COMPARISON OF TECHNIQUES FOR DETERMINING THE FRACTAL DIMENSIONS OF CLAY MINERALS

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Abstract—Small-angle X-ray scattering (SAXS), adsorption and nuclear magnetic resonance (NMR) techniques were used to determine the fractal dimensions (D) of 3 natural reference clays: 1) a kaolinite (KGa-2); 2) a hectorite (SHCa-1), and 3) a Ca-montmorillonite (STx-1). The surfaces of these clays were found to be fractal with D values close to 2.0. This is consistent with the common description of clay mineral surfaces as smooth and planar. Some surface irregularities were observed for hectorite and Ca-montmorillonite as a result of impurities in the materials. The SAXS method generated comparable D values for KGa-2 and STx-1. These results are supported by scanning electron microscopy (SEM). The SAXS and adsorption methods were found to probe the surface irregularities of the clays while the nuclear magnetic resonance (NMR) technique seems to reflect the mass distribution of certain sites in the material. Since the surface nature of clays is responsible for their reactivity in natural systems, SAXS and adsorption techniques would be the methods of choice for their fractal characterization. Due to its wider applicable characterization size-range, the SAXS method appears to be better suited for the determination of the fractal dimensions of clay minerals.

Key Words—Adsorption, Clay, Fractal, NMR, Small-angle x-ray scattering.

INTRODUCTION

Many reactions in soils are commonly associated with the surface chemical properties of clay minerals. These properties include cation exchange capacity (CEC), surface charge density, surface area and surface acidity. For instance, the adsorption of n-bytul-, n-dodecyl- and ethyldimethyl/octacedecenylammonium ions by K-saturated kaolinite, illite and montmorillonite has been shown to depend upon the CEC of the clays (Theng 1974). However, surface reactions do not depend only on the chemical properties. The geometry or morphology of the surface also affects its reactivity (Farin and Avnir 1989). The surface morphology determines the extent of the surface that is accessible to any potential adsorbate. Substances with rough or convoluted surfaces will have restricted accessibility depending upon their pore size and the size of the adsorbate molecules. Small molecules would penetrate the pores of the adsorbent whereas macromolecules would be excluded from narrow pores (Mayer 1994). However, substances with flat or smooth surfaces will have sorption sites equally accessible to both small molecules and macromolecules. In fact, macromolecules would outcompete low-molecular weight compounds for free mineral surfaces due to their greater potential range of interactions, including both coulombic and van der Waal's interactions (Ochs et al. 1994).

The surfaces of clay minerals have usually been described as smooth and planar. However, SEM has shown that clay minerals do not always have perfectly smooth or flat surfaces (White et al. 1991). These minerals contribute significantly to the surface reactivity of soils in natural systems where they are found in intimate association with soil organic matter (Keil et al. 1994; Mayer 1994; Collins et al. 1995). Thus, it is vital to be able to quantitatively characterize their surface morphology to better understand the interaction of clays with inorganic ions and various natural, as well as anthropogenic, organic substances in the environment. One way of characterizing surface morphology is by using fractal geometry.

Fractal geometry has been used to characterize the surface structure, characteristics and irregularities of solid materials. Fractal dimensions, D, are numbers used to quantify these properties. Avnir et al. (1984) reported that surfaces of most solid substances are fractals and are characterized by nonintegral dimensions with values between 2 and 3: $2 < D \leq 3$. These fractal dimensions are a measure of the space filling ability of the substance (van Damme et al. 1986). The larger the D value, the more irregular and space filling the surface is, and a substance with $D \sim 2$ has a smooth and planar surface morphology.

A fundamental characteristic of fractal geometry is that fractal substances are self-similar. The shape of the surface irregularities of these substances is invariant over a certain range of scale transformation (van Damme and Fripiat 1985). An increase in the resolving power used in the examination of the surface reveals smaller details morphologically similar to larger details previously observed. Regardless of the method used to measure the fractal dimension, fractality is detected by performing a resolution analysis, for exam-

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Table 1. Some fractal dimension results of selected materials.

Method	Material	Measured D	Reference
SAXS	Lahn river sediment	2.75 ± 0.10	Schmidt 1989
Adsorption	Soil (kaolinite, trace hallosite)	2.92 ± 0.02	Avnir et al. 1984
	Soil (mainly feldspars, quartz & limonite)	2.29 ± 0.06	
	Al-pillard montmorillonite	1.94 ± 0.10	Farin & Avnir 1989
NMR	Alcogel†	2.85	Devreux et al. 1990
	Aerogel 1‡	2.30	
	Aerogel 2‡	2.10	
	Crystallized silica	2.85	

† Obtained by gelation of silica solution.
‡ Obtained by evacuating solvent of silica solution under hypercritical conditions.

ple, analyzing the change in a measurable property as the resolving power is varied (Rojanski et al. 1986).

Various techniques have been used to characterize the surface morphology of solid materials. These include SAXS, adsorption- and NMR-based methods. Some D values obtained by each of the above methods are given for a variety of solid materials in Table 1. Small-angle X-ray scattering has been the most commonly employed technique. In a SAXS experiment, a beam of monochromatic X-rays is directed at the material to be characterized (Schmidt 1989). The intensity (I) of the scattered X-rays is measured as a function of the scattering angle which is usually expressed as the scattering vector, q. The intensity as a function of q ($I(q)$) is related to q by the power-law relationship in Equation 1:

$$I(q) \propto q^{-\alpha} \qquad [1]$$

The magnitude of the exponent α, which is obtained from the slope of a log-log plot of $I(q)$ versus q, is directly related to D. If $\alpha \leq 3$ then the substance is a mass fractal. A mass fractal is a substance whose surface and mass are both characterized by fractal properties. The power-law exponent, α, corresponds to the mass fractal dimension, D_m, and is less than or equal to 3 (Schmidt 1989). If $3 < \alpha \leq 4$ then the substance is a surface fractal. A surface fractal is one in which only the surface of the material exhibits fractal behavior. The surface fractal dimension, D_s, is related to α by the following: $\alpha = 6 - D_s$. The magnitude of α for a surface fractal is within the range $3 < 6 - D_s \leq 4$.

The unit of resolution for the SAXS method is q which is dependent on, and related to the scattering angle, θ, by Equation 2:

$$q = 4\pi\lambda^{-1} \sin \theta/2 \qquad [2]$$

where: λ is the X-ray wavelength. The range of resolutions for which a structure is fractal is determined by the geometry of the instrument and is expressed as $1/q_{max} < L < 1/q_{min}$, where q_{min} and q_{max} are the minimum and maximum values of q for which power-law scattering is observed (Schmidt 1989).

Avnir and co-workers (Avnir et al. 1983; Pfeifer and Avnir 1983; Avnir et al. 1984) proposed the use of adsorbed molecules for characterizing the fractal dimension of natural surfaces. This method is based upon the measurement of monolayer coverage, X_m, of the sample surface with some adsorbate molecule. The measurement is made either with probe molecules of increasing effective cross sectional area σ, or by using the same adsorbate molecule but varying the size, R, of sample particles. Monolayer coverage is dependent upon the size of the sample particles or probe molecules. They are related by the power-law:

$$X_m \propto (\sigma^{1/2}/R)^{-D_s} \qquad [3]$$

The fractal dimension is obtained from the slope of the log-log plot of X_m versus σ or R.

The use of a variety of molecular probes gives information on surface roughness, or irregularity and porosity at molecular scale, whereas using sample particles of different size gives information on surface roughness and porosity at the particle scale. Since the surface reactivity is characterized at the molecular level, we chose to use adsorbate molecules of varying cross sectional area to vary our resolving power for these experiments. The smaller the molecule the higher the resolution, that is, the more details of the surface irregularity that will be observed. The smallest and largest molecular probes constitute the limits of the resolution scale over which the material is fractal.

Recently Devreux et al. (1990) reported an NMR method for measuring the fractal dimension of Si containing materials. This method is based on the recovery of nuclear magnetization after saturation of the nuclear spin system of a substance containing a dilute amount of paramagnetic impurities which enhance nuclear relaxation in an NMR experiment. This is accomplished by applying a repetitive train of radio frequency pulses. The magnetization intensity, $m(t)$, is related to t, the time delay used between pulses, by a simple power-law:

$$m(t) \propto t^\alpha \qquad [4]$$

Table 2. Some properties of the clays used in this study (van Olphen and Fripiat 1979).

Clay	S_{BET} $(m^2\,g^{-1})$	CEC (meq/ 100 g)	Major cation	Fe_2O_3 (%)	FeO (%)	% Organic matter†
KGa-2	23.0	3.3	–	0.98	0.15	0.90
SHCa-1	57.2	43.9	Na	0.02	0.25	0.26
STx-1	78.3	84.4	Ca	0.65	0.15	0.64

† Determined by loss on ignition.

Table 3. Physico-chemical properties of probe molecules (Braker and Mossman 1971). Cross sectional areas (σ) are taken from McClellan and Harnsberger (1967).

Molecule	Formula	Mol. wt. (g/mol)	% Purity	σ (Å²)
Nitrogen	N_2	28.013	99+	16.2
Methane	CH_4	16.043	99.5	17.8
n-butane	C_4H_{10}	58.124	99+	44.8
n-pentane	C_5H_{12}	72.150	99+	49.2
n-hexane	C_6H_{14}	86.177	99+	56.2

where: the value of the exponent α is given by $\alpha = D/6$ (Devreux et al. 1990). A log-log plot of $m(t)$ versus t will be linear over a certain range of t values before reaching a saturation plateau. The value of D is calculated from the slope of the linear portion of this plot. This technique was employed to determine the fractal dimension of different forms of silica (Table 1) doped with Cr as an NMR relaxing agent.

The resolving power in the NMR method is the delay time, which is dependent upon and related to r, the distance of the nuclei in the lattice from the impurity responsible for relaxation, by Equation 5 below:

$$t \propto r^6 \qquad [5]$$

The purpose of this work was to compare and contrast the fractal dimensions of 3 natural reference clays measured by each of these 3 techniques to determine whether a systematic difference exists between them.

MATERIALS AND METHODS

Materials

The following reference clay materials were obtained from the Clay Minerals Society: a kaolinite (KGa-2), a hectorite (SHCa-1) and a Ca-montmorillonite (STx-1). These clays have been extensively characterized (van Olphen and Fripiat 1979) and some of their relevant properties are summarized in Table 2. These samples were used without further purification.

The surface hydroxyl distributions of these minerals have been characterized in our laboratory by both ^{29}Si cross-polarization magic-angle spinning (CPMAS) and ^{1}H Magic Angle Spinning (MAS) solid-state NMR (Malekani and Rice 1995). Silicon-29 CPMAS NMR results showed that the kaolinite surface is dominated by geminal silanol groups $[SiO_2(OH)_2]$ while surfaces of the hectorite and Ca-montmorillonite are dominated by single silanol $[SiO_3(OH)]$ groups. These clays have relatively low paramagnetic Fe contents, which is necessary for nuclear relaxation in the saturation recovery NMR experiments (Table 2). Large amounts of paramagnetic impurities greatly decrease relaxation times and make their measurements very difficult. All 3 clays have essentially no organic matter (Table 2) and therefore, any contribution to surface roughness by organic matter is considered to be negligible.

SAXS Determination

The SAXS measurements were performed on the Oak Ridge National Laboratory 10-m SAXS instrument (Wignall et al. 1990), with a sample-to-detector distance of 1.5 m using Cu-Kα radiation ($\lambda = 1.54$ Å) and a 20×20 cm² position-sensitive area detector with cells approximately 3 mm apart. The source was operated at a voltage of 40 kV and a current of 60 mA. The scattering intensity was stored in a 64×64 data array. Corrections were made for instrument background and detector efficiency, via an ^{55}Fe radioactive standard that emits γ-rays isotropically, on a cell-by-cell basis. The data were radially averaged and converted to an absolute differential cross section by means of pre-calibrated secondary standards (Russell et al. 1988). The scattering data were fitted to a power-law (Equation 1) and D obtained as described earlier.

Adsorption Determination

The surface area measurements were performed on a Micromeritics ASAP 2000 automatic surface area analyzer using the following probe molecules: nitrogen, methane, n-butane, n-pentane and n-hexane. Some physico-chemical properties of these adsorbates are given in Table 3. N-butane, n-pentane and n-hexane were purified by distillation before use.

Nitrogen was adsorbed at -196 °C, a liquid nitrogen bath, and methane at -186 °C, a liquid argon bath. Adsorption of the other probe molecules was carried out in an ice bath (0 °C). A clay sample of 0.3 to 0.5 g was outgassed under vacuum at 105 °C for 6 to 8 h before measurement. To obtain the monolayer capacity, the surface area was calculated using the linear Brunauer, Emmett and Teller (BET) plot of the adsorption isotherm at relative pressures (P/Po) of 0.05 to 0.3 (Gregg and Sing 1982). The fractal dimension was obtained from the slope of the log-log plot of surface area, A, versus σ as described earlier.

NMR Determination

Silicon-29 NMR spectra were obtained at 79.5 MHz on a Bruker ASX-400 spectrometer. The MAS of the samples was performed in ZiO_2 rotors at a frequency of 5 kHz. A train of 30 $\pi/2$ pulses of 3 μs duration was used to saturate the sample. The free-induction
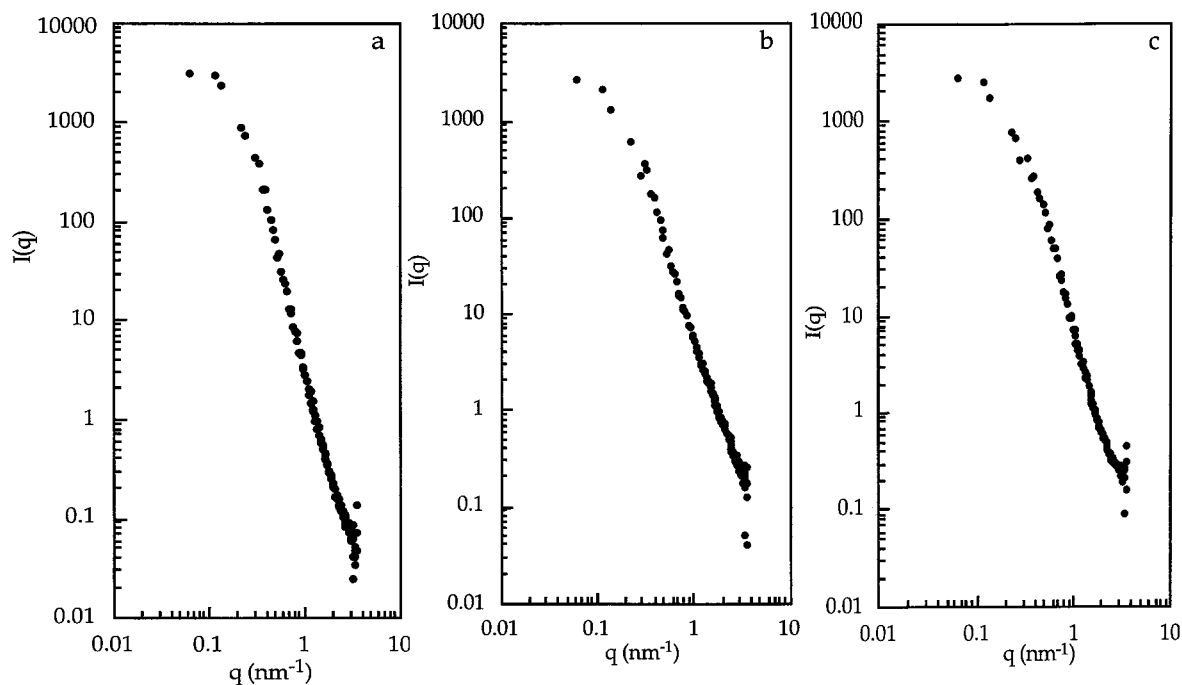
Figure 1.   SAXS curves for the a) kaolinite (KGa-2); b) hectorite (SHCa-1); and c) Ca-montmorillonite (STx-1).

decay was measured after variable delay-time ranging from 100 ms to 3000 seconds. The value of D is obtained from the slope of log-log plots of $m(t)$ versus t as previously described.

Scanning Electron Microscopy

Scanning electron micrographs were obtained with a Super IIIA (International Scientific Instruments) scanning electron microscope. Samples were prepared by sprinkling the clay material on an Al sample stub covered with double-sided tape, coated with a conducting Au-Pd film and then viewed.

X-Ray Diffraction

X-ray diffraction (XRD) traces were obtained on a Siemens Analytical X-ray Instruments Inc. diffractometer equipped with a Philips vertical goniometer and graphite monochrometer. The X-ray tube was operated at a voltage of 40 kV and a current of 20 mA. Clay samples were mixed with glycol, smeared onto a Metricel VM-1 membrane filter and viewed as oriented mounts.

RESULTS

SAXS Determination

The SAXS curves shown in Figures 1a–1c illustrate the characteristic behavior of the materials investigated in this study. The plots obey a power-law over an intensity range of approximately 4 orders of magnitude and cover a range of scattering vectors more than an

order of magnitude. The power-law exponents shown in Table 4 all fall in the range $3 < \alpha < 4$, indicating that all 3 clays used in this study are surface fractals. Kaolinite and hectorite are fractals over a length scale of 8 to 100 Å (Figures 1a and 1b) while Ca-montmorillonite (Figure 1c) is fractal over a shorter range of 8 to 50 Å. Kaolinte and Ca-montmorillonite exhibit D values (D_{SAXS}) of approximately 2.0, indicating a smooth, planar surface. The D_{SAXS} for hectorite is indicative of an irregular and more space filling surface. The SAXS instrument does not "see" any roughness on the surface of kaolinite and Ca-montmorillonite. This is not unexpected since, as already pointed out, basal surfaces of clay minerals have long been recognized as smooth. This observation is consistent with the crystal structure of kaolinite and smectite-type clays. The surface irregularity of hectorite could be attributed to impurities within the sample. The hectorite XRD trace in Figure 2b, in addition to the characteristic hectorite peak at 11.2 Å, exhibits peaks due to calcite, illite, chlorite and dolomite, with calcite apparently present in a large amount relative to the concentrations of the other impurities. These impurities could add more roughness to the surface of hectorite. The Ca-montmorillonite particles have minute impurities of opal-C (an amorphous crystobalite) that does not seem to affect its surface structure. The fractal dimension is therefore, closer to 2.0.

Adsorption Determination

The log-log plots of surface versus cross section σ are shown in Figure 3, while the corresponding cor-
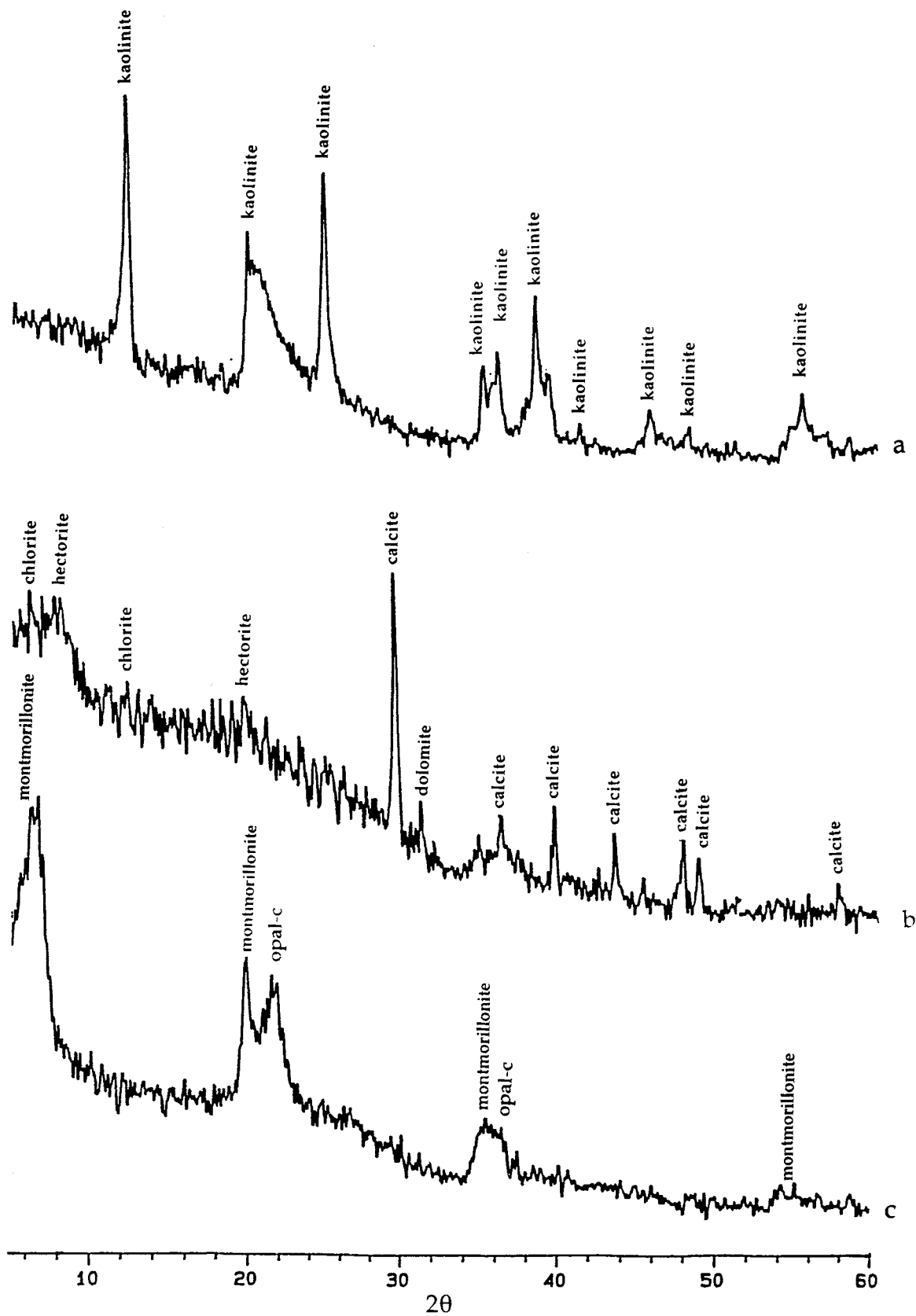
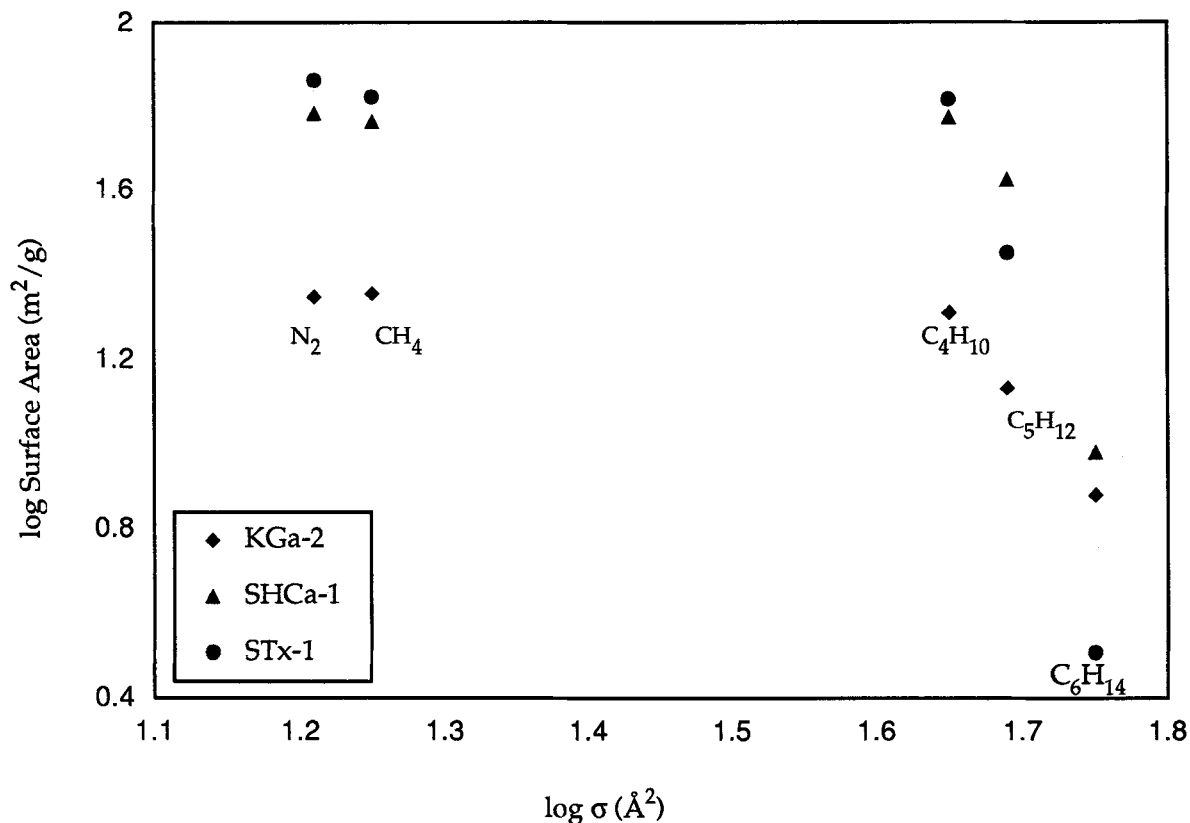Figure 2.   XRD of a) KGa-2; b) SHCa-1; and c) STx-1.

Figure 3. Log-log BET surface area versus cross sectional area σ for a) KGa-2; b) SHCa-1; and c) STx-1.

relation coefficients of the best-fit lines are listed in Table 4. N_2 and methane data points fell outside the linear portion of the power-law curve for all 3 materials studied. With the remaining points, all the data could be fitted to a straight line (r^2 varies from -0.947 to -0.998). This indicates that the power-law relationship does not extend down to ~4 Å, the approximate diameter for N_2 and methane molecules. The fractal regime ranges from 6 to 9 Å, which is very small compared to that of the SAXS method. However, this is typical of resolution scale ranges employed by the adsorption method, since the range is artificially limited by the range of adsorbate cross sectional areas

(Avnir et al. 1984; Avnir 1986). The adsorption $D(D_{ADS})$ results indicate a comparatively large fractal dimension for Ca-montmorillonite while those of kaolinite and hectorite are close to 2.0.

NMR Determination

Figures 4a–4c show log-log plots of ^{29}Si magnetization saturation recovery of the clays characterized in this study. The D value calculated from the NMR experiments (D_{NMR}) for kaolinite is 2.0 while that of hectorite is 2.3. The relaxation time, t, for STx-1 was so short that the magnetization-time plot levels off very early, making it impossible to determine D_{NMR} from the slope. Collecting more data points with delay times <100 ms could not overcome this difficulty. There were possibly some paramagnetic ferric ions in the interlamellar space shortening the relaxation time for this clay. After Ca-exchanging STx-1, D_{NMR} was found to be 2.2 and this is the value reported in Table 4.

DISCUSSION

The larger D_{ADS} value for Ca-montmorillonite suggests that the particle surfaces are dominated by micro- and/or mesopores whereas mesopores and mainly macropores would be dominant on KGa-2 and SHCa-1 surfaces that have D_{ADS} values closer to 2.0. The D_{ADS}
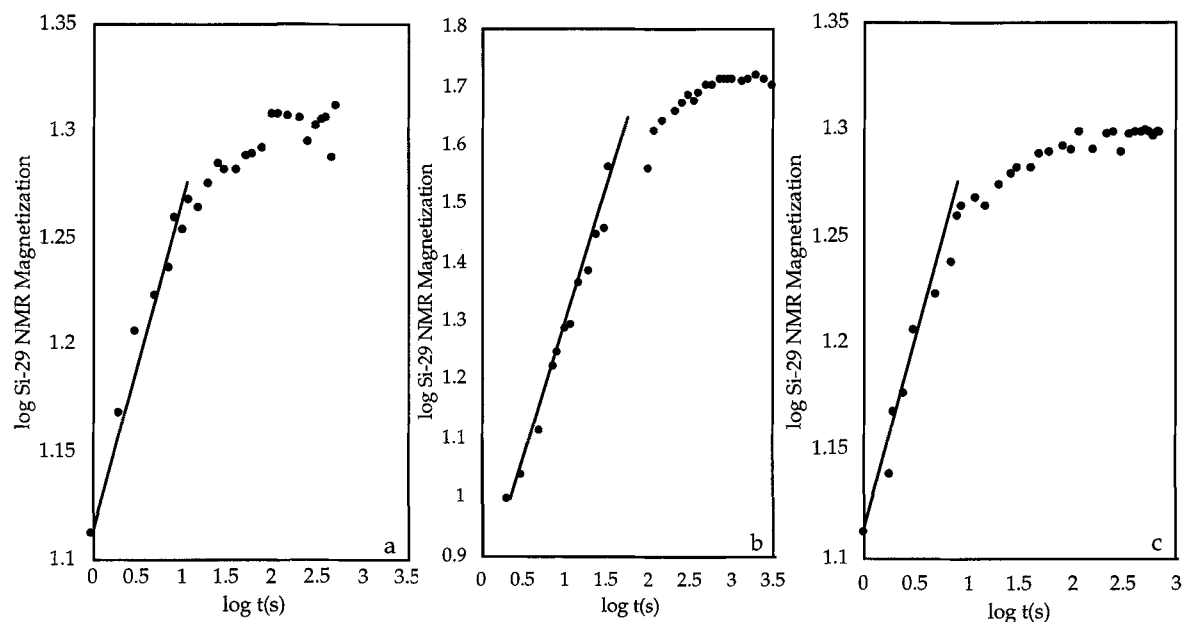
Table 4. Fractal dimensions of the kaolinite (KGa-2), hectorite (SHCa-1) and the Ca-montmorillonite (STx-1) obtained by each method[a][†].

| Sample | SAXS | | Adsorption | | NMR |
	Power-law exponent	D_{SAXS}	Corr. coeff., r^2	D_{ADS}	D_{NMR}
KGa-2	4.0	2.0	-0.998	2.1	1.9
SHCa-1	3.2	2.8	-0.947	1.9	2.3
STx-1	4.0	2.0	-0.982	2.8	2.2

† Absolute uncertainty associated with each D value is ±0.1.

Figure 4. Log-log plot of ^{29}Si magnetization saturation recovery versus delay time, t, for a) kaolinite; b) hectorite; and c) Ca-montmorillonite.

for Ca-montmorillonite is consistent with the fractal dimension result of 2.9 obtained by Ben Ohoud et al. (1988) for a bentonite montmorillonite clay.

The fractal dimension for KGa-2 obtained by adsorption is in good agreement with the value obtained by SAXS technique. The length scales for the 2 methods overlap, giving an "overall" range of fractal surface characteristics for KGa-2 particles of 6 to 100 Å. This observation suggests that smoothness is a fundamental characteristic of kaolinite particles. Highly-crystallized kaolinite is expected to have a fractal dimension of ~2.0 indicating a flat or smooth surface structure. KGa-2 is not highly-crystallized but the particles were found to have relatively smooth surfaces. Sokolowska et al. (1989) have also reported a fractal dimension of 2.12 for particles of Georgia kaolinite. The high degree of surface physical heterogeneity of most kaolinitic soils is probably due to substances adsorbed onto the surfaces of the clay particles such as soil organic matter, inorganic colloids and other minerals found in the soil. In fact, it has been shown that the removal of organic matter from clay minerals results in an increase in N_2-BET surface area (Mayer 1994) and a decrease in surface roughness. Indeed, organic matter does impart some roughness on the clay surface (see for example, the model Murphy et al. 1994, for organic matter adsorption onto mineral surfaces) and would limit the accessibility of N_2 molecules to small pores. The explanation for this trend is that upon removal of organic matter, there is a smoothening of the surface and exposure of small pores oth-erwise inaccessible to N_2 molecules, which results in an increase in surface area (Mayer 1994).

The results for STx-1 and SHCa-1 obtained by the 2 methods disagree. The SEMs support the adsorption results. The micrograph for hectorite, with the smallest D_{ADS} in Figure 5b shows a compact aggregation of clay particles. This would probably leave very little pore surface available for probing by adsorbate molecules. The 2:1 clays with monovalent cations as their exchange ions are known to form face-to-face aggregates (van Olphen 1963) which are usually compact. Ca-montmorillonite with the largest D_{ADS} (Figure 5c) has a pore structure that is more open than that of hectorite, therefore, exposing more surface for adsorption. The large D_{SAXS} value observed for hectorite can also be explained by realizing that while the narrow pores are inaccessible to adsorbed molecules the surface heterogeneity of this impure hectorite could be accessible in the scattering experiment (Farin and Avnir 1989). The SAXS technique probes the "overall" interface of the solid material by detecting the heterogeneity in electron density on the surface while adsorption has the advantage of probing the accessible or open surface, which is of more interest or relevance in the characterization of surface morphology of these clays (Reich et al. 1990). The fractal exponent obtained by this approach however, does not depend only upon the material's geometry and size of adsorbate used. It also depends upon the orientation of the adsorbed molecule relative to the surface. For example adsorbates lying flat on the surface and parallel to each
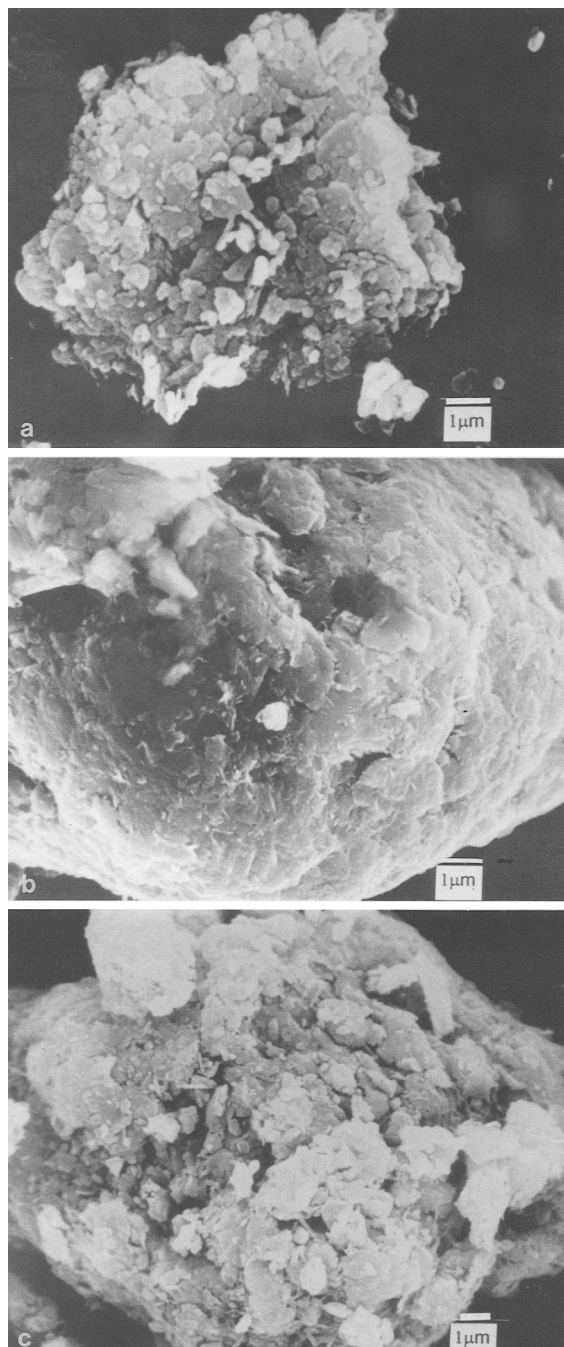
Figure 5.   Representative SEMs for a) KGa-2; b) SHCa-1; and c) STx-1.

other will give a D value that will be different from that obtained from randomly-oriented adsorbed molecules (Pfeifer and Avnir 1983).

The D_{NMR} for kaolinite is in good agreement with D_{SAXS} and D_{ADS}. Theoretically however, there does not appear to be any justification for this agreement.

SAXS and adsorption methods probe the material's surface irregularity while the NMR technique should give the mass distribution around the paramagnetic impurities in a fractal lattice (Devreux et al. 1990). Thus, while SAXS can be used to determine D_s and D_m and distinguish between surface and mass fractals and adsorption measurements can only be used to measure D_s, NMR measurements should only be capable of measuring D_m. While the NMR technique has been applied to the determination of fractal dimensions of synthetic silicas (Devreux et al. 1990), it is not apparent that it should be applicable to natural materials like clays for the following reason. Silica aggregation is usually a fractal process (Schaefer and Martin 1984; Keefer and Schaefer 1986; Schaefer 1989; Bottero et al. 1990). Thus, in a synthetic siliceous material it is possible to end up with a fractal distribution of paramagnetic impurities that can be related to D_m. However, in clay minerals the distribution of paramagnetic impurities, for example Fe, on exchange sites and/or substituted in the crystal lattice is a function of the clay's crystallography.

SUMMARY

The results of this study show that the surfaces of these natural reference clays are fractals with D values close to 2.0, indicating a fairly smooth, planar surface. This is consistent with SEM observations which also show the surfaces to be smooth. Thus, this investigation has shown that D can apparently be used to characterize the surface morphology from atomic (Å) to microscopic (μm) observation ranges. Some surface irregularities were observed for hectorite and Ca-montmorillonite probably as a result of impurities present in the material. Kaolinite was the only sample for which the value for the fractal dimensions determined by all 3 techniques are in agreement and is ~2.0. This observation is a validation for the 3 methods used in this work since kaolinite samples have been reported to have a D ~2.0 (Sokolowska et al. 1989). Small-angle X-ray scattering generates comparable fractal dimensions for kaolinite and Ca-montmorillonite. The range of resolution scale accessible with the SAXS method is significantly broader than the adsorption method. The length scale of the NMR method was not determined in this study. Devreux and co-workers (1990) measured r values for the synthetic silicas by electron paramagnetic resonance and found it to vary from 14 to 64 Å.

Results obtained by each of these methods should be compared with caution as each technique measures the fractal dimension through a phenomenon that "sees" the material from a different perspective. The scattering technique probes the chemical heterogeneity on the surface of the material through contrasts in electron density while the adsorption method probes the physical surface irregularity of the substance.

However, the NMR method seems to deal with the mass fractal distribution of certain structural sites in the material. Since the surface nature of clays is responsible for the reactivity in natural systems, SAXS and adsorption methods are better suited for characterizing their surface fractal dimensions. With its larger applicable characterization range, the SAXS method appears to be better suited for the determination of the fractal dimensions of clay minerals.

ACKNOWLEDGMENTS

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