BASELINE STUDIES OF THE CLAY MINERALS SOCIETY SOURCE CLAYS: SPECIFIC SURFACE AREA BY THE BRUNAUER EMMETT TELLER (BET) METHOD

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Abstract—Specific surface area measurements of The Clay Minerals Society source clays were made by the Brunauer, Emmett and Teller (BET) method of adsorption of nitrogen gas. Two replicate measurements of specific surface area were performed for each source clay. All pair values were within 3%, which is very good agreement for this type of measurement.

Key Words—BET, Hectorite, Kaolinite, Montmorillonite, Palygorskite, Source Clays, Specific Surface Area.

INTRODUCTION

The Clay Minerals Society source clay minerals include kaolinite (KGa-1b, KGa-2), hectorite (SHCa-1), montmorillonite (SAz-1, SWy-2), synthetic mica-montmorillonite (SYn-1), and palygorskite (PFl-1) (Van Olphen and Fripiat, 1979; Costanzo, 2001). Many properties of these source clays have been studied, including geological origin (Moll, 2001), chemical analyses (Mermut and Cano, 2001; Elzea Kogel and Lewis, 2001), layer-charge determination (Mermut and Lagaly, 2001), powder X-ray diffraction (Chipera and Bish, 2001), infrared spectra (Madejová and Komadel, 2001), thermal analyses (Guggenheim and Koster van Groos, 2001), cation exchange capacities (Borden and Giese, 2001), and colloidal and surface properties (Wu, 2001). One analytical aspect not covered in the 2001 special issue of this journal on the source clays is the measurement of their specific surface areas.

The pore size is specified as the pore width, or the radius of a pore which is assumed to be cylindrical. The widths of micropores are <2 nm, mesopores vary between 2 and 50 nm, and macropores are >50 nm (Gregg and Sing, 1982; Rouquerol *et al.*, 1999). The shapes of mesopores in clays having Type II isotherms can be cylindrical, parallel-sided slit, wedge, cavity or cone in a bottle. In mesopores, capillary condensation takes place after multimolecular adsorption. Capillary condensation begins from the narrowest pore during adsorption and capillary evaporation begins from the largest pore during desorption. These differences may cause the hysteresis between adsorption and desorption isotherms at high relative pressures.

Pores within the mineral cover a broad range of sizes. For similar types of pore systems, there are different definitions in the literature, depending on the discipline of the research. For example, petrographers define pores with diameters >10 μm as macropores, and pores with diameters <10 μm as micropores. However, pores with diameters >50 nm are called macropores in colloid chemistry (Fischer and Gaupp, 2004). These authors used the IUPAC classification (1985), which defined macropores as pores with diameters >50 nm, mesopores as pores with diameters of 2−50 nm, and micropores as pores with diameters of 0.02−2 nm. In this paper, pores >10 μm will be referred to as petrographical macropores.

In the determination of specific surface area, there are only two methods applicable to mesopores: mercury intrusion porosimetry (MIP) and the Brunauer, Emmett and Teller (BET) method of adsorption of an inert gas. Only adsorption methods are able to detect microporous surface areas. The MIP method is valid for the study of the diameters and surface areas of macro and mesopores (Ritter and Drake, 1945a, 1945b; Rootare and Prenzlow, 1967; Wardlaw and McKellar, 1981; Fischer and Gaupp, 2004). In the MIP method, pores in the sample are filled by liquid mercury under increasing pressure. This results in a capillary pressure function, which describes the volume of infiltrated mercury as a function of applied pressure. If a pore geometry model is assumed, the pore radii and the internal surface area are computable. The radius of cylindrical pores is given by the Washburn

a KGa-1b (1) $y = 1104.46702x + 18.78868$

$R^2 = 0.99853$

b KGa-1b (2) $y = 991.23097x + 12.05131$
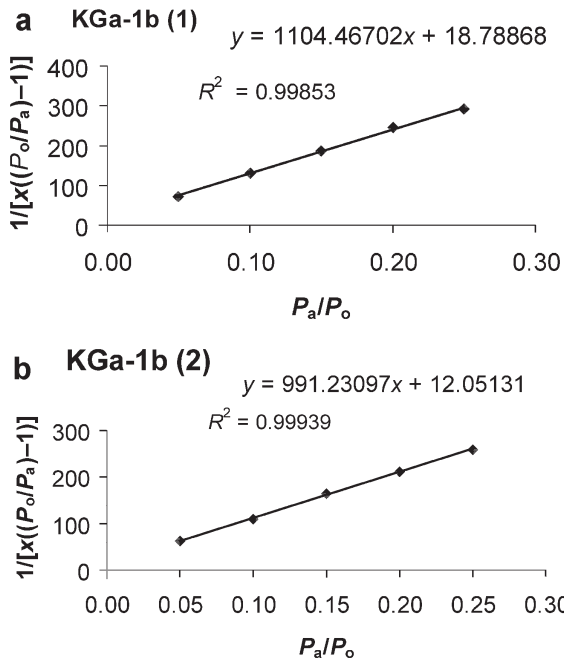
$R^2 = 0.99939$

Figure 1. BET specific surface area measurement of the source clay KGa-1b: (a) the first BET plot; and (b) the second BET plot.

equation (Washburn, 1921) from measurements of capillary pressure (p), $r_p = (-2\gamma/p)\cos\theta$ (m). For this calculation, the surface tension of mercury (γ) and the contact angle between mercury and the solid surface (θ) must be known. Errors or limitations of this method
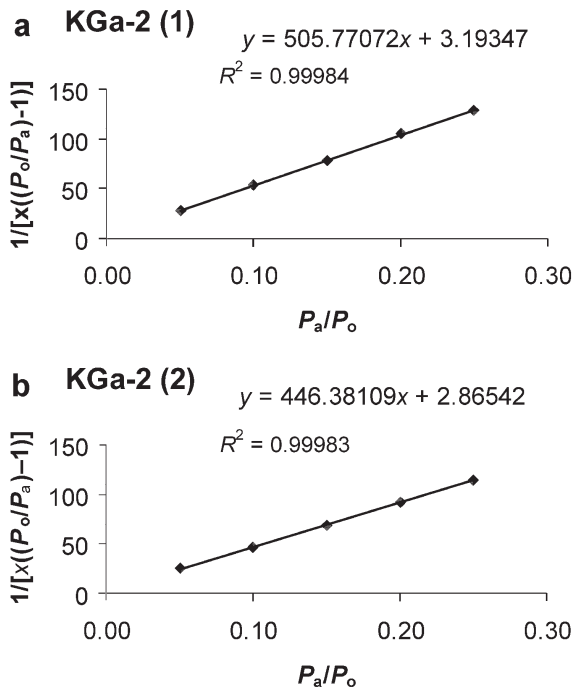
a SHCa-1 (1) $y = 437.21350x - 5.42954$

$R^2 = 0.99987$

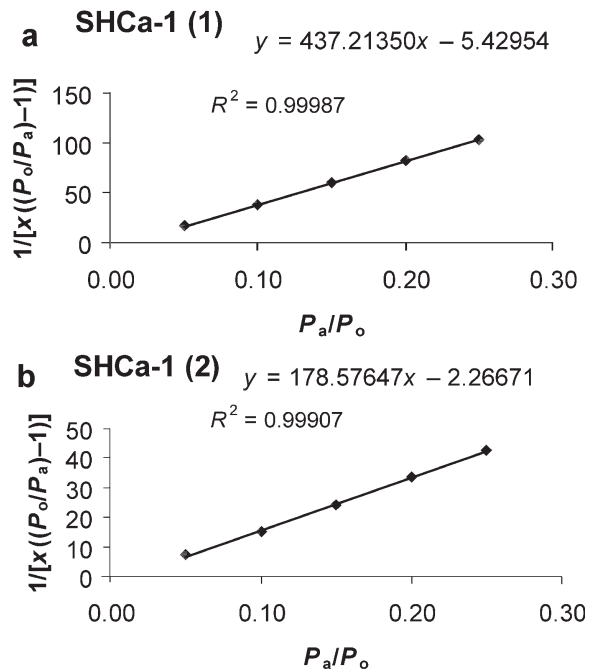**b** SHCa-1 (2) $y = 178.57647x - 2.26671$

$R^2 = 0.99907$

Figure 3. BET specific surface area measurement of the source clay SHCa-1: (a) the first BET plot; and (b) the second BET plot.

include: (1) the pore geometry model, *e.g.* a cylindrical pore shape is insufficient to describe true pore shapes; (2) the occurrence of the so-called ink-bottle-shaped pores, which give the appearance of more pores with a diameter of the tight bottle necks; and (3) the pore-
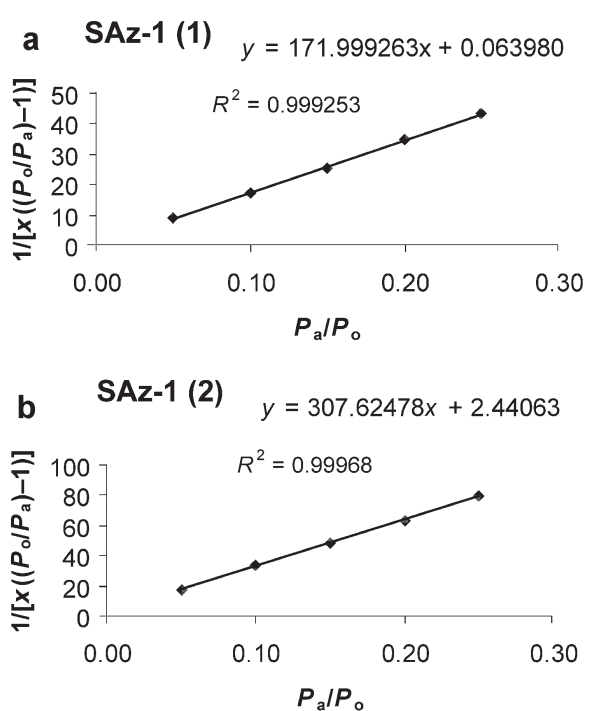
a KGa-2 (1) $y = 505.77072x + 3.19347$

$R^2 = 0.99984$

b KGa-2 (2) $y = 446.38109x + 2.86542$

$R^2 = 0.99983$

Figure 2. BET specific surface area measurement of the source clay KGa-2: (a) the first BET plot; and (b) the second BET plot.

a SAz-1 (1) $y = 171.999263x + 0.063980$

$R^2 = 0.999253$

b SAz-1 (2) $y = 307.62478x + 2.44063$

$R^2 = 0.99968$

Figure 4. BET specific surface area measurement of the source clay SAz-1: (a) the first BET plot; and (b) the second BET plot.

SWy-2 (1)

$$y = 704.46970x + 1.18024$$
$$R^2 = 0.99990$$

SWy-2 (2)

$$y = 604.01593x - 0.80680$$
$$R^2 = 0.99930$$
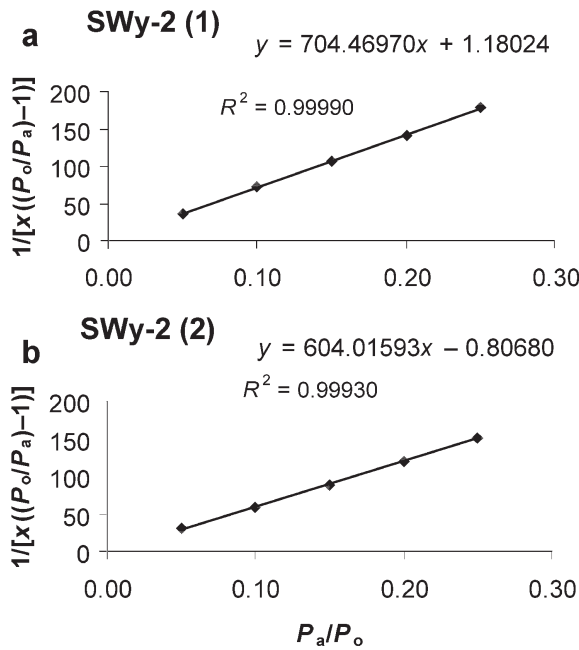

Figure 5. BET specific surface area measurement of the source clay SWy-2: (a) the first BET plot; and (b) the second BET plot.

in mesopores and micropores (Emmett and Brunauer, 1937; Brunauer *et al.*, 1938; Brunauer *et al.*, 1940; Gregg and Sing, 1982; IUPAC, 1985). The first applications of the BET method were the measurements of the surface areas of soils (Makower *et al.*, 1937; Nelson and Hendricks, 1944), and a comparison of internal surface areas of different clay minerals as a function of the adsorbate gas (Grim, 1968).

MATERIALS AND METHODS

The source clays of The Clay Minerals Society, including (1) KGa-1b (replaces KGa-1), well ordered kaolinite from Washington County, Georgia, USA; (2) KGa-2, poorly-ordered kaolinite from Warren County, Georgia, USA; (3) SHCa-1, hectorite (contains calcite) from San Bernandino County, California, USA; (4) SAz-1, montmorillonite from Apache County, Arizona, USA; (5) SWy-2 (replaces SWy-1), Na-rich montmorillonite from Crook County, Wyoming, USA; (6) SYn-1 (Barasym SSM-100, synthetic mica-mont-morillonite from NL Industries; and (7) PFl-1: palygorskite from Gadsden County, Florida, USA, were selected as materials for this study.

Specific surface areas of these source clays were determined using the multi-point BET method. Nitrogen vapor adsorption data (77 K) were obtained for relative vapor pressures (P/P_o) of 0.05, 0.10, 0.15, 0.20 and 0.25. The cross-sectional area of a nitrogen molecule was assumed to be 16.2 Å^2.
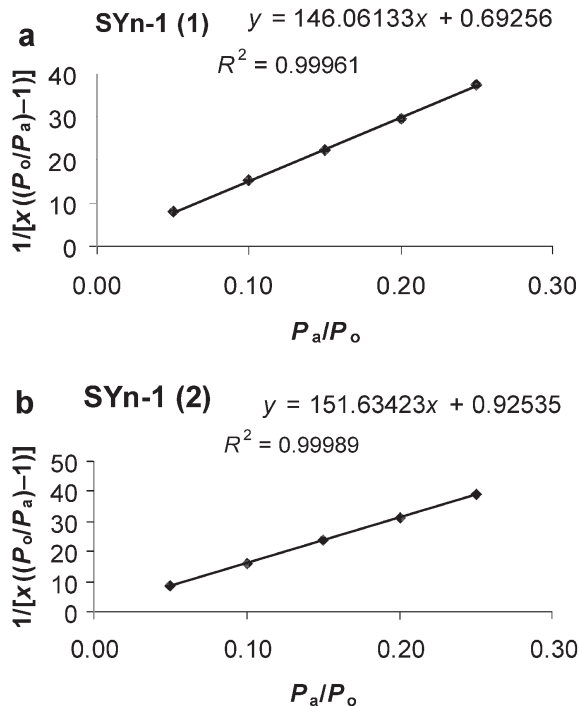
space-deforming effects of high mercury intrusion pressures.

The BET method uses adsorption of chemically inert gases, such as nitrogen, argon or krypton, to measure the entire surface area, including the surface area contained

SYn-1 (1)
$$y = 146.06133x + 0.69256$$
$$R^2 = 0.99961$$

SYn-1 (2)
$$y = 151.63423x + 0.92535$$
$$R^2 = 0.99989$$

Figure 6. BET specific surface area measurement of the source clay SYn-1: (a) the first BET plot; and (b) the second BET plot.

PFl-1 (1)
$$y = 87.896501x - 0.111054$$
$$R^2 = 0.999821$$

PFl-1 (2)
$$y = 202.445880x + 0.518380$$
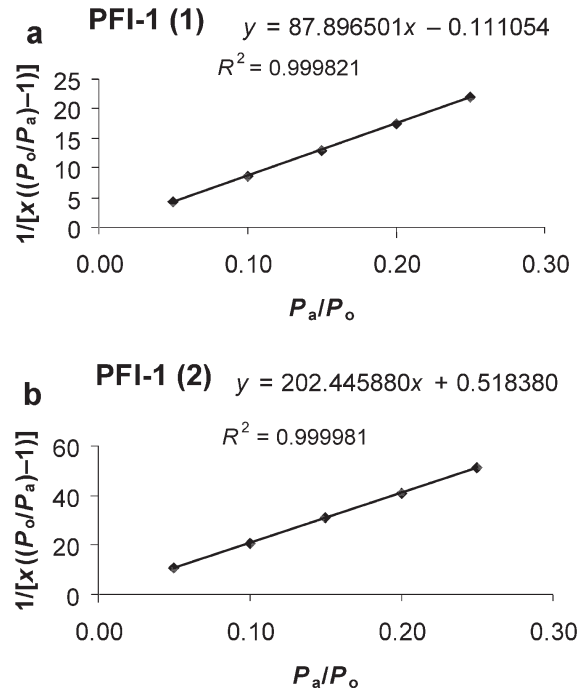$$R^2 = 0.999981$$

Figure 7. BET specific surface area measurement of the source clay PFl-1: (a) the first BET plot; and (b) the second BET plot.

The method for specific surface area determination and the experimental procedures employed were validated using two surface area reference materials: 8570 Calcined Kaolin, and 8200 Alumina (both from NIST). The specific surface areas determined for the Calcined Kaolin and Alumina were 11.2 m²/g and 258.8 m²/g, respectively, both in good agreement with the values (10.9 m²/g and 256 m²/g, respectively) reported by NIST. The specific surface areas were determined from the estimated (by BET) amount of nitrogen required for monolayer coverage, the cross-sectional area of a nitrogen molecule, and the sample weight.

The source clays of The Clay Minerals Society were outgassed at 130°C for 6 h under a vacuum of 0.1 mm Hg and then were conditioned with nitrogen (flowing stream) at 35°C for ~20 h. After outgassing, nitrogen adsorption was determined for every sample over the relative equilibrium adsorption pressure (P/P_o) range of 0.05−0.25, as explained above. In the expression (P/P_o), P is the absolute adsorption equilibrium pressure and P_o is the condensation pressure of nitrogen at laboratory conditions. These experiments were conducted by using a Quantasorb Surface Area Analyzer and Gas Mixing Unit (Quantachrome Corporation, Boynton Beach, Florida). No particle-size fractionation was performed. Supplementary information on the computations of the specific surface areas can be obtained from the corresponding author.

The source clays were also examined in detail using an Hitachi S-4000 field emission scanning electron microscope (SEM) equipped with iXRF energy dispersive spectrometer (EDS) to determine morphology, composition and possible impurities. For SEM, an accelerating voltage of 5 kV was used, and for EDS, an accelerating voltage of 15 kV was used.

RESULTS AND DISCUSSION

The BET equation describes multimolecular vapor adsorption (Brunauer *et al.*, 1938), and is based on the application of the Langmuir equation to the first and subsequent layers of adsorbate on the surface. The linear form of the BET equation is as follows:

$$x/(n(1 − x)) = 1/n_m c + ((c − 1)/n_m c)x \qquad (1)$$

where, $x = P/P_o$, n_m (mol g⁻¹) is the monolayer capacity and c is a constant related to the heat of adsorption. The BET plots for the source clays are given in Figures 1−7. Two equations were obtained for each clay and the two specific surface area results were averaged.

The specific surface area, S (m²g⁻¹), was calculated using the equation:

$$S = n_m L a_M \qquad (2)$$

where, $L = 6.022 \times 10^{23}$ mol⁻¹ and is the Avogadro number, and $a_M = 16.2 \times 10^{-20}$ m² and is the area occupied by an adsorbed N_2 molecule in the completed monolayer.

Table 1. Specific surface areas (S_1 and S_2) of the source clays from The Clays Minerals Society. S_1 and S_2 represent the first and the second BET measurements, respectively.

Source clay	S_1(m²g⁻¹)	S_2(m²g⁻¹)	S_{mean}(m²g⁻¹)
KGa-1b	12.99	13.18	13.1
KGa-2	21.43	22.01	21.7
SHCa-1	35.13	36.07	35.6
SAz-1	65.96	64.45	65.2
SWy-2	22.34	22.99	22.7
SYn-1	116.06	118.97	118
PFl-1	171.02	175.83	173

The results of the specific surface area analyses are reported in Table 1. S_1 represents the first BET measurement and S_2 represents the second BET measurement. Sample-to-sample reproducibility was very good, since all pair values were within 3%. This would be expected given the high coefficients of determination for the BET plots ($R^2 \geqslant 0.9985$).

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