Clay Minerals (1987) **22**, 351–356

NOTE

RELATIONSHIPS BETWEEN THE MEAN AREA, VOLUME AND THICKNESS FOR DISPERSED PARTICLES OF KAOLINITES AND MICACEOUS CLAYS AND THEIR APPLICATION TO SURFACE AREA AND ION EXCHANGE PROPERTIES

In the course of constructing a graphical representation of the physical dimensions of dispersed clay particles as determined by quantitative transmission electron microscopy techniques, a linear relationship between the logarithms of the mean particle volume and area was observed for kaolinites and micaceous clays (sericites, illites, interstratified illite-smectites). That a general relation should exist was, of course, anticipated, but such a high degree of correlation was somewhat unexpected given the large variation in the size of individual particles. Because this relationship between mean values may be of general use it is examined in some detail here.

Materials and methods

The values of mean particle diameter, $D_m = (\text{length} \times \text{width})^{1/2}$, and thickness T_m, based on particle measurements from twelve kaolinites (A, B, E, I, and fine fractions from mines

TABLE 1. Mean and standard deviation values for thickness and area of dispersed particles from some kaolinites.

Sample	Particles measured	T_m nm	sd	A_m 10^4 nm^2	sd
A[1]	14	120	—	31·81	—
B[1]	17	60	—	14·9	—
E[1]	14	90	—	31·36	—
I[1]	22	60	—	18·49	—
M19[1]	200	112	—	24·5	—
M21[1]	97	47	—	11·97	—
M15[1]	66	36	—	8·70	—
Avant[1]	200	54	—	13·62	—
Cornwall[1]	200	151	—	41·47	—
GK1[2]	1000	50	—	9·0	—
K[3]	—	67·2	—	17·82	—
D[3]	—	22·3	—	2·98	—
GK2[4]	10	52·87	31·28	7·74	3·12
TKs[5]	24	4·64	4·44	0·53	0·36

[1] Bates (1971).
[2] Conley (1966).
[3] Robertson *et al.* (1954).
[4] Poorly crystallized Georgia kaolinite <1 μm fraction.
[5] Nadeau (1985).

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15, 19, 21, Avant, and Cornwall; Bates, 1971), well-crystallized Georgia kaolinite, GK1 (Conley, 1966) and Pugu kaolinites K and D from Tanganyika (Robertson *et al.*, 1954) were used to calculate the mean particle area, $A_m = D_m^2$, and mean particle volume, $V_m = T_m \times A_m$. Also included were A_m and T_m values from poorly crystallized Georgia kaolinite, GK2, and an interstratified kaolinite-smectite, Tks (Schultz *et al.*, 1971), with 25% expandable layers determined using the methods of Nadeau (1985). T_m and A_m values of these kaolinites are shown in Table 1. For the micaceous clays, A_m and T_m values were taken for four sericites from hydrothermal deposits in the Silverton Caldera, San Juan Mountains, Colorado, USA (SG 4, RM 3, RM 30, RM 13; Eberl *et al.*, 1987) as well as a diagenetic sandstone illite, Rot, and eight interstratified illitic clays with 70–90% expandable layers from bentonites (Tgb, Dib, Lpb, Sfb, Ccb), sandstones (Ran, Mag), and a synthetic clay, Sms (Nadeau, 1985). T_m and A_m values of the micaceous clays are shown in Table 2. To accommodate the large range in particle sizes represented by these materials and obtain a normal distribution of the data, the logarithms of the mean values (A_m in nm^2, V_m in nm^3) were plotted (Fig. 1). Lines of equivalent mean particle thickness of 1, 10, 100 nm are also shown for reference. Where there is some positive correlation between particle area and thickness for the clay sample, it should be noted that the mean volume values from individual particle measurements (Nadeau, 1985) will be somewhat larger than V_m as calculated here (i.e. $V_m = T_m \times A_m$).

Results

An interesting feature of the data is that they form two linear trends with approximately the same slope. That the slope >1 suggests a relationship between mean particle area and thickness. In other words, the shape or aspect ratio of the particles is on average constant for the samples of the two data sets. The general form of this relationship can be written:

$$T_m = A_m^h / i$$

TABLE 2. Mean and standard deviation values for thickness and area of dispersed particles from some micaceous clays.

Sample	Particles measured	T_m nm	sd	A_m 10^4 nm^2	sd
SG4[1]	27	42·7	27·8	214·5	199·8
RM3[1]	19	18·7	23·4	79·3	78·4
RM30[1]	30	10·2	7·8	22·97	23·57
RM13[1]	22	7·9	4·0	35·99	70·98
Rot[2]	38	9·22	4·33	41·16	39·21
Ran[2]	30	3·7	1·42	9·57	6·28
Mag[2]	20	3·13	1·8	7·01	10·01
Tgb[2]	47	4·94	2·62	3·84	3·34
Dib[2]	55	3·82	1·54	3·78	2·92
Lpb[2]	36	3·52	1·78	3·89	3·77
Sfb[2]	41	2·57	0·8	1·94	1·53
Ccb[2]	52	2·03	0·8	2·68	2·85
Sms[2]	30	2·93	1·01	1·59	0·83

[1] Eberl *et al.* (1987); [2] Nadeau (1985).

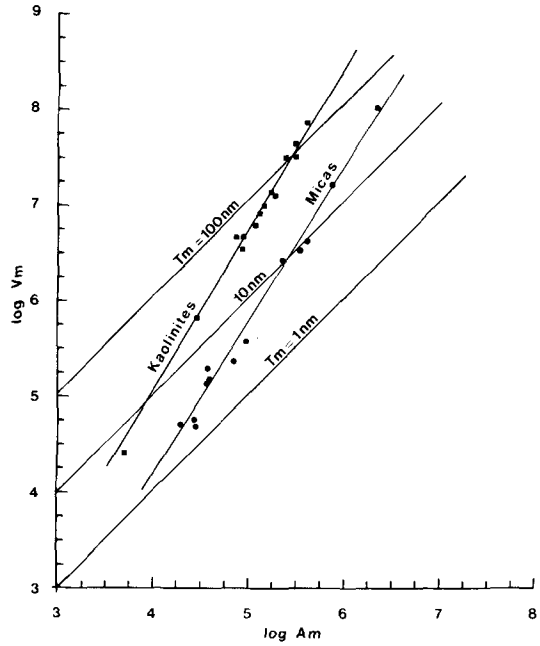

FIG. 1. Logarithmic relationship between the mean particle area (A_m) in nm^2, and volume (V_m) in nm^3 (1 nm = 10Å) for kaolinites (squares) and micaceous clays (circles). The lines of the best fit equations, as well as lines of equivalent mean particle thickness (T_m) for 1, 10, and 100 nm, are also shown.

TABLE 3. Correlation between the standard deviation (sd) and mean particle area (A_m) and thickness (T_m) for micaceous clays.

	Slope	Intercept	R^2
A_m vs. sd	0·94	3·1	0·97
T_m vs. sd	0·72	0·28	0·83

where h and i are constants, h determining the slope of the line and i being related to the intercept. If we consider that the value of h is about 1/2 in both instances, then T_m becomes a function of the mean particle diameter D_m, since $A_m^{1/2} = D_m$. In fact, Bates (1971) noted that for kaolinite T_m is about 1/6 the mean particle diameter. The best-fit equation for kaolinites gives values for $h = 0{\cdot}657$ and $i = 38{\cdot}7$ ($R^2 = 0{\cdot}988$) and for micaceous clays $h = 0{\cdot}571$ and $i = 127{\cdot}9$ ($R_2 = 0{\cdot}985$). The data indicate that in general kaolinites are substantially thicker per unit area than the micaceous clays. It must be stressed however that this relationship holds for mean values only. Plots of area and volume for individual particles show larger variations (standard deviation values for T_m and A_m are also given in Tables 1 and 2) and there is usually a much lower, and often very little, correlation between particle area and thickness, particularly for micaceous clays.

Another feature of the data for the micaceous clays is the relationship between the mean and standard deviation values. The correlation parameters (Table 3) show that the standard deviation (sd) is approximately equal to A_m, and somewhat smaller than T_m.

Discussion

Because particle area is readily determined from transmission electron micrographs, particularly with advancements in digital image analysis, the above relationships allow the mean particle thickness and volume parameters to be extrapolated from mean values of such area measurements. Furthermore, equivalent mean volume, mass and perimeter values as well as edge, basal and particle surface areas can also be estimated. For example if one considers that the mean particle volume (V_m) in nm^3 is given by

$$V_m = A_m^{(h+1)}/i$$

then the mean particle mass (M_m) is given by

$$M_m = V_m \rho 10^{-21}$$

when ρ is the density (about 2·6) in g/cm^3. The reciprocal of M_m gives the number of particles per gram (N_g). Further considering that the mean perimeter (P_m) assuming regular hexagons is given by

$$P_m = 3{\cdot}72 A_m^{1/2}$$

then it is possible to calculate the basal surface area (S_b), edge or lateral surface area (S_l) and total specific surface area (S) in m^2/g by:

$$S_b = 2A_m 10^{-18} N_g$$
$$S_l = T_m P_m 10^{-18} N_g$$
$$S = S_b + S_l$$

The relationships between S and A_m are shown in Fig. 2. An interesting consequence of the thinner nature of the micaceous clays is that the basal surface area represents about 95% of the total surface area as compared to 65–85% for kaolinites. Such observations are important

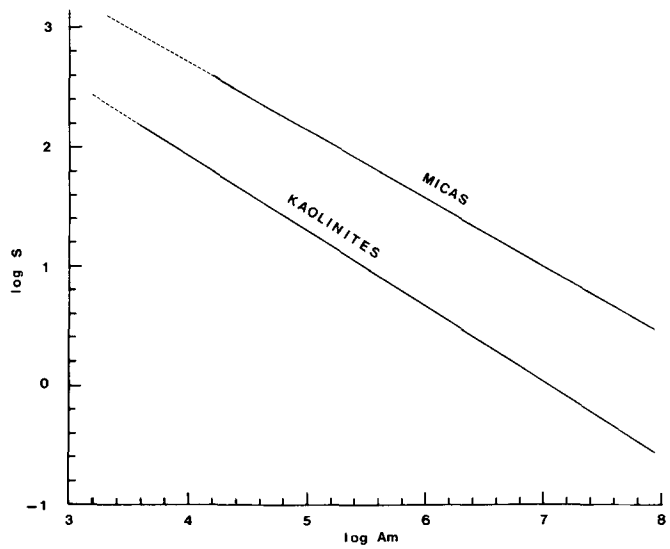

FIG. 2. Calculated logarithmic relationships between mean particle area (A_m) in nm^2 and specific surface area (S) in m^2/g for kaolinites and micaceous clays.

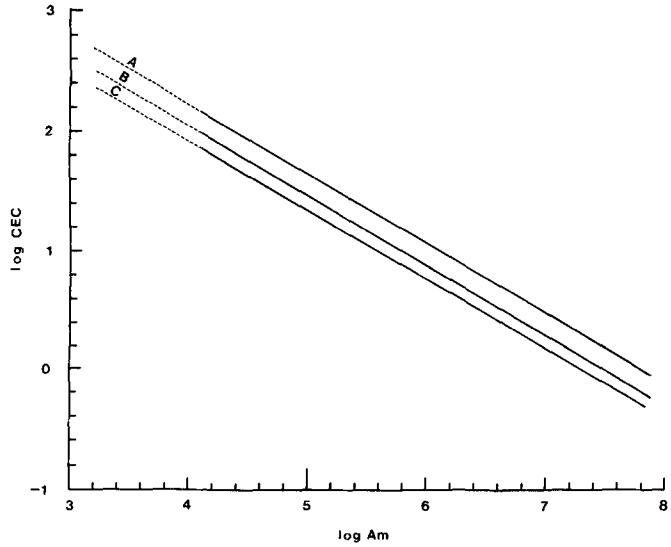

FIG. 3. Calculated logarithmic relationship between mean particle area (A_m) in nm^2 and cation exchange capacity (CEC) in mEq/100 g for micaceous clays, assuming charge density of 0·5 nm^2/site (A); 0·75 nm^2/site (B); and 1·0 nm^2/site (C).

in evaluating the cation exchange capacity (CEC), charge density (Cd in nm^2/site), and surface layer charge of illitic clays (Nadeau, 1985; Nadeau & Bain, 1986).

An example of the relationship between CEC and mean particle area for micaceous clays is shown in Fig. 3. Here, the CEC in mEq/100 g is given by:

$$\mathrm{CEC} = \frac{(2A_m/\mathrm{Cd})\, N_g \times 100}{6{\cdot}02 \times 10^{20}\ \mathrm{sites/mEq}}$$

where $2A_m$/Cd is the mean number of monovalent exchange sites attributable to basal surfaces per particle, and $N_g \times 100$ is the number of particles per 100 g. The values for charge density (Cd) used to calculate the CEC in Fig. 3 are comparable to those for mica (A) (0·5 nm^2/ site), vermiculite (B) (0·75 nm^2/site), and smectite (C) (1·0 nm^2/site).

The above relationships may also be of value in conjunction with X-ray diffraction parameters such as crystallinity or percent expandable layers where there is some correlation with T_m, A_m or D_m (Robertson *et al.*, 1954; Bundy *et al.*, 1966; Lietard *et al.*, 1980; Nadeau, 1985; Cases *et al.*, 1986; Eberl *et al.*, 1987). Furthermore, to the extent that the dispersed particles are representative of the bulk specimens, these relationships may be of general use in characterizing clay materials.

The trends for the dimensional relationships of kaolinites and micaceous clays reported here should be treated as provisional and it is hoped that future improvements based on more numerous observations will be undertaken. Furthermore, sub-trends may exist within the overall trends noted here. For example, diagenetic illitic clays from sandstones are usually larger in area than comparable clays from bentonites, this difference being possibly related to the greater availability of free pore space within the sandstone diagenetic environments. Also, for kaolinites, it is generally thought that secondary clays have a more blocky morphology than primary clays.

The reasons for the observed correlations are not yet fully understood and may be related to dispersion and fractionation techniques, interlayer bonding, surface energy considerations, and/or mechanisms of crystal growth associated with the physical and chemical parameters of the environment of formation. In any case, it is interesting to note that the interstratified clays plot on these trends, and are thus similar in shape, only smaller in size, relative to the larger particles of the non-interstratified clays. This evidence could be taken in support of the fundamental particle and neoformation concepts for interstratified clays (Nadeau *et al.*, 1984a, b, c, 1985; Nadeau & Bain, 1986), particularly if the relationships are a consequence of crystal growth aspects of these phyllosilicate minerals.

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