of Cerahydrate ( $\gamma$  AlOOH) for various mixtures.

Also, for cristobalite imperfect forms exist — L. D. Swindale (1955), O. W. Flörke (1955). The X-ray spectra of pure kaolinite from various origin show, that there are large differences in the intensities of the various samples — see figure 3 and the earlier research of W. von Engelhardt 1955. Badly crystallized kaolinite (ball clay from Dorsetshire and kaolinite from Thailand) cannot be distinguished from somewhat better ordered halloysite (Capalbio) — see for details: H. Beutelspacher and H. W. van der Marel (1961).

The  $d = 7.1$  Å reflection of kaolinite is still the best suited for quantitative analyses because of its large intensity and thereby being not overlapped by the



strong 3.33 Å reflection of quartz by which it is mostly accompanied in soils. By checking against the O. G. Griffin, 1954 cerahydrate ( $\gamma$  AlOOH) Standard, an inverse relation was found to exist between peak intensity or integrated intensity and the sp. surf. of kaolinite samples from various origin — H. W. van der Marel, 1960. The samples investigated contained after chemical analyses only 5 to 15 % impurities ( $\text{H}_2\text{O}^-$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Mn}_3\text{O}_4$ ) The results show (figure 4) that for fine kaolinite with a sp. surf. of about 70 m<sup>2</sup>/g, the decrease in peak intensity and integrated intensity was from 1.10 to 0.46 and from 1.50 to 1.0 (relative values) respectively as compared to that of kaolinite with a sp. surf. of about 16 m<sup>2</sup>/g. The latter are the most common found in many commercial deposits — (Cornwall, Mesa Alta, Bath Carolina, etc. — Zettlitz = 38 m<sup>2</sup>/g). The very fine ball clay from Dorsetshire, England

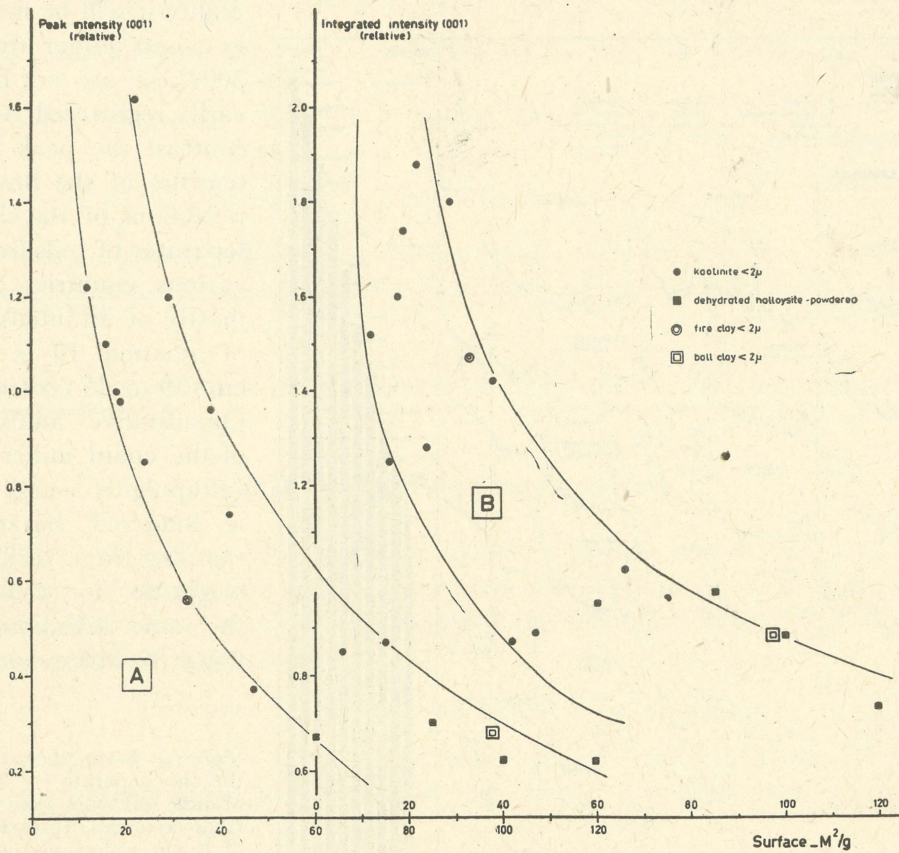


Figure 4: Peak intensity (A) and integrated intensity (B) of  $d = 7.09 \text{ \AA}$  (001) reflection of various kaolinites, dehydrated halloysite, fire clay and a ball clay relative to ditto of  $\gamma$  AlOOH.



and the various halloysites which have a sp. surf. of 60 to 100 m<sup>2</sup>/g have a peak intensity of only 0.28 to 0.22 (relative values) and an integrated intensity of only 0.95 to 0.73 (relative values).

Many authors have already attended on the large variability of the intensity of the Bragg-reflections of clay minerals. R. S. Dyal and S. B. Hendricks 1952, D. Schroeder 1954, O. G. Griffin 1954, R. L. Gordon and G. Nagelschmidt 1954, W. von Engelhardt 1955, Jarvis N. L. et al. 1957, H. W. van der Marel 1960. It is mainly caused by disorder in the crystal structure and an amorphous Beilby layer on the crystal surface. In figure 5 is demonstrated the large differences which exist between the intensities of the Bragg reflections of (common) well crystallized minerals and of soil clay minerals. Halloysite the most disordered clay mineral has the lowest intensity = about 60 to 75 cts/sec. Kaolinite has 300 to 525 cts/sec, calcite has 775 to 1500 cts/sec. Vermiculite has even 6000 to 7200 cts/sec. which equals with a peak height of 2000 to 2400 cm. In

reality it will be more as counts larger than 5000/sec., are not linearly registered. As a contrast the peak intensities of the Bragg reflections of the clay separates of soils from various countries are mostly of an intensity of maximal 10 to 15 cm (30 to 45 cts/sec.). Quantitative analysis of the chain minerals (attapulgite, sepiolite) is hindered because samples from various origin do not deliver the same reflections - figure 6. Meerschaum

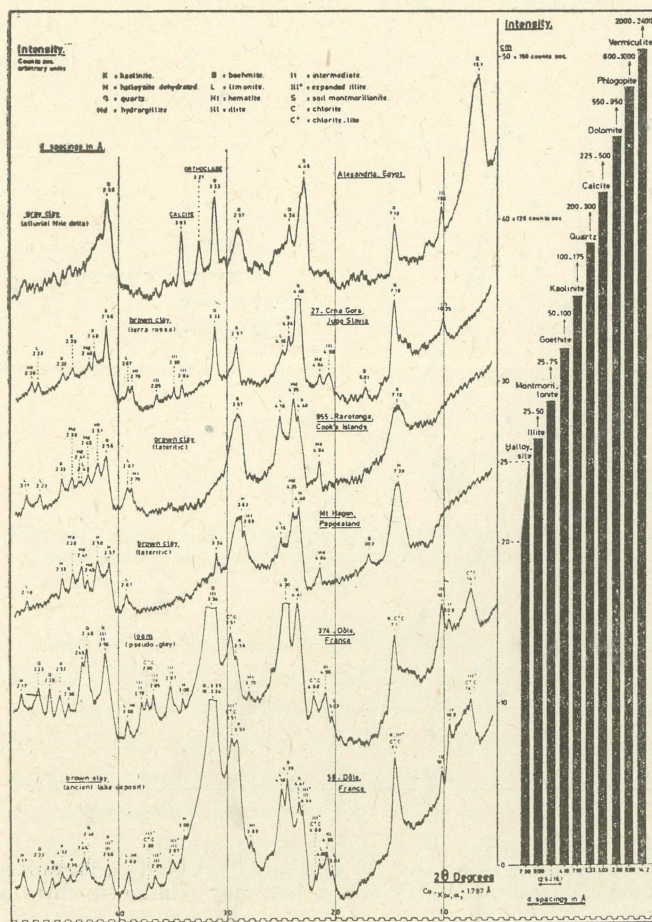


Figure 5: X-ray spectra of the clay separate ( $< 2 \mu$ ) of some soil types from various countries. Intensities of Bragg reflections compared with those of various minerals. Linearity assumed to exist also for counts  $> 5000/\text{sec}$ .



which contains very small and poorly developed fibers has its X-ray spectrum also the poorest developed — see also for the variability of sepiolites from various origin — J. Galan et al., 1958.

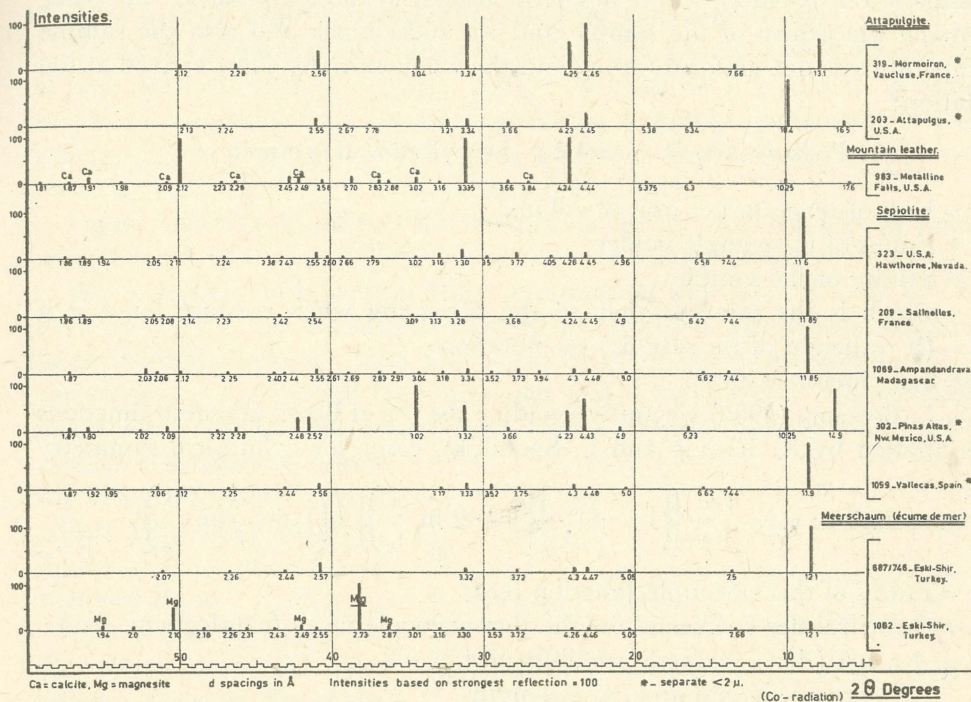


Figure 6: X-ray spectra of attapulgite mountain leather, sepiolite and meerschaum from various countries.

### 3) Differential thermal analysis

The peak area which is enclosed by the base line and the curve of the differential temperature ( $\Delta T$ ) as recorded versus initial time ( $t_1$ ) and final time ( $t_2$ ) of a thermal reaction, is related to the heat of reaction ( $\Delta H$ ) which is evolved during that process:

$$\text{peak area } (\int_{t_1}^{t_2} \Delta T dt) = \Delta H M / g \lambda \text{ — S. Speil 1945.}$$

$M$  = mass of sample (g);  $g$  = geometrical factor (cm) which accounts for temperature gradient distribution in the sample;  $\lambda$  = heat conductivity of sample (cal/deg. cm. sec.).

$$\text{Thus the "calibration factor" } (\psi) = \frac{\text{peak area}}{(\Delta H)} = M / g \lambda$$



R. Kronig and F. Snoodijk (1953) derived a theoretical formula for the relation of peak area and heat of transformation based on the physical character of the dissipation process of heat in the sample investigated during d. t. a. Dissipation of reaction heat is not proportional to the temperature difference between the centre of the sample and the nickelblock and also the sample temperature is not uniform throughout the whole sample. They arrived at the relation:

$$\text{Peak area} = L \rho a^2 / 4 \lambda \text{ — for cylindrical symmetry.}$$

$L$  = heat of reaction per unit of volume

$a$  = radius of the sample holder

$\rho$  = density of the sample

which is the same as that of the foregoing when reading for  $4 \pi h$  ( $h$  = height of the sample) the notation

$g$  = body factor of Speil.

S. L. Boersma (1955) elegantly avoiding the use of Bessel potential functions (as applied by R. Kronig and F. Snoodijk), came for cylindrical symmetry

$$\text{to the relation: } \psi = \frac{\rho a^2}{4 \lambda} \left\{ \left( 1 - \frac{r_0^2}{a^2} \right) \left( 1 + 2 \ln \frac{a}{r_0} \right) \right\} / \left( 1 + \frac{4}{\lambda} \ln \frac{a}{r_0} \right)$$

$r_0$  = radius of thermocouple junction (cm)

$\Delta$  = heat transfer coefficient for the thermocouple wires (cal/deg. cm. sec.)

=  $\Delta t \cdot A / l$  ( $\Delta t$  = temperature difference in  $^{\circ}\text{C}$ ,

$A$  = cross sectional area,  $C$  = length).

From the above follows that quantitative analyses are possible if ( $\Delta H$ ) is a constant for a certain clay mineral from various origin. Moreover  $\lambda$  for the clay samples and for the reference material (usually  $\alpha \text{ Al}_2\text{O}_3$ ) should also be constant during the whole 100 to 1000  $^{\circ}\text{C}$  trajectory.

The  $\lambda$  of the samples should neither vary with the packing density of the sample and uniformity of the particle size of the sample. But especially illite and quartz have a  $\lambda$  which differs considerably from that of  $\alpha \text{ Al}_2\text{O}_3$ , kaolinite and bentonite — G. Josselin de Jong (1957). This error can be avoided by diluting the sample with an excess of inert material, and then packing it to such a degree that its density and heat conductivity properties will be determined principally by those of the inert material. Thus heat transfer will remain unchanged during the analysis regardless of shrinking, sintering or liquefaction of the test material-dilution technique of R. W. Grimshaw and A. L. Roberts (1953). But by the large dilution, the thermal effect is largely decreased. Therefore it is better to place the thermocouples outside the sample holder instead of as usually, inside it. A further advantage in this case is that the thermocouple is not attacked by the sample when heated — Boersma d. t. a. principe (1955).



However the heat flow through the thermocouple wires is neither constant for various thermocouples. Variations to even 30 % were found — G. Josselin de Jong (1957). Thus quantitative determinations of clay minerals by calibration against well known chemical substances of constant heat of reaction, should be done with the same thermocouple and in the same sample hole.

However the thermal effect (heat of reaction) of a sample when heated and as measured from  $dt/T - (dH)$ ,  $dp/T - (\Delta F)$  or  $dk/T - (\Delta E^*)$  measurements is not constant for a certain clay mineral. It will be the largest when the mineral occurs in its most ordered state. In nature there is a strive to the most ordered crystal structure e. g. the highest crystal energy.

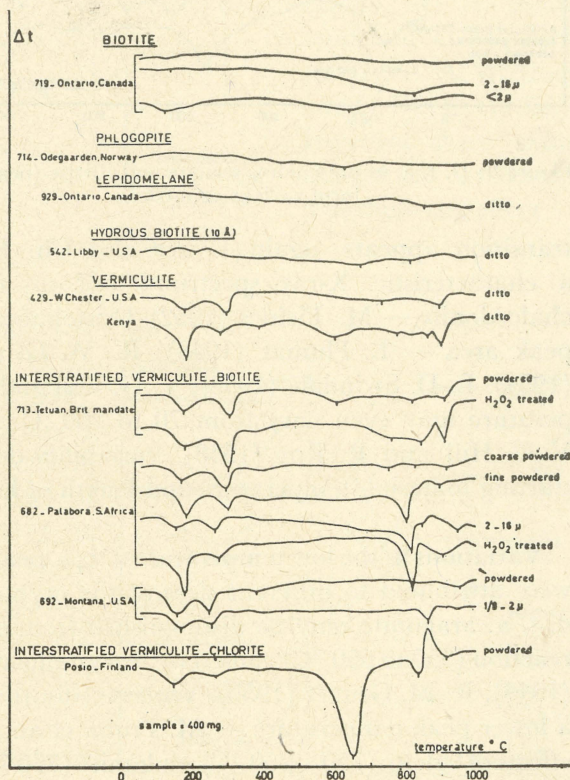
Figure 7 shows that the thermal effect of the loss of structural OH by biotite when heated, is small and thereby smeared over a large tract.

When ground, this thermal effect is somewhat increased. The d. t. a. of vermiculite or of the vermiculite-chlorite interstratified minerals do not show large thermal reactions either. The peaks at 150 to 220 °C and 250 to 325 °C are caused by interlayered  $H_2O$  molecules and by interlayered  $H_2O$  molecules coordinated around Mg respectively. The latter molecules therefore are of zeolitic character. By grinding or by  $H_2O_2$  the thermal effects are largely changed. These minerals show a particle size effect.

The d. t. a. of muscovite also show the particle size effect — figure 8. The shape and the peak intensity is not similar for sericite and illite samples from various origin. The same holds for montmorillonite-beidellite saponite and nontronite — figure 9. And for glauconites and celadonite — figure 10.

By the d. t. a. method quartz and cristobalite can be distinguished from each

Figure 7: D. t. a. of biotite, phlogopite, lepidomelane, hydrous biotite, vermiculite, interstratified vermiculite-biotite and interstratified vermiculite-chlorite from various origin.





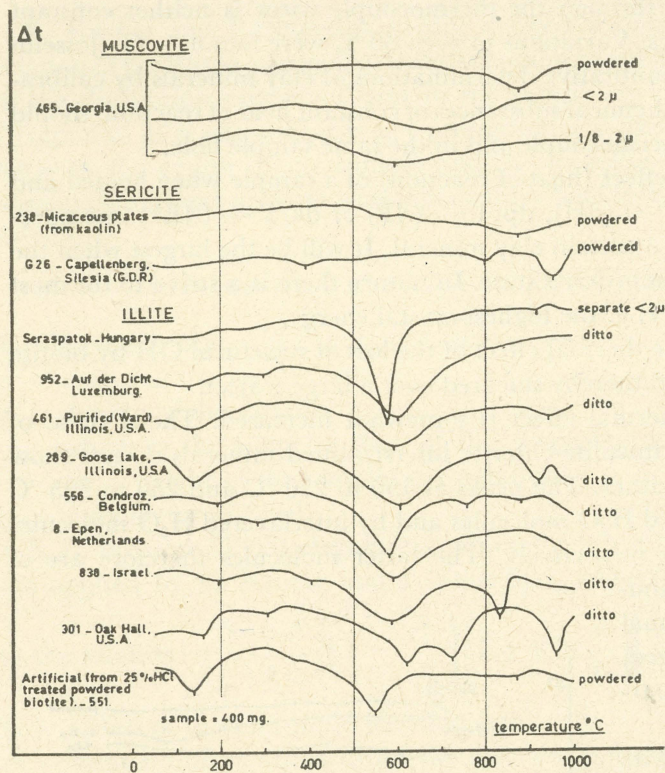


Figure 8: D. t. a. of muscovite, sericite and illite (nearly pure) from various countries.

the transition appears again — see also Ch. R. Pelto (1956). Quartz with a characteristic X-ray spectrum, but no thermal effect is indicated as chalcedonite — M. Fieldes (1952) Cristobalite also shows wide variations in peak area — E. Plumet (1948), R. W. Grimshaw (1953), M. J. Buerger (1954), L. D. Swindale (1955), V. G. Hill and R. Roy (1958). The peak temperature may even vary from 70 to 260 °C — O. W. Flörke (1955). After V. G. Hill and R. Roy (1958), variability depends on the structure of the starting material, temperature and length of heat treatment.

Variations in the low temperature d. t. a. peaks of opal (rigid silicic-hydrogel) were attributed to different sizes of the cryptopores — J. Konta (1952). By d. t. a. aragonite may be distinguished from calcite by the small exothermal reaction (350 to 550 °C) caused by recrystallization to calcite — M. Pruna et al. (1949), R. M. Gruver (1950). Vaterite (disordered calcite) has this reaction at a lower peak temperature — M. Pruna et al. (1949). The other endothermal effects of calcite (750—960 °C), dolomite (760—825, 800—920 °C) and magne-

other by their transition reactions  $\alpha/\beta$  quartz = 573 °C, and ca. 4 cal/g  $\alpha/\beta$  cristobalite = 230—270 °C and ca. 3.5 cal/g — R. W. Grimshaw and A. L. Roberts. (1953). However the transition effect of quartz may be largely decreased and even suppressed in fine grained crypto-crystalline forms — L. H. Berkelhamer (1944), O. F. Tuttle (1949), H. G. Midgley (1951). After M. L. Keith and O. F. Tuttle (1952) it is caused by crystal defects from which a strained lattice at both sides of the boundary results. When the mineral is powdered the



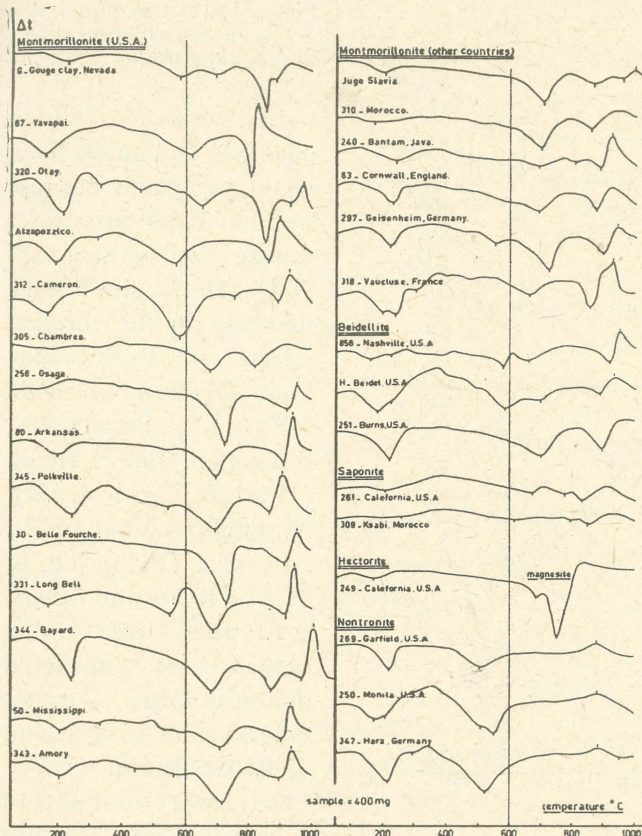


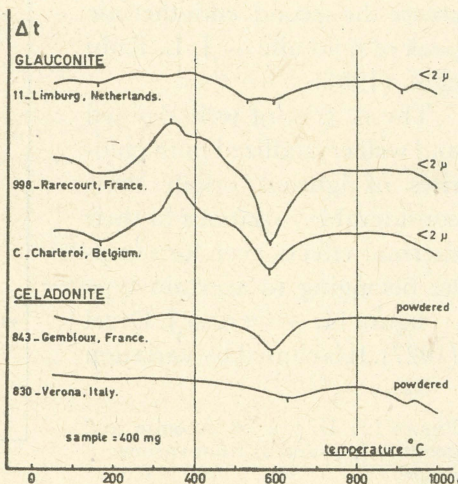
Figure 9: D. t. a. of separate  $< 2 \mu$  of montmorillonite, beidellite, hectorite and nontronite from various countries.

site (500—690 °C) are large = 400—440, 85—125, 185—235 and 300—320 cal/g respectively.

The overlapping of the double dolomite peak may be decreased and therefore peak area measurements more accurate by analysis under  $\text{CO}_2$  pressure — R. A. Rowland and D. R. Lewis (1951), R. A. Rowland and C. W. Beck (1952), R. A. W. Haul and H. Heystek (1952). However there exists also for the carbonates a particle size effect —

see for calcite J. L. Kulp et al. (1951), C. M. A. De Bruyn and H. W. van der Marel (1954), Th. L. Webb (1958); for dolomite G. T. Faust (1948), D. L. Graf (1952), W. F. Bradley et al. (1953). After Th. L. Webb (1958) differences in particle size may give for calcite a variation of 40 %, for magnesite of 50 % and for dolomite even of 60 %. It was furthermore found that pure calcites from various countries, but ground to about the same particle size ( $< 149 \mu$ ) delivered a peak area which

Figure 10: D. t. a. of glauconite and celadonite, from various origin.





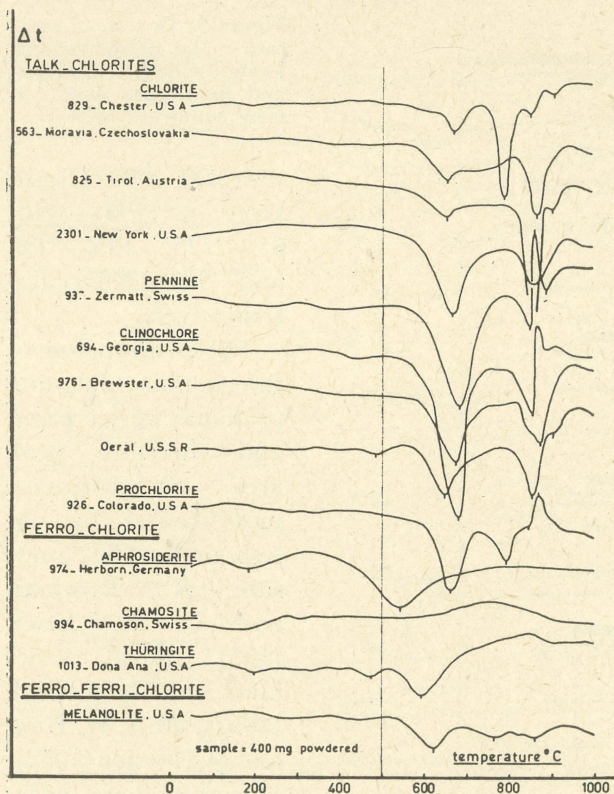


Figure 11: D. t. a. of pure minerals of the chlorite-group from various origin.

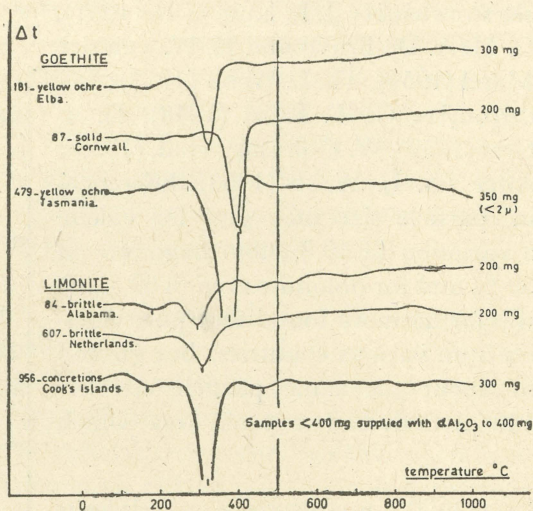
varies between 62.8 to 80.8 cm<sup>2</sup>. Dolomites show wider variations because small included impurities during their genesis f. i. NaCl, MgCl<sub>2</sub> give a large decrease in the thermal effects — P. P. Budnikov and D. P. Bobrovnik (1938), L. G. Berg (1943), S. Caillère and S. Hénin (1948), D. L. Graf (1952), M. Földvári-Vögl and V. Koblencz (1955), Th. L. Webb (1958) and others.

Another cause is the existence of disordered dolomite forms — protodolomite - D. L. Graf and J. R. Goldsmith (1956). Lastly small amounts of calcite decrease the first

peak — H. H. Heady (1952), and small amounts of Fedecrease the second endothermic peak of dolomite — J. L. Kulp et al. (1951).

The d. t. a. of well defined and well crystallized pure chlorites of igneous origin show considerable variations in their thermal effects, even for samples belonging to ascertain type — figure 11. — see also J. Orcel (1927). It is caused by variation

Figure 12: D. t. a. of limonite and goethite (powdered) from various origin.





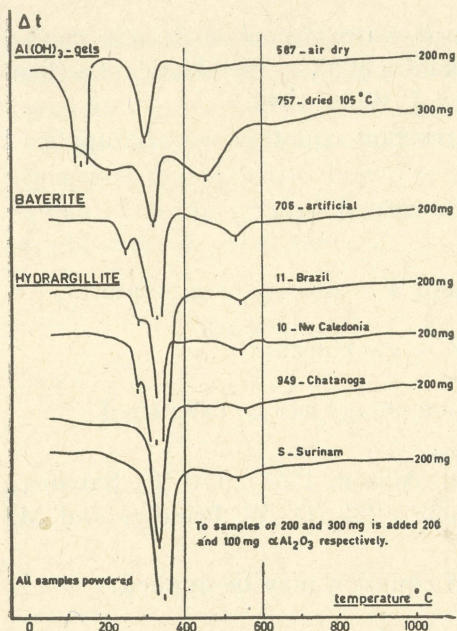


Figure 13: D. t. a. of  $\text{Al}(\text{OH})_3$  gels, bayerite and hydrargillite from various origin.

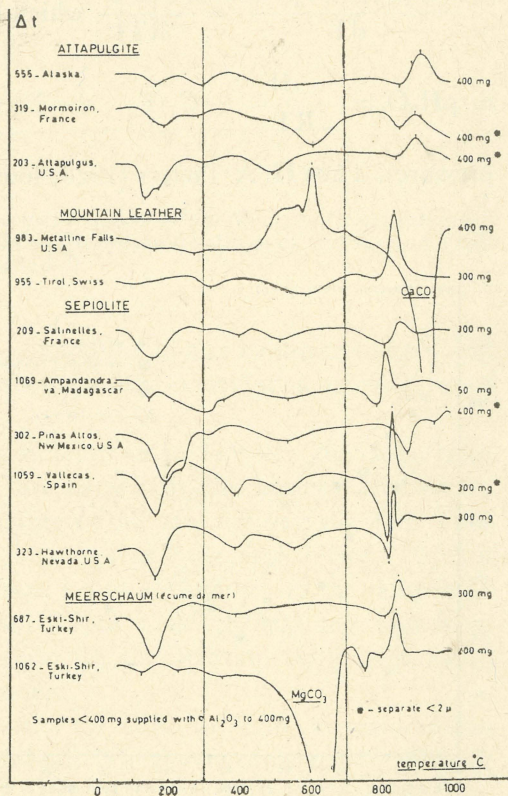
in the chemical composition especially of Fe and Mg. These chlorites thereby show a large particle size effect — see also Sabatier (1951).

The d. t. a. of goethite and limonite from various origin, show wide variations in their thermal effects — figure 12; see also J. L. Kulp and A. F. Trites, 1950, W. C. Kelly, 1956, U. Schwertmann, 1959. In addition the hydrargillite samples from various origin have their weaker 280 °C and 550 °C peaks — the first resulting from bayerite and the latter

from boehmite decomposition, more or less pronounced — figure 13; see also K. Sasvári and J. Hergedüs 1955 and K. Sasvári and A. Zalai 1957.

The d. t. a. of attapulgite and sepiolite which minerals may be found to occur in the clay separate of soils in acid climates associated with dolomite, magnesite and serpentine, also show wide variations in the thermal effects in each group — figure 14. They are caused by loss of absorbed water, zeolitic water, structural OH and recrystallization effects which are not sharp but smeared over a large tract. The loss of structural OH groups from kaolinite when heated, can be considered

Figure 14: D. t. a. of attapulgite, mountain leather, sepiolite and meerschaum (powdered) from various countries.





to follow, if it is not disturbed by entrapped water vapour such as in coarse crystallites — G. W. Brindley and M. Nakahira 1957 — the kinetics of a (first order) chemical reaction — P. Murray and J. White 1949.

For thermogravimetric analyses the Arrhenius equation may be applied:

$$\frac{d \ln k}{dT} = \frac{-\Delta E^*}{RT^2} \text{ which becomes in its integrated form:}$$

$$\ln k = \frac{-\Delta E^*}{RT} + C \quad (k = \text{rate constant, } T = \text{absolute temperature}),$$

$E^*$  = activation energy (cal/mole),  $R$  = gas constant

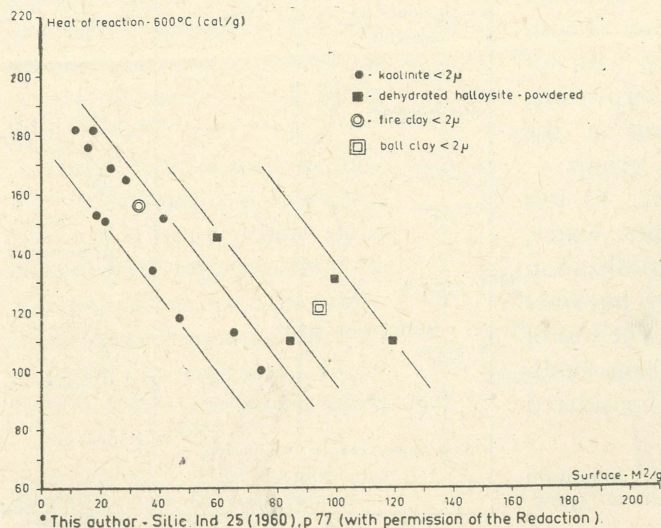
By a plot of  $\log k$  versus  $\frac{1}{T}$  the activation energy can be calculated.

Thus for kaolinite was found 213 (E. B. Allison, 1954), 170 (G. Sabatier, 1955), 173 (P. Murray and J. White, 1955), 252 (G. W. Brindley and M. Nakahira, 1957) cal/g.

For volumetric analyses the Van't Hoff equation may be applied:

$$\frac{d \ln p_{H_2O \text{ vapour}}}{dT} = \frac{-\Delta F}{RT^2} \text{ which becomes in its integrated form:}$$

$\ln p_{H_2O} = \frac{-\Delta F}{RT} + C$  ( $F$  = the Free energy of formation,  $p$  = vapour pressure). Thus H. A. Pieters (1928) found 300 cal/g for kaolinite.



By calibration of the peak areas of kaolinite against those of substances of well known heats of reactions, I. Barshad 1952 found for the heat of decomposition of kaolinite = 253 cal/g. After the same method — H. W. van der Marel 1960 found for 85 to 95%

Figure 15: Heat of reaction (cal/g) of various kaolinites, dehydrated halloysite, fire clay and a ball clay, compared to their specific surface (M2/g).



pure kaolinites from various origin = 100—180 cal/g. Moreover the heats of reaction were inversely related to the sp. surf. of the samples investigated — figure 15.

A. R. Carthew 1955 found for 4 kaolinites of different origin, the slope ratio ( $\tan \alpha / \tan \beta$ ) to be linearly related to the ratio: peak area (A)/width of the peak at half its height (W). As furthermore the ratio A/W was proportional to the weight of the pure kaolinites which were analysed, it is supposed to be possible

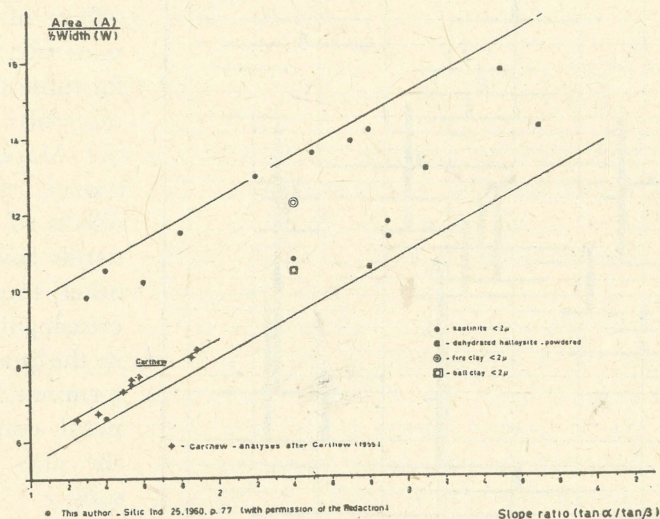


Figure 16: Quotient of the area of the endothermal reaction at 600 °C (in cm<sup>2</sup>) and the width of the peak at  $\frac{1}{2}$  of its height of various kaolinites, dehydrated halloysites, fireclay and a ball clay compared with their slope ratio ( $\tan \alpha / \tan \beta$ ).

to estimate quantitatively the amount of kaolinite in any kaolinite sample and also regardless of its surface area or perfection of the crystal structure (degree of ordering).

Figure 16 shows that only a rough relation exists between the slope ratio and the A/W quotient. These results, are caused by the larger variation in particle size and degree of crystal ordering of the samples investigated. Thus the calorimetric effect in the samples investigated here varied from 14.6 to 26.2 cm<sup>2</sup>/150 mg and the slope ratio from 1.3 to 2.9 against for the samples in the experiments of A. R. Carthew from 9.7 to 12.4 cm<sup>2</sup>/800 mg and from 1.25 to 1.88 respectively. The slope ratio for the relation A/W/slope ratio, however is the same for both investigations.

Figure 17 shows the thermal reactions of the most common clay minerals in soils and also those of some related minerals. They were obtained by diluting samples from various origin with  $\alpha$  Al<sub>2</sub>O<sub>3</sub> à 150 : 250 and calibration of the



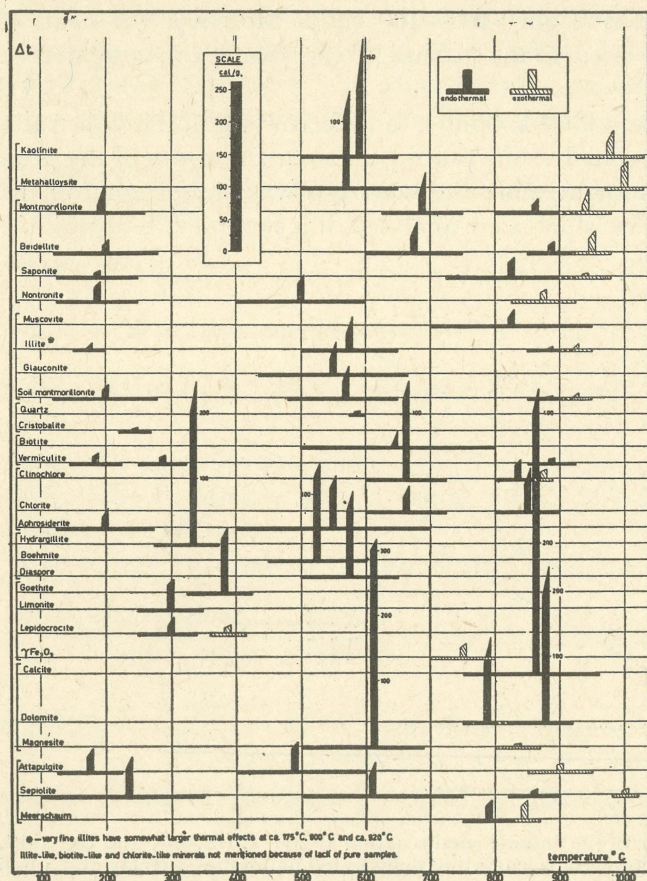


Figure 17: D. t. a. of most common minerals in the clay separate of soils and some related minerals (after De Bruyn and Van der Marel 1954).

#### 4) Infra-red-analysis

When a certain amount of energy is added to the atoms of a molecule or a crystal which are continuously vibrating at  $10^{13}$  to  $10^{14}$  Hz., they will absorb this energy when its level is of the same order as that of the energy of their own specific vibration level (resonance principle). For the ideal case of two free, highly symmetrical moving atoms, the following relation exists (R. B. Barnes et al. — 1944):  $h$  - Planck constant =  $6.62 \times 10^{-27}$  erg. sec.,  $E$  (vibra-

$$\text{tion}) = (n + \frac{1}{2}) \frac{h}{2\pi} \sqrt{\frac{f}{\mu}} \text{ (eV)}, f = \text{force constant between the two atoms}$$

$$\text{(dyne cm}^{-1}\text{)}, \mu = \text{the reducing mass} = \frac{m_1 \times m_2}{m_1 + m_2} \text{ (} m_1 = \text{mass atom } m_1 \text{ and } m_2 = \text{mass atom } m_2 \text{ in g.)}$$

peak areas against  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ . The latter delivers when losing 4 molecules crystalwater (between 100 to 180 °C) = 220 cal/g. Wide variations are found for the thermal effects of the various minerals; in particular for those of the kaolin minerals — H. W. van der Marel 1956. Moreover the thermal effects of various minerals overlap each other, thus further increasing the difficulties in the quantitative determination of the mineral composition of the clay separate of soils.



The vibration energy ( $E$  in eV) is mostly expressed in  $\text{cm}^{-1}$  ( $1 \text{ cm}^{-1} = 1/\lambda$  which equals  $1.986 \times 10^{-6}$  erg.).

From the above follows that in the ideal case, the vibration frequency of two atoms varies inversely with the root of their atomic mass. Thus if Al is substituted by Fe, the absorption band shifts to a lower energy level. Vibrational energy depends also on the bond force constant ( $f$ ) between the two atoms.

For atoms in tetrahedral configuration ( $\text{AB}_4$ ) the following relation is suggested — W. Gordy 1946:

$$\text{bond stretching force constant } (f_{\text{AB}}) = 3.29 \left( \frac{x_{\text{A}} x_{\text{B}}}{r^2} \right)^{3/4} - 0.40$$

( $x_{\text{A}}$  and  $x_{\text{B}}$  = electronegativities,  $r$  = distance between atoms). Thus  $f$  for Si-O and Al-O in tetrahedral configuration = 5.85 and  $5.06 \times 10^5$  dynes/cm respectively ( $r = 1.63 \text{ \AA}$ ,  $X_{\text{Si}} = 1.8 \text{ eV}$ ,  $X_{\text{Al}} = 1.5 \text{ eV}$ ,  $x_0 = 3.45 \text{ eV}$ .)

Consequently there will be a shift of the I. R. band to lower  $\text{cm}^{-1}$  values when Si has been increasingly replaced by Al.

However in reality the above equations give only a simple representation of what actually happens. For, a crystal consists of a frame work of densely compacted atoms and atomgroups. Thus the vibration energies of two atoms in a crystal may be damped and they depend moreover on the interactional forces of the atoms and atomgroups by which they are surrounded. For bending, wagging, rocking, twisting, etc. vibrations the calculations of the vibrational energies are very complicated. Apart from the fundamental and their weaker combination and overtone vibrations ( $\text{CO}_2 : \nu_1 + \nu_2 = 3716 \text{ cm}^{-1}$ ,  $2\nu_2 + \nu_3 = 3609 \text{ cm}^{-1}$ ;  $\text{H}_2\text{O} : 2\nu_1 = 7251 \text{ cm}^{-1}$ ,  $3\nu_1 = 10631 \text{ cm}^{-1}$  and  $\nu_1 + \nu_3 = 533 \text{ cm}^{-1}$ ) which result from a certain configuration of atoms, also other vibrations of somewhat higher or somewhat lower energy level exist. These result from perturbations by neighbouring atoms, crystal defects, strain, Doppler effects, interaction with skeletal vibrations of low level, vacant holes, isomorphous substitutions of incident character. The effect is a broadening of the bands.

The intensity of an absorption band depends on the energy of the dipole moment ( $\mu$ ) of the atoms or the atomgroups during their vibrational movements. Therefore the absorption band of HCl is stronger than that of HJ [ $\mu \times 10^{18} = 1.03$  and  $0.38$  (e. s. e.  $\times \text{cm}$ ) respectively].

Also in this case the surrounding atoms and atomgroups have influence on the intensity of a certain vibration between two atoms. Thus the O-H stretching band of phenol decreases to 1/3 of its original intensity and its energy level is thereby lowered from ca.  $10400$  to  $10200 \text{ cm}^{-1}$  when benzaldehyd is used as a solvent instead of cyclohexanon — W. Lütke and K. Mecke (1949). The O-H stretching vibration is even absent in organics like m-nitrophenol, salicyl-



aldehyd and 2.6-dihydroxybenzoic-acid because the protons are in this case in a "chelated" position between two oxygen ions — Hilbert et al. 1935.

When particle size is larger than the wave length of the incident rays in this case = 2.6 to 24  $\mu$ , there will be a decrease of the intensity of the I. R. band because of reflection. However, this will not happen for the clay separate (< 2  $\mu$ ) of soils which are moreover ground in a vibration grinder with KBr before the I. R. analysis. A decrease of the intensity of the transmitted rays may be caused by Tyndall scattering of the rays by very fine particles. After A. H. Pfund 1934, ZnO particles of 0.088  $\mu$  diameter (specific surface = 400 m<sup>2</sup>/g when spheres) scatter rays of wave lengths from 0.4 to 2.4  $\mu$  following Rayleigh equation after which intensity of scattering is inversely related to the 4th power of the wave length.

Raleigh's scattering equation — see J. Valesek, 1949 ( $r < \lambda$ )

$$I_s = \frac{I(n^1 - n)^2}{n^2} \left( 1 + \cos^2 \Theta \right) \frac{\pi N V^2}{R^2 \lambda^4}$$

$I_s$  — intensity scattered rays;  $I$  = intensity incident rays

$n^1$  = refraction index of the scattering particles

$n$  = refraction index of the embedding medium

$V$  = volume of scattering particles

$N$  = number of scattering particles

$\lambda$  = wave length used

$\Theta$  = scattering angle

$R$  = distance from the sample to the observer.

Scattering was found to be negligible below a particle size of about 0.030  $\mu$  (sp. surf. = 1127 m<sup>2</sup>/g when spheres) as in this case the phase differences between the scattered rays are too small. Therefore only there will be some scattering effect at the higher cm<sup>-1</sup> wave numbers for the clay separate of soils which mostly have a specific surface of 15 to maximal 200 to 300 m<sup>2</sup>/g ( $r = 1\mu$  to maximal 0.09 to 0.05  $\mu$ ).

Absorption bands suited for quantitative analyses should be of high intensity and not be overlapped by neighbouring bands of other minerals. Moreover the base-line should be small in order to know the exact point where resonance absorption by specific groups in the crystal of the mineral has practically ended and background absorption caused by scattering and the conversion of radiation in unordered, thermal motion of the various crystal atoms, has commenced. But just because of the complicated nature of the absorption bands in clay minerals and to a lesser degree in the well defined common minerals, they are in contrast to those of liquids, and especially of gases, broad and thereby of low intensity — see figure 18. The same figure shows that the absorption bands of the clay separate of soils from various types are all broad, badly developed and thereby overlapping each other.



The I. R. bands of pure mono clay minerals and related minerals are somewhat better developed — see figure 19.

They show that quartz and cristobalite may be distinguished from each other by the  $780\text{ cm}^{-1}$ ,  $800\text{ cm}^{-1}$  and  $790\text{ cm}^{-1}$  bands. These bands are also the sharpest. Quartz amounts of 1% may thus be detected — J. M. Hunt and D. S. Turner, 1953.

The other bands (quartz =  $463\text{ cm}^{-1}$ ,  $696\text{ cm}^{-1}$ ,  $1084\text{ cm}^{-1}$ , cristobalite =  $478\text{ cm}^{-1}$ ,  $620\text{ cm}^{-1}$ ,  $1105\text{ cm}^{-1}$ ) are broad or they are thereby of small intensity (quartz =  $512\text{ cm}^{-1}$ ,  $1170\text{ cm}^{-1}$ , cristobalite =  $518\text{ cm}^{-1}$ ,  $1189\text{ cm}^{-1}$ ).

The existence of OH instead of O as is found in obsidians and perlites can be identified by a strong O-H stretching band at  $3430\text{ cm}^{-1}$  and absence of the O-H bending vibration at  $1636\text{ cm}^{-1}$ . By I. R. analysis calcite may be distinguished from aragonite by the  $888\text{ cm}^{-1}$ ,  $1430\text{ cm}^{-1}$  and  $859\text{ cm}^{-1}$ ,  $1480\text{ cm}^{-1}$  bands respectively. But aragonite is a rare mineral in the clay separate of sediments. Dolomite may be distinguished from calcite and magnesite by the  $726\text{ cm}^{-1}$ ,  $712\text{ cm}^{-1}$  and  $750\text{ cm}^{-1}$  band respectively. As only these bands are sharp and thereby not overlapped by others, they are the best suited for quantitative analyses. However there is a large decrease of the intensity of the incident rays by reflection and scattering and an increase in the intensity of the  $712$ ,  $888\text{ cm}^{-1}$  absorption bands (corrected for background) when the diameter of the calcite par-

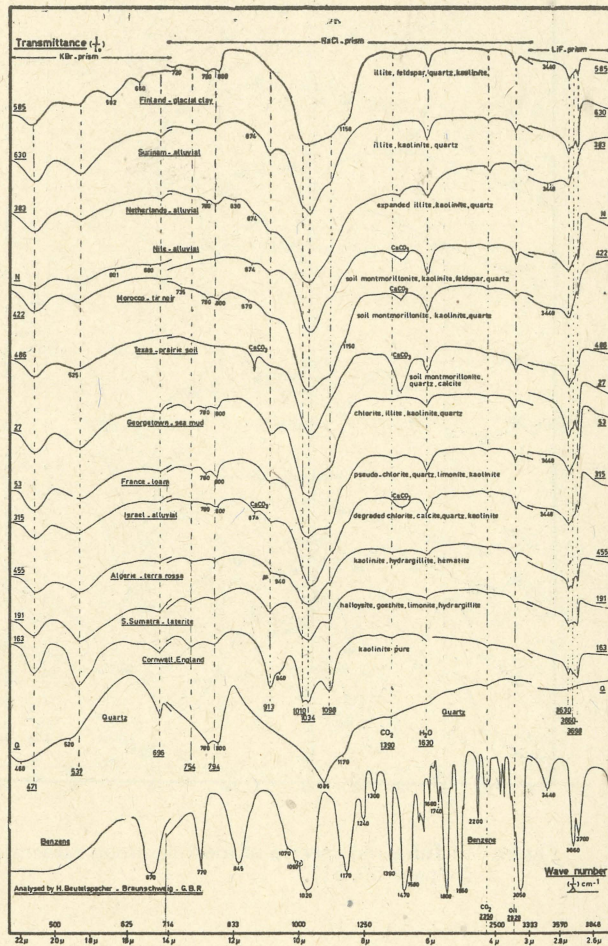


Figure 18: Infra-red spectra of separate  $< 2\text{ }\mu$  from various soil types and of benzene. Mineral composition in decreasing order of abundance.



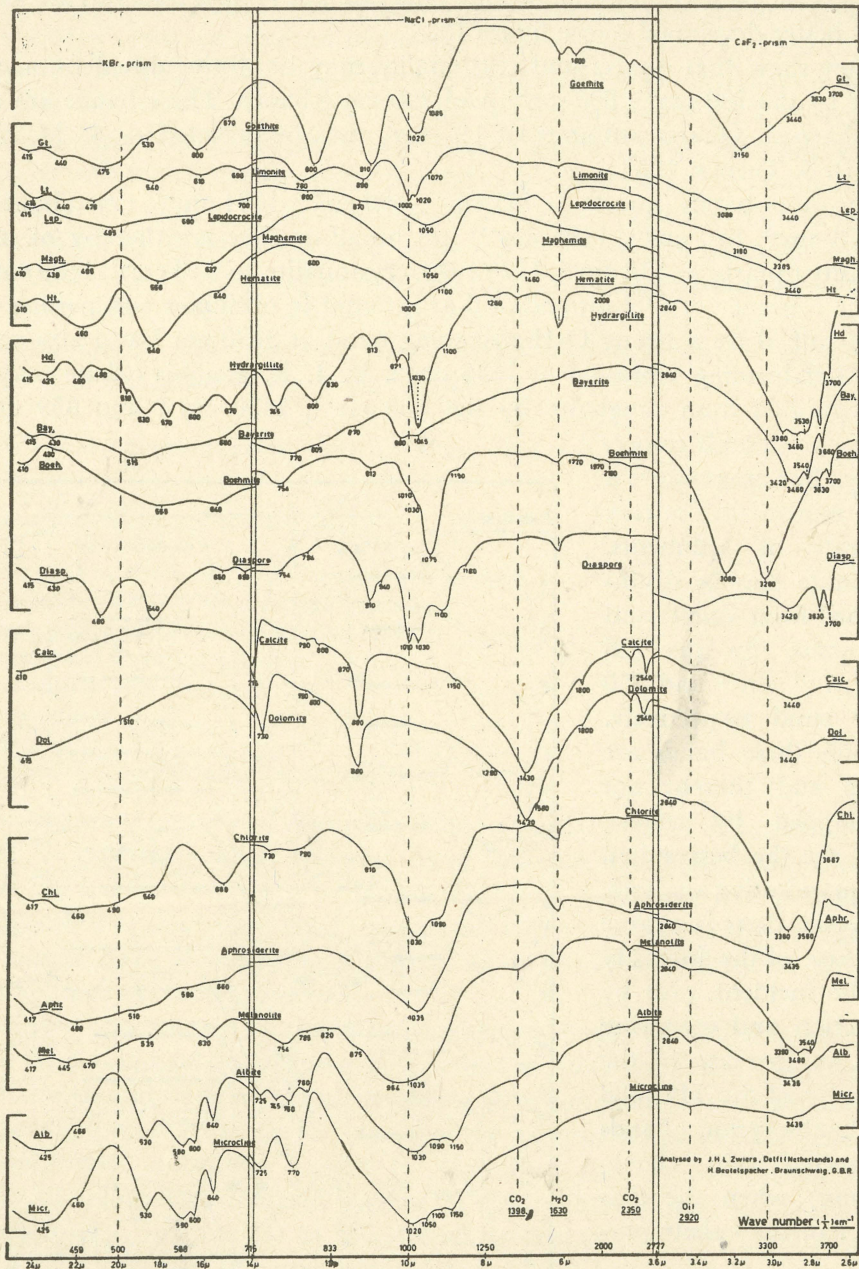
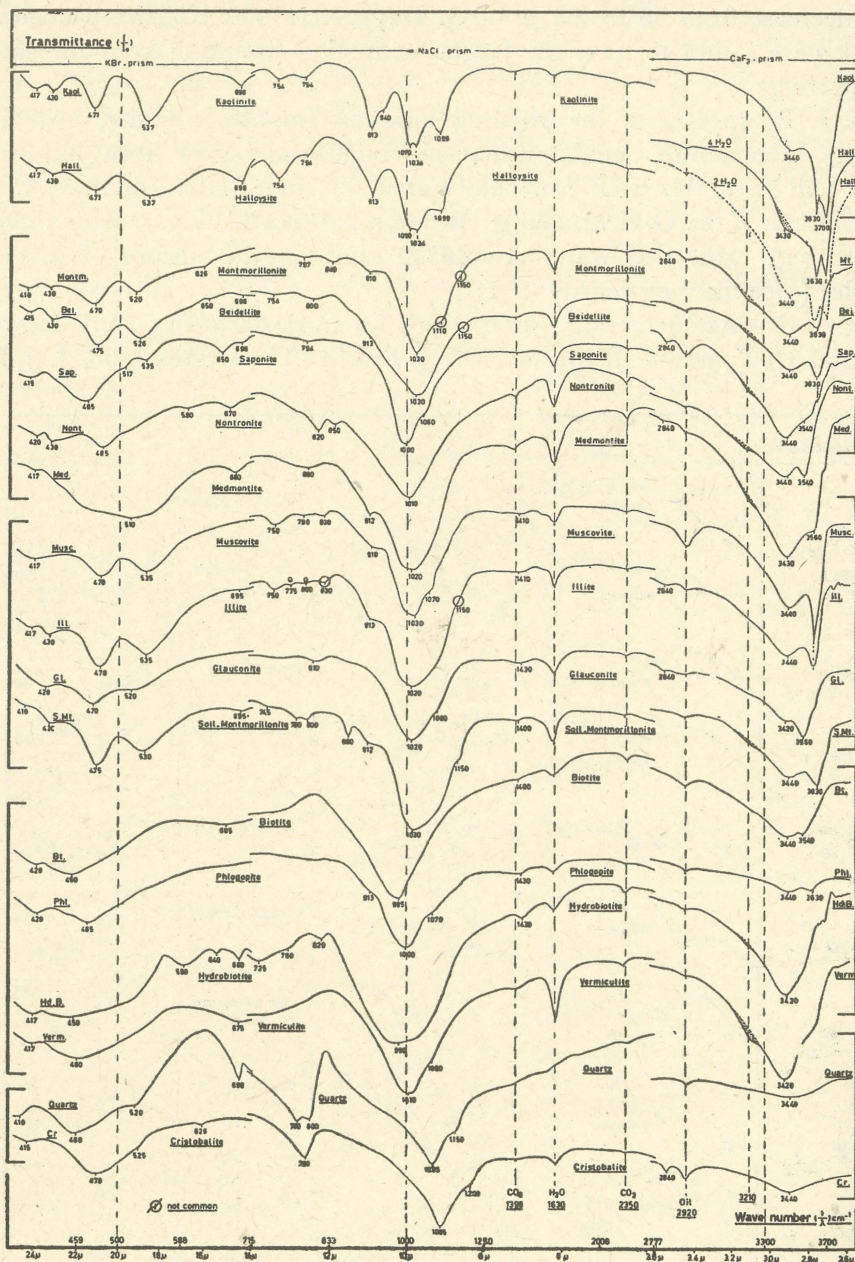


Figure 19: Infra-red spectra of most common minerals in the clay separate of soils (page 50, 51).







ticles decrease from 55 to  $2.1 \mu$  — G. Duykaerts 1959. Calcite particles of ca.  $0.1 \mu$  are found to have the largest extinction (resulting from absorption + scattering).

The I. R. spectra of the swelling minerals (montmorillonite, beidellite, saponite, nontromite, medmontite, soil montmorillonite) have all broad bands and thus this method is not suited for quantitative analyses. Very characteristic is the O-H stretching vibration band at  $3210 \text{ cm}^{-1}$  which results from strongly absorbed water (ca 40000 atm) on the surface of the clay particles („ice-like“ of density  $> 1$ ).

Absorbed water or crystal water yields an O-H stretching band between  $3500$  and  $3100 \text{ cm}^{-1}$  — J. Errera 1937, J. Errera and H. Sack 1938, J. J. Fox

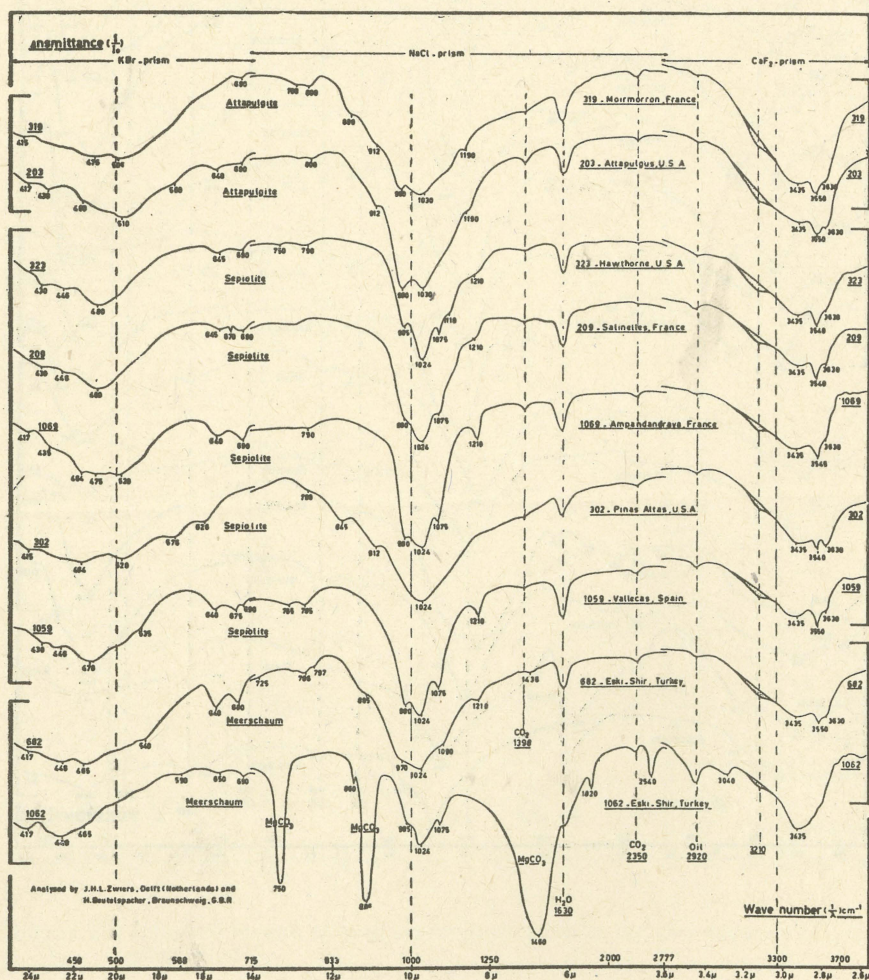


Figure 20: Infra-red spectra of attapulgite, sepiolite, and meerschaum from various origin.



The I. R. spectra of attapulgite, sepiolite and meerschaum show that sharp bands which just are needed for quantitative analyses are failing — see figure 20. Moreover for each group there are some differences in the  $\text{cm}^{-1}$  data of the several bands. Zeolitic and crystal water in the samples (see for the structural formulas of attapulgite — W. F. Bradley 1940 and that for sepiolite — B. Nagy and W. F. Bradley 1955, K. Brauner and A. Preisinger 1956, J. L. Martin Vivaldi and J. Cano-Ruiz 1953, 1956, A. Preisinger, 1959) is indicated by the O-H stretching bands at  $3120\text{--}3250\text{ cm}^{-1}$  (absorbed water has  $3430\text{ cm}^{-1}$ ).

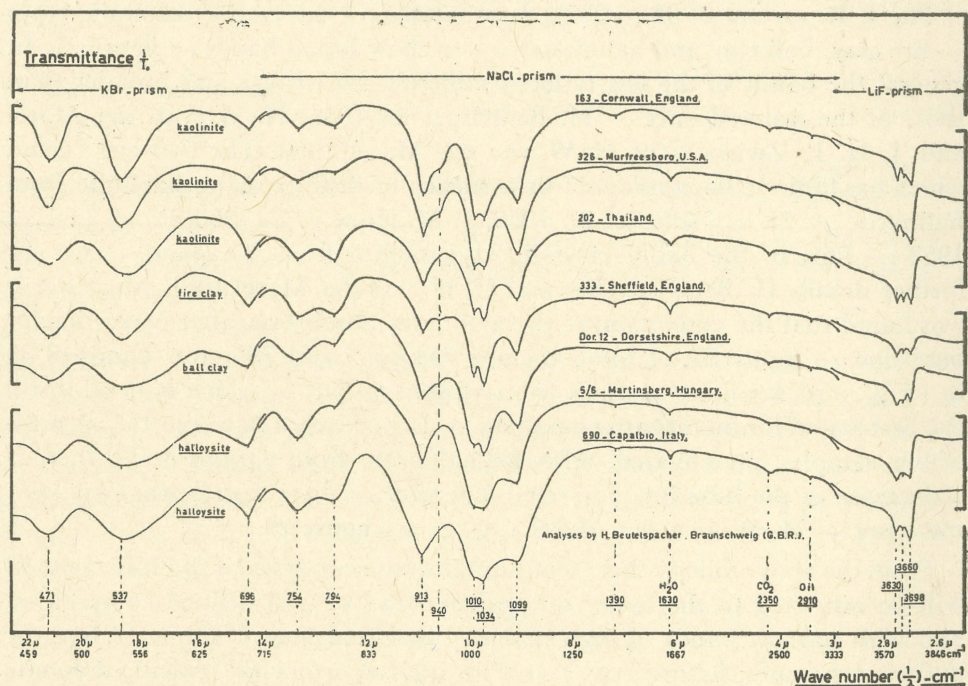


Figure 21: Infra-red spectra of kaolinite ( $< 2 \mu$ ), fire clay, ball clay ( $< 2 \mu$ ) and halloysite from various origin. — Beutelspacher and van der Marel 1961.



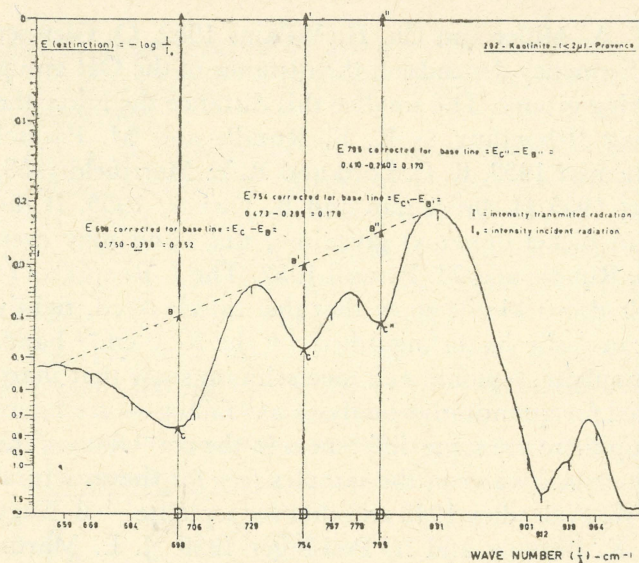


Figure 22: Correction of maximum extinction of 698  $\text{cm}^{-1}$ , 754  $\text{cm}^{-1}$  and 795  $\text{cm}^{-1}$  absorption bands of kaolinite (and halloysite), after the N. Wright 1941 and J. J. Heigl et al. 1947) procedure.

The I. R. spectrum of goethite is far better developed than that of the lesser ordered limonite. Bayerite, hydrazurillite and boehmite, common minerals in bauxite deposits may easily be distinguished from each other. Rather,

also in this case sharp bands which are not overlapped by neighbouring bands fail.

The I. R. spectra of 85 to 95 % pure samples of the various kaolinite types — fire clay, ball clay and halloysite — also show broad bands — figure 21. In general the bands of the less ordered minerals are weaker and broader than those of the ordered ones — H. Beutelspacher 1956, H. W. van der Marel and J. H. L. Zwiers 1959, H. W. van der Marel 1960. The 940  $\text{cm}^{-1}$  band which has hitherto be considered as a means of distinguishing kaolinite from halloysite — H. H. Adler et al. 1950, J. M. Hunt et al. 1950, Ph. J. Launer 1952 — fails in the badly crystallized kaolinite from Thailand — see for further details H. Beutelspacher and H. W. van der Marel 1961. Moreover it was found that the extinction at its maximum absorption after correction for base line — figure 22. of the 698  $\text{cm}^{-1}$ , 754  $\text{cm}^{-1}$  and 795  $\text{cm}^{-1}$  bands of 85 to 95 % pure kaolinite samples from various origin — which mineral is still the best suited for quantitative analyses — is inversely related to the sp. surf. of the samples investigated. Also for halloysite from various origin there is a decrease in the base line corrected intensity of these bands when sp. surf. increases — H. W. van der Marel 1960 — see figure 23.

From the above follows that (semi) quantitative analyses by the I. R. method will be restricted to the better ordered minerals of well defined composition and with narrow bands of high intensity and sharpness f. i. quartz, hydrazurillite, carbonates, sulfates, etc. — see for quartz, orthoclase, calcite, dolomite — J. M. Hunt and D. S. Turner 1953, for fluor apatite — R. B. Fischer and Ch. E. Ring 1957, for quartz — M. Gade and K. F. Luft 1959.



However a wide field of fruitful investigations in the study of crystal structure still remains for the I. R. method — H. Scholze and A. Dietzel 1955, L. A. Romo 1956, F. Laves and St. Hafner 1956 -- Beutelspacher 1956, J. M. Serratos and W. F. Bradley 1958, J. M. Serratos 1960, H. W. van der Marel and J. H. L. Zwiers 1959, W. M. Tuddenham and R. J. P. Lyon 1959, R. G. Milkey 1960, V. Stubican and R. Roy 1961.

## 5) Cation exchange capacity (C.E.C.)

The site of the power to exchange cations of clay minerals is mostly attributed to the existence of an electric double layer on the negative charged clay particles. After H. Helmholtz, 1879, the inner and the outer layer are closely opposite each other and thus form a condenser. M. Gouy 1910 and D. L. Chapman 1913, developed the theory of the diffuse double layer. The relation between the differential of the electric field and the net charge density in this diffuse layer at a certain point, can be represented by the Poisson—Boltzmann equation — E. J. W. Verwey and J. Th. G. Overbeek, 1948.

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi}{\epsilon} p = -\frac{4\pi}{\epsilon} C_k \exp.\left(-ve \frac{\psi}{kT}\right)$$

$\psi$  = electric potential in e. s. e. at a distance = x (cm)

p = net charge density at a distance x

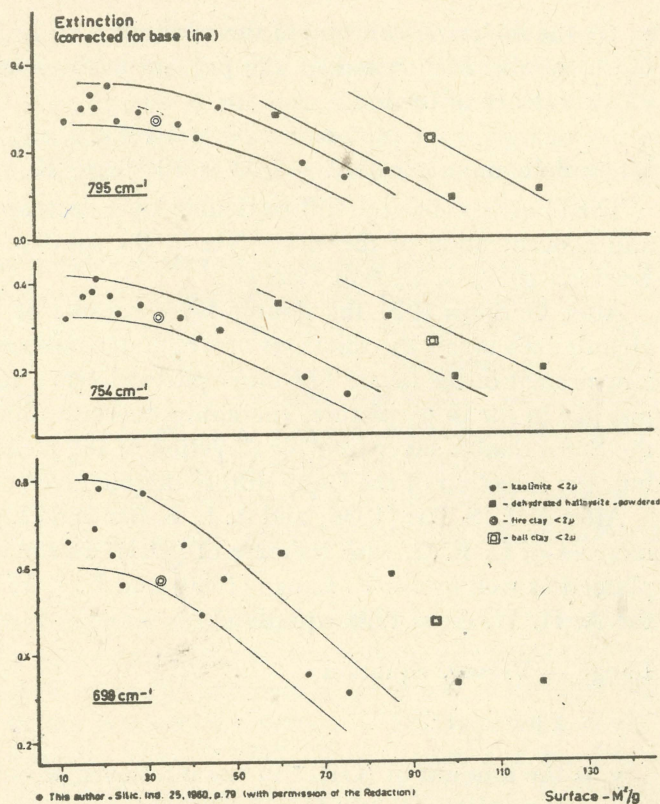


Figure 23: Extinction =  $\log \frac{I \text{ (intensity transmitted rays)}}{I \text{ (intensity incident rays)}}$  at maximum absorption of I. R. bands at 795  $\text{cm}^{-1}$ , 754  $\text{cm}^{-1}$  and 698  $\text{cm}^{-1}$  of various kaolinites, dehydrated halloysites, fire clay and a ball clay compared with their sp. surf. in  $\text{M}^2/\text{g}$ .



$\epsilon$  = the dielectric constant of the medium  
 $C_k$  = number of monovalent ions per  $\text{cm}^3$  in the solution  
 $v$  = valence of the ion  
 $e$  = charge of the proton =  $4.80 \times 10^{-10}$  e. s. e.  
 $k$  = Boltzmann constant =  $1.38 \times 10^{-16}$  erg/ $^\circ\text{K}$ .

The thickness of Gouys diffuse double layer decreases with increasing valence and concentration of the electrolyte in the solution — see for details A. E. Erickson 1952, G. H. Bølt 1955 etc.

After O. Stern 1924 the double layer consists of an inner part similar to Helmholtz's layer, the thickness of which depends on the volume of adsorbed ions present in the layer. The other part delivers a structure of the ion swarm just like in the Gouy picture. Increasing concentration in the solutions changes the Stern double layer into the direction of the Helmholtz layer and dilution into the direction of the Gouy diffuse double layer.

After A. L. S. Bär (1936) and A. L. S. Bär and H. J. C. Tendelo (1936) the increase of C. E. C. with increase of  $(\text{OH})^-$  in the outer solution can be explained as well by the E. Lange (1930) and E. J. W. Verwey (1934) — as by the A. H. W. Aten 1935 equation.

Lange — Verwey equation

$$y = k \log x + C$$

$y$  = the amount of  $(\text{OH})^-$  in the interlayer,  $x$  = the amount of  $(\text{OH})^-$  in the outerlayer and  $C$  = a constant.

Aten equation

$$\log \frac{cM}{cH} \times \frac{CH}{CM} = K_1 cM + K_2$$

$cM$  and  $CM$  = amount of exchangeable cations and of cations in the solution respectively.

$cH$  and  $CH$  = amount of exchangeable H ions and of H ions in the solution respectively.

For, a transport of  $(\text{OH})^-$  from the outer solution to the inner layer [inner layer consisting of  $(\text{OH})^-$  after Lange-Verwey] is the same as that of replacement of exchangeable H by K, Na etc. because of increased  $(\text{OH})^-$  concentration in the solution- (innerlayer charge = constant after Aten). Many authors have found the C. E. C./pH relation to exist for clay minerals — see also M. A. Cook et al. 1953.

Thus C. E. C. determinations should preferentially be done at a well defined pH. Acid solutions are not allowed because of adsorption of H ions which are only partly exchangeable. Neither are alkalic solutions allowed because of dispersing action of especially amorphous sesquihydroxides which than be-



come cation exchange active because of preferential  $(\text{OH})^-$  adsorption on an increased surface — H. W. van der Marel 1935. Therefore C. E. C. determinations will give the best reliable results if the salt solutions used are weakly acid, neutral or weakly alkaline and thereby buffered.

The negative charge on the surface of the clay particles may result from the following:

**a) Broken bonds and lattice distortions.** It is assumed that  $(\text{OH})^-$  of the outer solution is preferentially adsorbed at the broken Si-O, Al-O or Al-OH linkages which in turn attracts an exchangeable counter cation from the solution — K. Endell and P. Vageler 1932, U. Hofmann et al. 1934, U. Hofmann and W. Bilke 1936, A. L. Johnson and F. H. Norton 1942, A. L. Johnson 1949. After the last mentioned, each unit cell of montmorillonite and kaolinite contained after C. E. C. and particles size determinations (with the electron microscopie) about  $8.5 \times 10^{14}$  and  $7.8 \times 10^{14}$  bonds per  $\text{cm}^2$  of lateral surface which amounts were also expected to exist on theoretical calculations.

**b) Isomorphous substitutions with the lattice layers.** A negative charge on the surface of a clay mineral should result from substitution of trivalent Al for quadrivalent Si — in the tetrahedral layer and of divalent Mg (or Fe) for trivalent Al in the octahedral layer — L. Pauling 1930, W. K. Lewis et al. 1935, J. B. van der Meulen 1935, W. P. Kelley and H. Jenny (1936), C. E. Marshall 1935, E. A. Hauser and C. E. Reed 1937, G. Nagelschmidt 1938, R. E. Grim 1939 etc.

The counter ions balancing the negative charges should be stronger tightened for the tetrahedral substitutions in which they are nearest to the surface, than for the octahedral substitutions. If the interlayer charge thereby is large, such as for the mica minerals, the first will be strongly bond and become non exchangeable.

**c) Amorphous gels of silicic acid and aluminium hydroxide (iron-hydroxide) coating the surface of the clay minerals.** After S. Mattson 1931, the greater the acidoid/basoid ratio, the lower the isoelectric point, the greater will also be the cation exchange capacity and vice versa. From the experiments of J. M. van Bemmelen (1890, 1904, 1910), D. J. Hissink (1915), K. K. Gedroiz (1931), R. H. J. Roborgh (1935), it follows that after the removal of an easier HCl soluble part, a more resistant residue is left which is thereby of constant composition e. g. the unweathered crystalline kernel — see also L. D. Baver 1940. This residue thereby has a constant adsorption capacity when calculated on 100 g particles  $< 2 \mu = 45 \text{ me}$  (called the Way factor) by J. Hudig and R. H. J. Roborgh 1936. Also the amorphous artificial permutites deliver a fairly constant  $\text{SiO}_2 : \text{Al}_2\text{O}_3$  ratio = ca 3 : 1 when they are



made from different ratios of silicic acid and aluminium hydroxide = 1 : 1 to 1 : 20 — R. Gans 1913, A. A. J. von Sigmond 1915.

From the above follows that in contradiction to what is suggested in literature here and there, C. E. C. of a clay mineral is not a characteristic which can be used for its quantitative determination — see also R. E. Grim 1953. On the contrary, there exists a close relation between sp. surf. and C. E. C. as has been observed by several investigators. Thus A. L. Johnson and W. G. Lawrence (1942) found  $83 \text{ \AA}^2$  for kaolinite (spec. surf. estimated by electro-microscopy); M. M. Mortland (1954) and H. W. van der Marel (1960) found  $95 \text{ \AA}^2$  and  $67 \text{ \AA}^2$  for kaolinite (spec. surf. estimated after the Dyal—Hendricks ethylene glycol method). In this investigation was found after the same spec. surf. method  $73 \text{ \AA}^2$  for kaolinite, illite, glauconite, soil montmorillonite, montmorillonite and nontronite — see figure 24.

C. E. C. of the attapulgite and sepiolite samples is not related to their sp. surf. However, in this case of chain minerals with canals, the highly polarizable ethylene glycol molecules ( $\alpha_D = 4.86 \text{ \AA}^3$ ) are tightly bond to the inner surfaces. The same holds also but to a weaker grade for halloysite. Moreover the ethylene

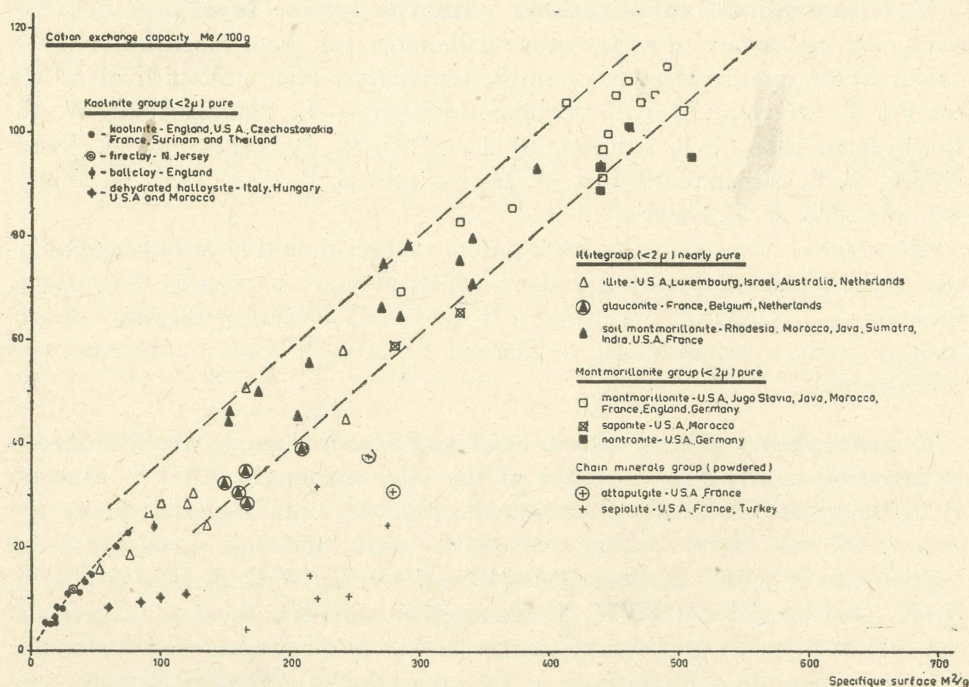


Figure 24: Cation exchange capacity (me/100 g) and specific surface (M2/g) of the clay separate (< 2 μ) of minerals of the kaolinite-, illite- and montmorillonite group and powdered attapulgite and sepiolite from various origin.



glycol molecules can even substitute crystal water molecules — J. Ottemann 1953. Thus for attapulgite sepiolite and halloysite a too large specific surface is found relative to their C. E. C.

From the above follows, that the suggestion of G. Beilby 1921, S. Mattson 1931 and J. Hudig and R. H. J. Roborgh 1936 about the existence of an amorphous layer of permutite-like structure and constant C. E. C. on the surface is the most substantiated by the experimental results. Apart from this phenomenon, coarse non clay minerals with isomorphous substitution of lower for higher valence cations like the vermiculites, can also exchange cations because they have on their surface points of weak negative charge. Also the expanded illites have these negative points but the C. E. C. resulting therefrom is only weak (after experience maximal = ca 15 % of their total C. E. C.) as against that resulting from the amorphous film which coats their surface.

The actual charge density on the surface of the amorphous layer should not be homogeneous but unequally distributed to explain the results of titration curves — see for kaolinite: A. K. Ganguly and S. K. Mukherjée 1951, R. P. Mitra and K. S. Rajagopalan 1952, R. K. Schofield and H. R. Samson 1953, J. R. Goates and K. H. Anderson 1955, for kaolinite and montmorillonite J. J. Fripiat et al. 1954, for beidellite R. M. Garrels and C. L. Christ. 1956. Also M. M. Mortland 1954 came to the same conclusion but from  $\Delta H$  absorption data of ammonia by montmorillonite. As a consequence cation exchange equations based on a homogenous double layer — Gapon 1933, Erikson 1952, Bolt 1955, can not be used to describe exchange reactions of the clay separate of soils over large trajects of cation concentrations.

## DISCUSSION

From the above examples it follows, that the quantitative determination of clay minerals in soils is a very difficult problem. Differences in the grade of structural ordening in the crystallites, and an amorphous (Beilby) layer of permutite-like composition covering the naked surface of the crystalline kernels of the clay particles, are the main factors which hinder quantitative analyses.

Other disturbing factors are amorphous organic and inorganic substances which may be found to large amounts in various soil types in addition to the clay mineral particles of crystalline composition — see for details: H. Beutelspacher and H. W. van der Marel — This journal.

The amorphous material hinders the short wave X-rays ( $\text{Co} = 1.787 \text{ \AA}$   $\text{Cu} = 1.5405 \text{ \AA}$ ) to reach the inner crystalline kernel because of large scattering. Heat conductivity of the sample is changed by this matter and thus the registered peak area of the d. t. a. is also influenced. The much longer



wave I. R. rays (2.5 to 24  $\mu$ ) are the least effected by these amorphous organic and inorganic material. But rather this method is the least suited for quantitative analyses because of absence of sharp well defined bands of high intensity in the various clay minerals.

At last the many stages which are found in nature between related minerals (f. i. illite and (expanded) swelling illite) and minerals formed by interleaving of brucite-like layers of sesquihydroxide composition in an (expanded) swelling illite or in a soil-montmorillonite (minerals most common in the clay separate of soils) is a further source of many difficulties. As a consequence of the bad defined nature of the above minerals, literature is overflowed at present with new names indicating certain minerals which were indentified by the authors named after a certain method.

In the following is given a brief example of the various minerals which belong to illite and the illite-related minerals. They were identified and classified by the X-ray method which in this case permits to distinguish various types. The d. t. a. and I. R. method fail here — See for the dta. method figure 25.

**I. Illite.** The indication illite was proposed by R. E. Grim et al 1937, for mica or sericite-like minerals as a general term, and not for a specific mineral of a certain structural type. Illites should differ from muscovite or sericite by a larger loss of  $H_2O$  on ignition, but a lesser contents of  $K_2O$ . Its structure should be  $KAl_2[(AlSi_3)O_{10}(OH)_2]_n H_2O$  — S. B. Hendricks and Alexander 1939. Earlier S. L. Galpin 1912 introduced the name hydromica for the same kind of mica.

Illites mostly occur as 1 M structure but when poorly ordered = degraded illite — S. B. Hendricks and E. Teller 1942, they have 1 Md (randomly stacked one layer monoclinic) — H. S. Yoder and H. P. Eugster 1955. Illite from Fithian Illinois = 1 Md + 2 M, from Gilead Illinois = 2 M, from Ballater = 3 T — H. S. Yoder and H. P. Eugster 1955.

Other names: Hydromica — S. L. Galpin 1912 — H. V. Anderson and K. G. Chesley 1931 — D. M. C. Mac. Ewan 1951 — J. Erdélyi et al 1957, A. A. Levinson 1955. Potassium bearing clay mineral — C. S. Ross and P. F. Kerr 1931. Sericite-like mineral — R. E. Grim et al 1937. Glimmerton — K. Endell et al 1935. Glimmerartige Tonmineralen — E. Maegdefrau and U. Hofmann 1938. Clay muscovite — G. F. Walker 1950. Hydroglimmer — P. Schachtschabel 1951, Hydrous mica — G. Brown and K. Norrish 1952, H. Heystek 1954. Potassium mica of sericite type (mica worms) — E. Norin 1953, Detrital muscovite — H. S. Yoder and H. P. Eugster 1955, Leverrierit — coarse, worm-like crystals in coals — A. Schüller and H. Grassmann 1949, A. Schüller 1953, K. Hoehne 1957.



Varieties of illite are:

(a). Al-illite(Fe-poor) — Sarospatakite (Nagybörzsöny near Sarospatok — Hungary) — J. D. Sedletsky 1940 — after H. S. Yoder and H. P. Eugster 1955 = mixed layer 1 M — muscovite + montmorillonite 10%.

(b). Iron illite (Fe) — H. E. Stremme 1951. Till the present rarely found and investigated, but large areas of soils derived from „Feuerletten“ (red coloured shales in Germany) should contain this mineral.

(c). Brammalite (Na) — F. A. Bannister 1943. A very rare mineral sometimes in flakes to about 100  $\mu$  — after J. Erdélyi et al 1958 = Hydroparagonite with tetrahedral OH.

(d). Glauconite (Fe-Mg) — J. Murray 1891, A. Lacroix 1893, K. Glinka 1896, J. W. Gruner 1935, J. De Lapparent 1937, S. B. Hendricks and Cl. S. Ross 1941 — after J. F. Burst 1958 = 1M or 1 Md. Glauconite is a common clay component in many W. European soils — Clermont (Belgium), Rarécourt (France), Slenaken (Netherlands).

(e). Celadonite (Mg-Fe) — E. F. Glocker 1847, previously described as terra verta — R. De Lish 1783 and Grünerde-Hoffmann 1788 is found in rock fillings. Structure similar to that of glauconite — S. B. Hendricks and Cl. S. Ross 1941 — after H. S. Yoder and H. P. Eugster 1955 = 1M.

The better ordered illites have resulted from crystallisation under favourable conditions. Thus the hydrothermal Sarospatok (Fe poor) illite consists of large well developed laths. As a contrast the fine Israel illite is very bad developed. Between these end members there are numerous intermediates. Plate 1.

**II. Minerals related to illite** A. When illite loses its interlayered potassium (charge) by gain of H — M. Fieldes and L. D. Swindale 1954, A. Weiss et al 1956, J. Erdélyi et al 1957, or by replacement of Al by Si in the tetrahedral layers (silification) because the Si-O tetrahedral configuration has a larger free energy than the Al-O one, the following minerals may be formed in order of decreasing interlayer charge.

(1) Basal spacing broadened with tail extending towards low angles — G. Nagelschmidt 1944, D. M. C. Mac Ewan 1948, 1949.

Name: Hydrated illite — R. E. Grim 1953, P. Gallitelli 1955. Other names: broadened illite — D. M. C. Mac Ewan 1948, M. Munoz Taboada 1953.

(2) Second order line intermediate between illite and expanded 14 Å illite collapsing when heated at 350 °C. Degree of contraction when saturated with K<sup>+</sup> depending on amounts of expanded 14 Å mineral in the sample, non swelling — figures 25 and 26.

Name: Interstratified illite-expanded (14 Å) illite. Other names: Degraded illite — S. B. Hendricks 1942, S. B. Hendricks and E. Teller



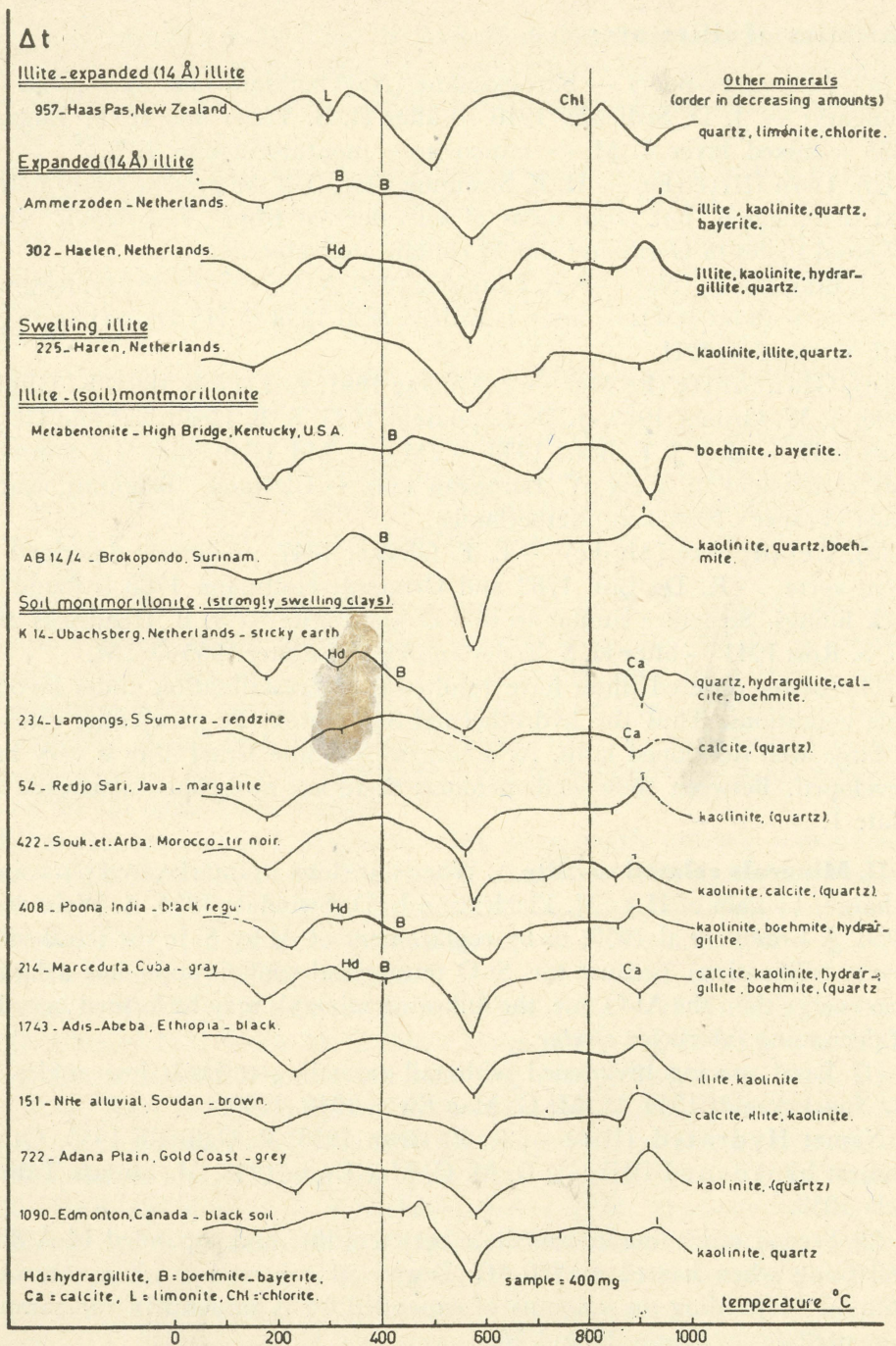
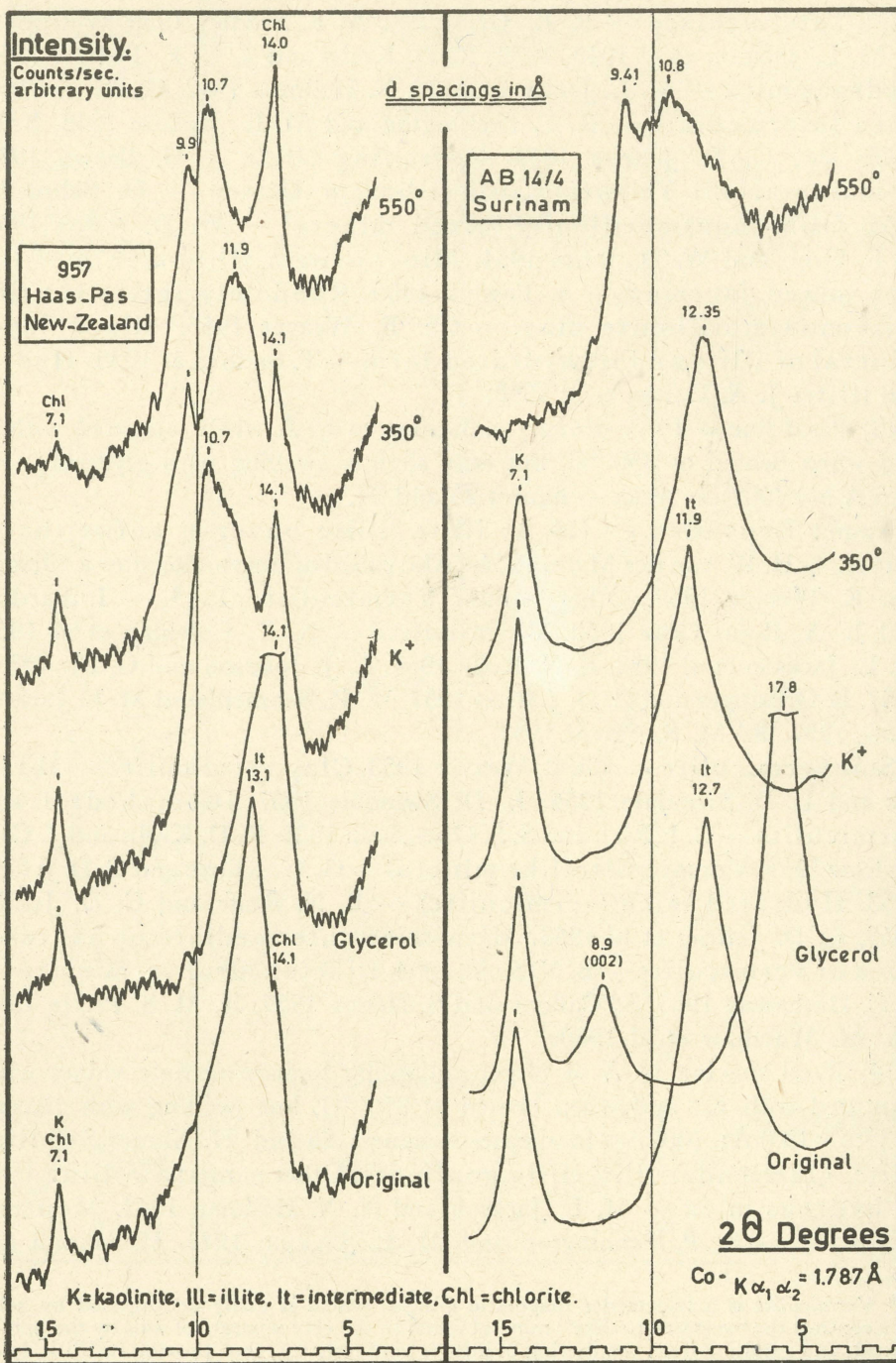


Figure 25: D. t. a. of separate  $< 2 \mu$  of various soils with mainly illite — expanded illite (14 Å) — intermediate, expanded illite (14 Å) swelling with glycerol but contracting with KCl. Furthermore of soil-montmorillonite.



**Figure 26:** X-ray spectra of separate  $< 2\mu$  of soils with illite-expanded (14 Å) illite (957) and illite-(soil)montmorillonite (AB 14/4) intermediates.





1942, R. E. Grim 1953, M. C. Powers 1954, J. F. Burst 1958, D. M. Hirst 1958, G. D. Nicholls and D. H. Loring 1960, S. Pawluk 1960; Hydrous mica intermediate — R. E. Grim and W. F. Bradley 1939, Grundite — M. L. Jackson et al 1948, 1952, R. D. Krebs and J. C. F. Tedrow 1957, Hydrous mica — M. L. Jackson and N. N. Hellman 1942, G. Brown 1951. Mica intermediate — R. P. Pennington and M. L. Jackson 1948, B. N. Rolfe and C. D. Jeffries 1953. Degrading illite — G. Brown 1954. Tonmineral mit Teilweise aufweitbarem Gitter — D. Schroeder 1954. Illite-montmorillonite-mixed mineral — W. D. Keller 1953, R. E. Grim and W. D. Johns 1954. Mineral with illite-montmorillonite mixed layering — S. Pawluk 1960. Randomly interstratified illite-montmorillonite clay — Ch. E. Weaver 1956. Mixed layer mineral of illite and its hydrated form — T. Sudo et al 1958. Hydrated illite. J. A. Dalton et al 1958.

(3) Basal line = 14 Å strongly collapsing to 10 Å when saturated with K and when heated at 350 °C, but only slightly swelling with glycerol — to 17.6 Å but (002) = weak — figures 25 and 27.

Name: Expanded — (14 Å) illite (illite ouverte, aufweitbarer illite). — H. W. van der Marel 1954. (Also called ammersooite after a village.) Ch. E. Weaver 1959. Other names: Vermiculite clay\* — I. Barshad and L. A. Rojas Cruz 1950. Vermiculite — N. T. Coleman et al 1950, M. L. Jackson et al 1952, B. N. Rolfe 1954, L. J. Johnson and C. D. Jeffries 1957, E. Grissinger and C. D. Jeffries 1957, W. R. Schmehl and M. L. Jackson 1956, 1957, R. M. S. Perrin 1957.

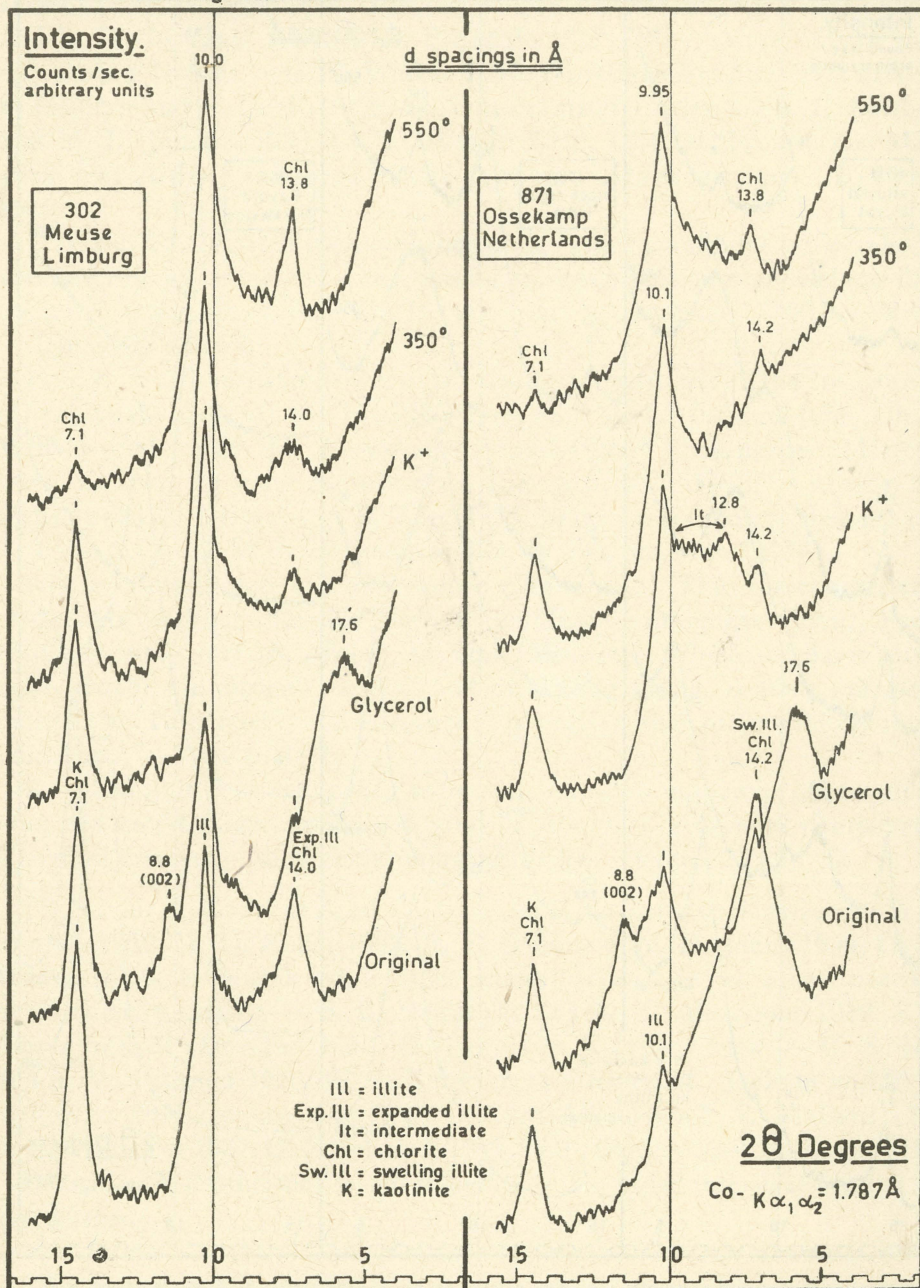
Soil vermiculite — Ch. E. Weaver 1953, Clay vermiculite — M. Fiedes and L. D. Swindale 1954, L. D. Swindale 1957. Dioctahedral soil vermiculite — C. I. Rich and S. S. Obenshain 1955, R. D. Krebs and J. C. F. Tedrow 1957. Vermiculite-like mineral — G. W. Kunze and C. D. Jeffries 1953. Hydrated mica (vermiculite) — B. N. Rolfe and C. D. Jeffries 1953, C. D. Jeffries et al 1953. Mica-mica intermediate or hydrated mica or vermiculite — B. N. Rolfe 1954. Dioctahedral vermiculite — J. C. Hathaway 1955, S. Callère and S. Hénin 1957, R. M. S. Perrin 1957, Ch. M. Warshaw et al 1960.

(4) Basal spacing 14 Å or larger collapsing to intermediate values when saturated with K<sup>+</sup> and when heated at 350 °C, but swelling with glycerol to 17.6–18.0 Å; (002) = moderate — figures 25 and 27. Name: Swelling illite, Quellender illit, illite gonflante. Other names: Swelling type of hydrous mica — M. L. Jackson and N. N. Hellman 1942, Montmorillonite — R. P. Pennington and M. L. Jackson 1948, H. Hamdi and

\* Vermiculite is a trioctahedral magmatic mineral which is easily decomposed by acids. As a contrast the "vermiculite-like" mineral found in the clay separate of soils by the authors named, and resulting from weathering of illite is acid resistant, thus proving its illitic origin



Figure 27: X-ray spectra ( $< 2\mu$ ) of soils with expanded (14 Å) illite (302) and with swelling illite (871).









W. Epprecht 1955. Quellbare Tonmineralen mit Wechsellagerungsstruktur — D. Schroeder 1954, 1955. Clay vermiculite — M. Fieldes and L. D. Swindale 1954, L. D. Swindale 1957. Clay vermiculite with expanded layers — G. F. Walker 1957. Dioctahedral vermiculite — S. Caillère and S. Hénin 1957. Soil montmorillonite — B. L. Sawhney and M. L. Jackson 1958, Ch. E. Weaver 1958, 1959, H. W. van der Marel 1959. Expanding mineral of the montmorillonite type — H. Hamdi 1959.

B. When Fe, Mg-rich rocks weather under moist conditions a dioctahedral swelling mineral is formed which has an analogue structure as swelling illite, included its swelling power which may even be increased, (002) = strong — figures 25 and 28.

Name: Soil montmorillonite (Boden montmorillonite, montmorillonite de sol) — B. L. Sawhney and M. L. Jackson 1958, Ch. E. Weaver 1958, 1959, H. W. van der Marel 1959. Other names: Mineral very nearly an end member of the montmorillonite series but approaching illite — J. B. Page 1943. Missouriite (after Missouri clay — U. S. A.) — C. M. A. de Bruyn and H. W. van der Marel 1954.

Soil montmorillonite is a wide-spread clay mineral. Thus the clay separate of strongly swelling soils like black regur (India), margalite (Java), Badob (Sudan), black turf (S. Africa), tir noir (Morocco), which all have caused many troubles in agriculture, civil and rural engineering, contain soil montmorillonite. Its particle — size comes very near to that of (common) montmorillonite\* — see plate I.

C. When illite is interstratified with other minerals numerous intermediates may be formed. Characteristics depend on amounts of mineral components. The most known are those with montmorillonite — figures 25 and 26.

(1) Name: Interstratified illite — (soil) montmorillonite — W. F. Bradley 1950, W. D. Keller 1953, R. E. Grim and W. D. Johns 1954, Ch. E. Weaver 1956, S. Pawluk 1960. Other names: Mixed layer montmorillonite hydrous mica — S. B. Hendricks and L. T. Alexander 1939, I. C. Brown and M. Drosdoff 1940. Ordovician K-bentonite — C. S. Ross and E. V. Shannon 1926, W. P. Kelley et al 1931, M. L. Jackson and N. N. Hellmann 1942. Bravaisite (from Noyant Allier) — F. E. Mallard 1878, R. E. Grim et al 1937, G. Nagelsmidt 1944, W. F. Bradley 1945, A. Rivière 1946

In case of hydrothermal origin minerals with regular interstratification are also formed.

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\* This name should be restricted to an analogue swelling mineral but which has resulted from hydrothermal weathering of volcanic material — figure 28, No. 344. Another characteristic is the large difference in spec. surface (200—250 M<sup>2</sup>/g and 400—800 M<sup>2</sup>/g respectively) and d. t. a. reactions (1 and 2 or 3 peaks respectively in the 500—1000 °C temperature tract) — see figure 25.



(2) Name: Regularly interstratified illite-montmorillonite. Other names: Montmorinic dioctahedral illite  $28.5 \text{ \AA}$  — Y. Hseung and M. L. Jackson 1952. Regular mixed layer clay mineral 1:1 hydrous mica and montmorillonite — H. Heystek 1954.

The above is only a brief example of the main stages which may be found in nature belonging to a certain small group of clay minerals. The same holds for trioctahedral illite. Also the chlorite group has many members etc. Details about the identification and classification of these groups will be published elsewhere.

Consequently many clay minerals may be found in soils of varying characteristics and composition; one being somewhat better defined than the other, but most of them have to the present never been found to occur as a pure mono clay mineral. Moreover by the loss of interlayer  $K^+$ , the intensity of the basal spacing is increased because of increase of  $Ca^{++}$ ,  $H^+$  or H bonded to O. The intensity of this spacing also depends on the degree of structure ordering which is not the same for samples from various origin.

The general conclusion of this paragraph can thus only be — in addition to the results of all the experiments treated in the foregoing paragraphs — that quantitative analyses of minerals in the clay separate of soils can only be estimated very roughly. Ciphers about the mineral composition of soil clays, each kind of mineral specified to an accuracy of 5% even for those which have to the present never been found to occur in a pure state (as mentioned in many publications) — should therefore be regarded with the utmost criticism.

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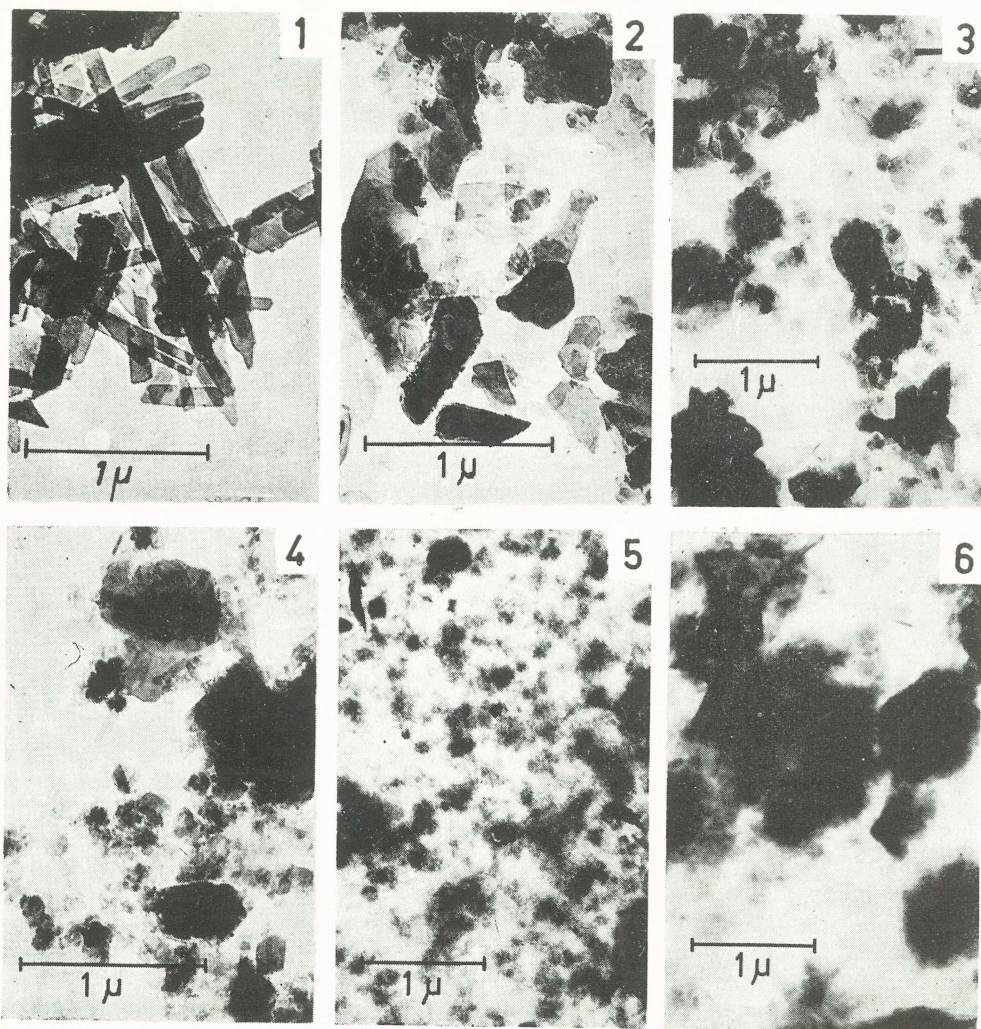
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Plate 1 : Electronmicrographs of illite (1 to 5) and of soil -  
montmorillonite (6) from various countries.



1 - Sersapatok, Hungary, 2 - Luxembourg, 3 - Netherlands,  
4 - Illinois, 5 - Israel, 6 - Java.

Micrographs : H. Beutelspacher, Braunschweig, Germany and  
J. Kramer, Delft, Netherlands.



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