

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

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**Abstract**—The Clay Minerals Society published a complete characterization scheme for its ‘Source Clays’ but not for its ‘Special Clays’. To address this issue, the specific surface areas (SSAs) of the 16 special clays from The Clay Minerals Society were determined using the Brunauer, Emmett and Teller (BET) method of adsorption of an inert gas. Two BET measurements were performed for each of the 16 special clays, and the average BET SSA of each of the special clays was determined. The BET SSA of cookeite is reported for the first time. In the present study, special clays from The Clay Minerals Society are classified under three groups based on their BET specific surface area values as Group-I special clays, with BET values of 0.1–10 m<sup>2</sup>/g, Group-II special clays, with BET values of 10–100 m<sup>2</sup>/g, and Group-III special clays, with BET values >100 m<sup>2</sup>/g. Comparisons which proved interesting were the those involving the mixed-layer clays and the synthetic clays. The systematic approach employed in this paper will allow for better comparisons to be made between different clays and will provide a comprehensive database for future applications of such material (*e.g.* as catalyst carriers, as adsorbents in waste treatments, *etc.*).

**Key Words**—Beidellite, BET, Cookeite, Illite, Illite-smectite, Montmorillonite, Nontronite, Rectorite, Ripidolite, Special Clays, Specific Surface Area, Synthetic Hectorite, Laponite.

### INTRODUCTION

In 2001, a special issue of *Clay and Clay Minerals* (volume 49, number 5) was dedicated to the Baseline Studies of the Source Clays of The Clay Minerals Society. A BET SSA characterization was not included so this was presented by Dogan *et al.* (2006). The source clays are: well ordered kaolinite, KGa-1b; poorly ordered kaolinite, KGa-2; hectorite, SHCa-1; montmorillonite, SAZ-1; Na-rich montmorillonite, SWy-2; synthetic mica-montmorillonite, SYn-1; and palygorskite, PFl-1.

In the determination of SSAs, methods applicable to mesoporous and/or microporous materials include: mercury intrusion porosimetry (MIP), small-angle X-ray scattering, adsorption of a dye from solution, and the BET method of adsorption of an inert gas. Mercury intrusion methods assume that the pores are cylindrical. The presence of pores which are slits or the presence of ‘ink-bottle’ pores can cause serious inaccuracies. Also, only mesopores are accessible by mercury intrusion porosimetry. Small-angle X-ray scattering techniques rely on Porod’s Law. However, the applicability of the

original Porod Law or the need to use a modified form of the Porod Law is dependent on the morphology of the material. The exact form necessary requires either a trial and error procedure or *a priori* knowledge of the exact morphology. Additionally, small-angle X-ray scattering can measure pores which are too small to be accessed by a nitrogen molecule. While the existence of such pores is interesting from the standpoint of the structure of the solid, the measurement of such pores can lead to estimates of SSA which are irrelevant for most ‘real world’ applications, *i.e.* most adsorbates of interest cannot enter a pore which is inaccessible to nitrogen. Techniques involving the adsorption of a dye from solution require that the area that the dye occupies on the surface of the clay be accurately known. This is difficult and frequently ambiguous. Large molecules may not lie flat on the surface, and are also apt to adopt different conformations in different solvents. An additional problem results from the competition for surface interaction sites between the dye and the solvent. This competition can make it difficult to determine whether a complete monomolecular layer of dye is present on the surface at maximum dye adsorption.

The BET method uses the adsorption of chemically inert gases, such as helium, nitrogen, argon or krypton, to measure the total surface area contained in or on micropores, mesopores, macropores and flat surfaces (Emmett and Brunauer, 1937; Brunauer *et al.*, 1938;

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DOI: 10.1346/CCMN.2007.0550508

Gregg and Sing, 1982; IUPAC, 1985). The BET method addresses most of the inadequacies or difficulties of the previously mentioned methods. As the BET model is not based on pore filling, there is no assumption pertinent to the geometry of the pores, and ink bottle pores do not cause a problem at the reduced pressures employed. Similarly, particle morphology is largely irrelevant. The inert gas, nitrogen in these experiments, does not have to compete for surface adsorption sites because only nitrogen, helium (carrier gas), and the adsorbent are present in the sample cell. At 77 K, helium is well above its critical temperature. Finally, small molecules, such as the N<sub>2</sub> molecule, have a known geometry. The combination of a known geometry and the frequency with which nitrogen gas is employed in BET SSA measurements leads to a very reliable value for the area occupied by an N<sub>2</sub> molecule on solid surfaces (16.2 Å<sup>2</sup>). It is interesting to note that some of the very 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 type (Grim, 1968).

In the present study, the surface areas of 16 special clay minerals from The Clay Minerals Society were determined using the BET method of adsorption of an inert gas.

## MATERIALS AND METHODS

### Materials

The 16 special clays from The Clay Minerals Society, listed in Table 1, were selected for this study.

### Methods

The large samples were broken into 1 cm pieces, or smaller, using a steel hammer. The smaller pieces were

milled in a Fritsch Planetary Micromill (model Pulverisette 7) using four stainless steel 1.5 cm diameter balls. The instrument was run for 1.5 min at a moderate speed setting of 5. For samples NAU-1 and NAU-2, an additional 30 s of grinding were necessary at a speed setting of 8 to reduce the samples to a useable powder. Samples NAU-1 and NAU-2 required more intensive grinding conditions because of their quartz contents. Approximately 1 g of each resulting powder was spread in a thin layer over the bottom of a glass dish. The powders were dried under 0.01 atm vacuum at 135°C for 6 h. Each powder was brought back to room temperature in a desiccator containing calcium sulfate. The dried samples were individually filled into a clean, dry Quantasorb sample tube and purged with nitrogen at 35°C for 20 h. After purging, the SSA analysis was performed. Two independent determinations of SSA were made for each powder. Virtually all of the powder prepared was consumed between the duplicate measurements of SSA. This eliminated concerns pertinent to the sample removal protocol, as all of the powder that was prepared was measured.

Specific surface areas of these special clays were determined using the multi-point BET method. Nitrogen vapor adsorption data (77 K) were obtained for relative vapor pressures ( $P/P_0$ ) 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<sup>2</sup>.

The method for SSA determination and the experimental procedures employed were validated using two surface area reference materials: 8570 calcined kaolin, and 8200 alumina (both from NIST). The SSAs determined for the calcined kaolin and alumina were 11.2 m<sup>2</sup>/g and 259 m<sup>2</sup>/g, respectively, both in good agreement with the values (10.9 m<sup>2</sup>/g and 256 m<sup>2</sup>/g, respectively) reported by NIST. The error for the low SSA standard was 2.8%, while the error for the high SSA

Table 1. Mineralogy and localities of the special clays from The Clay Minerals Society.

Special clay	Mineralogy	Locality
SCa-3 (white)	Montmorillonite	California, USA
SCa-3 (purple)	Montmorillonite	California, USA
SAz-2	Ca-montmorillonite	Arizona, USA
SBI-d-1	Beidellite	Idaho, USA
NAu-1 (green)	Nontronite	Australia
NAu-2 (brown)	Nontronite	Australia
NG-1	Nontronite	Germany
SYnH-1	Synthetic hectorite	United Catalysts Inc.
SYnL-1	Synthetic Laponite	Southern Clay Products Inc.
IMt-1	Illite	Montana, USA
IMt-2	Illite	Montana, USA
CAR-1	Cookeite	Arkansas, USA
CCa-2	Ripidolite (Fe chlorite)	California, USA
RAR-1	Rectorite (regular mixed-layered)	Arkansas, USA
ISMt-1	Illite-smectite (60/40 ordered)	Mancos shale, USA
ISCz-1	Illite-smectite (70/30 ordered)	Czechoslovakia

standard was 1.1%. The SSAs 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. Details of the calculations involved have been presented previously (Dogan *et al.*, 2006).

The special clays were outgassed at 130°C for 6 h under a vacuum of 0.1 mm Hg and then 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 ( $P/P_0$ ) range of 0.05–0.25, as explained above. In the expression ( $P/P_0$ ),  $P$  is the absolute adsorption equilibrium pressure and  $P_0$  is the condensation pressure of nitrogen at laboratory conditions. These experiments were conducted using a Quantasorb Surface Area Analyzer and Gas Mixing Unit (Quantachrome Corporation, Boynton Beach, Florida).

## RESULTS AND DISCUSSIONS

The main thrust of this study was to measure the SSAs of the special clays by the BET method. The BET equation describes multimolecular vapor adsorption (Brunauer *et al.*, 1938). This model was based on the application of the Langmuir equation to the first and subsequent layers of adsorbate on the surface. A critical assumption of the model is that all of the adsorption sites in the first layer are energetically equivalent. This can be a troublesome assumption for surfaces having both polar and non-polar sites when a polar adsorbate, such as H<sub>2</sub>O, is used. Thus, nitrogen was used in these studies to measure SSA.

Although BET measurement of SSA is subject to criticism when used on materials which swell appreciably upon hydration, such as smectites, the most logical alternative method has a comparable problem. Specific surface areas for materials which swell in aqueous media can be determined from solution-phase adsorption studies, with the subsequent application of the Langmuir equation. While the condition of the clay may now more closely resemble its physical state in product-oriented applications, the issue becomes the determination of a reasonable cross-sectional area for the adsorbate as it exists on the surface. Most solutes will have molecular weights of ~80 or more. Such solute molecules, which are appreciably larger than N<sub>2</sub> molecules, do not always have a predictable orientation on the surface and, even if they do, the assumption of a closest-packing arrangement on the surface is more tenuous. Thus, it is felt that nitrogen vapor adsorption, while imperfect, is the best way to measure SSA for comparisons which will be made for a range of materials.

For either vapor-phase or solution-phase methods of SSA determination, sample pretreatment is a matter of concern. This is especially true when the samples must

first be milled. However, it is important to recognize that the extent of the problem is influenced by the proportion of the SSA which is external and the proportion of the SSA which is internal (pores, inter-lamellar spaces, *etc.*). When most of the SSA of a powder is external, the SSA is highly influenced by the particle size of the powder. When most of the SSA of a powder is internal, the SSA is little influenced by the particle size of the powder. An example of this is provided by activated carbons. Activated carbons typically have particle sizes in the low micron range. Thus, a geometric calculation of the external SSA of an activated carbon would yield a specific surface area in the range 1–3 m<sup>2</sup>/g. However, most activated carbons have SSAs in the range 500–2000 m<sup>2</sup>/g (as measured by N<sub>2</sub>-vapor BET). Thus, it is clear that the vast majority of the surface is located in the micropores of the activated carbons. As a result, the particle size has little influence on the measured SSA.

The discussion above has implications for this work. Given the grinding conditions employed, it would be expected that the particle sizes would be in the low-to-mid micron range. Thus, it would be expected that the external SSA would be 0.5–2 m<sup>2</sup>/g (approximately). For those samples which exhibited BET SSAs of 0.4–1.3 m<sup>2</sup>/g, it is evident that essentially all of the SSA is external, and the particle size very important. Duplication of the SSA results would require duplication of the mean particle size and particle-size distribution. For those samples having SSAs in the range 34.3–279 m<sup>2</sup>/g, it is clear that most of the SSA is internal, and that the particle size will have little impact on the measured SSA. In fact, for these samples, the external SSA is of the same magnitude as the intrinsic error of the measurement. Thus, these SSAs can be considered to be characteristic of the materials. For those samples having SSAs in the range 7.6–20.5 m<sup>2</sup>/g, the impact of the external surface area on the total SSA is not as clear cut. However, even for this range of SSAs, the internal surface area constitutes the largest fraction of the total SSA (~75% or more). As a result, even for this last group of materials, the SSAs obtained can be considered to be characteristic of the materials.

### *Montmorillonite*

The montmorillonite SCA-3 (both white and purple) originated in San Diego County, California, USA. The earlier reports related to 'Otay' bentonite or montmorillonite include Kerr (1949), Cleveland (1960), Grim and Kulbicki (1961), Weaver and Pollard (1973), Grim and Güven (1978), and Post (1981). The average BET SSA of the special clay SCA-3 montmorillonite (white) is 43.2 m<sup>2</sup>/g; 65.3 m<sup>2</sup>/g for SCA-3 montmorillonite (purple); and 41.0 m<sup>2</sup>/g for Ca-montmorillonite from Arizona (SAz-2). The average SSAs of the source clays SAz-1 montmorillonite from Apache County, Arizona; SWy-2 Na-rich montmorillonite from Crook County, Wyoming;

and SYn-1 synthetic mica-montmorillonite, were reported to be 65.2 m<sup>2</sup>/g, 22.7 m<sup>2</sup>/g, and 118 m<sup>2</sup>/g, respectively (Dogan *et al.*, 2006). The minimum and maximum SSAs for montmorillonite minerals were reported as 22.7 m<sup>2</sup>/g (Dogan *et al.*, 2006) and 350 m<sup>2</sup>/g (Kloprogge *et al.*, 1994), respectively. For montmorillonite intercalated with Al- and Cr-hydroxy oligomers, BET surfaces measured between 250 m<sup>2</sup>/g to 300 m<sup>2</sup>/g (Auer and Hofmann, 1993). The thermal treatment of hydroxy-Al and hydroxy-Ga pillared montmorillonite increased the BET surface area from 35 m<sup>2</sup>/g to 350 m<sup>2</sup>/g (Kloprogge *et al.*, 1994). Adsorbents with SSAs of 100 m<sup>2</sup>/g to 236 m<sup>2</sup>/g were prepared on the basis of montmorillonite and basic salts of Fe (Komarov *et al.*, 1995). The platinum catalysts modified the textural properties of the Al-pillared montmorillonite and led to a significant decrease in the SSA (Gil *et al.*, 2001; Vicente *et al.*, 2002). Nanoparticles (SnO<sub>2</sub>, tin content of 15 to 50 wt.%) were prepared by hydrolysis in an aqueous medium and stabilized by montmorillonite, and as temperature was increased, the SSA of the catalysts (801–210 m<sup>2</sup>/g) decreased markedly (Korosi *et al.*, 2004).

#### Beidellite

The special clay, beidellite, SBId-1, originated from the DeLamar Mine, Idaho, USA, and was described by Post *et al.* (1997). The average BET SSA of the SBId-1 beidellite is 12.7 m<sup>2</sup>/g. The SSA of 230 m<sup>2</sup>/g was reported in dealuminated beidellite (Delacaille and Fripiat, 1991). Milling experiments, creating a new positively charged surface, resulted in increases in SSA (Sondi and Pravidic, 1996, 1998; Sondi *et al.*, 1997).

#### Nontronite

The nontronites, NAu-1 (green) and NAu-2 (brown), originated in the Uley graphite mine of South Australia, and NG-1 in Hohen Hagen, Germany. Keeling *et al.* (2000) characterized NAu-1 and NAu-2 nontronites, and Schneiderhoehn (1965) characterized the NG-1 nontronite. The results of average BET SSA of NAu-1 is 52.8 m<sup>2</sup>/g; of NAu-2 is 10.6 m<sup>2</sup>/g; and of NG-1 is 13.9 m<sup>2</sup>/g.

The oxidation state of Fe in the crystal structure of smectite minerals profoundly affects their physical and chemical properties (Lear and Stucki, 1989). The process of Fe reduction involves the transfer of an electron to octahedral Fe(III) modifications, and these changes play a dominant role in altering the clay surface chemistry (Stucki *et al.*, 2002; Elsner *et al.*, 2004; and Stucki and Kostka, 2006). In marine hydrothermal smoker chimneys, Fe-oxidizing, sheet-forming bacteria play a decisive role in nontronite formation at these sites (Kohler *et al.*, 1994). The bacteria isolated from soil and sediments catalyze the rapid reduction of structural Fe(III), in which the extent of Fe(III) reduction is large, from 46% to >90%; hence, particle surface area decreased by 26% to 46% in response to bacterial reduction (Kostka *et al.*, 1999).

#### Hectorite

The synthetic hectorite, SYnH-1, is made by United Catalysts Inc. Natural hectorite is relatively rare, having been originally found in Hector, California in a deposit believed to have formed by alteration of pyroclastics by Mg-, Li- and F-rich solutions. The average BET SSA of the synthetic hectorite (SYnH-1) is 244 m<sup>2</sup>/g. The minimum and the maximum SSAs of hectorite were reported to be 5 m<sup>2</sup>/g (Carrado *et al.*, 1996) to 300 m<sup>2</sup>/g (Auer and Hofmann, 1993), respectively. The BET surfaces of hectorite intercalated with Al- and Cr-hydroxy oligomers measured between 250 m<sup>2</sup>/g and 300 m<sup>2</sup>/g (Auer and Hofmann, 1993). Synthetic hectorite was hydrothermally crystallized with direct incorporation of series of water-soluble polyvinyl alcohols and removal of the polymer does not alter the extended synthetic clay network, and the BET surface area increases from 5 m<sup>2</sup>/g to 200 m<sup>2</sup>/g (Carrado *et al.*, 1996). Hectorite particles are larger and more anisotropic than those of Laponite, and the pore volume is smaller than that of Laponite (Alcover *et al.*, 2000). The platinum catalysts modified the textural properties of the Al-pillared hectorite and led to a significant decrease in the SSA (Gil *et al.*, 2001; Vicente *et al.*, 2002). Nanocomposites (*i.e.* TiO<sub>2</sub>, SnO<sub>2</sub>) prepared using hectorite clay mineral platelets showed that as temperature increases, the SSA of the catalysts (80–210 m<sup>2</sup>/g) decreased markedly (Mogyorosi *et al.*, 2003; Korosi *et al.*, 2004). The average SSA of the source clay SHCa-1 hectorite from San Bernardino County, California, was reported to be 35.6 m<sup>2</sup>/g (Dogan *et al.*, 2006).

#### Laponite

The synthetic Laponite, SYnL-1, is made by Southern Clay Products Inc. and its average BET SSA is 279 m<sup>2</sup>/g. Comparing it with hectorite at a given relative humidity, Laponite tends to hold more water (Al-Mukhtar *et al.*, 1999) and mechanical stress strongly reduces the number of macropores but does not affect micropores; mesopores, and hydraulic stress increases the number of macropores (Alcover *et al.*, 2000). A comparison with the SSA measured by adsorption of ethylene glycol monoethyl ether indicates that methylene blue adsorbs as a monomer regardless of the aggregation number in solution, and suggests that dimers are formed in the contact region between two aggregating particles (Avena *et al.*, 2001). A novel Laponite RD clay-based Fe nanocomposite consists mainly of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> and shows a large SSA (472 m<sup>2</sup>/g) (Feng *et al.*, 2003a, 2003b). Synthesis and modification of Laponite-related materials by surfactants and globular cations shows increased pore volume and enhanced SSA (Powell *et al.*, 2004).

#### Illite

The special clay illites (IMt-1, IMt-2) came originally from Cambrian shale of Silver Hill, Montana, USA, and were characterized by Hower and Mowatt (1966). The

structures of these illites were reported as  $(K_{1.37}Mg_{0.09}Ca_{0.06})(Al_{2.69}Fe_{0.76}^{3+}Mg_{0.43}Fe_{0.06}^{2+}Ti_{0.06})Si_{6.77}Al_{1.23}O_{20}(OH)_4$ . The average values of the BET SSA of special clays IMt-1 and IMt-2 illites are 20.5 m<sup>2</sup>/g and 17.5 m<sup>2</sup>/g, respectively. The BET SSA measurements on fully water-saturated claystones and siltstones (Boom clay from Belgium, Opalinus Clay from Switzerland, and Tertiary mudstone from offshore Norway, in which the major clay minerals were illite and smectite) ranged from 20 m<sup>2</sup>/g to 48 m<sup>2</sup>/g (Hildenbrand *et al.*, 2002). The effects of coatings of organic matter and Fe- and Al-oxides on a series of electrochemical properties and heavy metal sorption of illite showed that the coatings increased the SSA (Zhuang and Yu, 2002). The BET SSA measurement performed on loess-derived surface soils of Central Germany (illite contents >80%) showed that organic matter accumulates in the fractions of smallest size and largest surface area (Kahle *et al.*, 2002). The total SSA of Tunisian bentonite, which contains 15% illite, was found to be 711 m<sup>2</sup>/g (M'Bodj *et al.*, 2003).

The organic carbon content of soil is positively related to the SSA, though large amounts of organic matter result in reduced SSA values. Kaiser and Guggenberger (2003) observed that sorption of organic matter reduced SSA, depending on the amount sorbed and the type of mineral; the reduction in SSA decreased in the presence of larger proportions of organic matter, specifically the SSA of the mineral soils was positively related to the Fe oxyhydroxides content and negatively related to the organic carbon content. The BET surface area measurement after acidimetric titration suggested that edge faces and basal planes of illite participated in dissolution of structural components (Liu *et al.*, 2003). In preferential association between organic matter and clay particle edges (clay contains illite), siliceous clay faces contribute most of the surface area and form pore walls (Mayer *et al.*, 2004). Illite grinding results in a decrease in the BET SSA (Yang *et al.*, 2005). The BET experiment performed on ceramic products contained illite, and SSA varied between 13 and 76 m<sup>2</sup>/g (Garcia *et al.*, 2005). Suspended particulate matter within the estuarine turbidity maximum in the Humber Estuary system, UK, consisted of silt and clay. The clay mineralogy was dominated by illite and the mean SSA was between 22 and 26 m<sup>2</sup>/g (Uncles *et al.*, 2006).

#### Cookeite

The special clay, cookeite (CAR-1), was found at Jeffrey Quarry, North Little Rock, Pulaski County, Arkansas, USA by Miser and Milton (1964). Bailey (1975) investigated cation ordering and pseudo-symmetry in layer silicates including cookeite. Cookeite (CAR-1) has a very small BET SSA value, averaging 0.85 m<sup>2</sup>/g (Figure 1a,b). Our literature search did not find any publication that reported the BET SSA of the cookeite. Therefore, the BET value of cookeite is reported here for the first time.

#### Ripidolite

Special clay, ripidolite (CCa-2), an Fe chlorite, was originally found at Flagstaff Hill, El Dorado County, California, USA, by Post and Plummer (1972). It has a very small BET SSA value, averaging 1.3 m<sup>2</sup>/g. The effects of mechanical particle disintegration by dry milling and high-impact ball milling, mimicking physical weathering and natural water wear, have been examined in the case of ripidolite. The milling caused considerable changes in the morphology and surface properties, followed by loss of crystallinity of the treated minerals. Dry milling experiments resulted in 12.3-fold increases in SSA (Sondi and Pravdic, 1996). Major changes in SSA were produced by high-energy ball milling in ripidolite (Sondi *et al.*, 1997). By milling, new positively charged surfaces were created in ripidolite; however, the SSA value was found to be much smaller than that of beidellite (Sondi and Pravdic, 1998).

#### Rectorite (regular mixed-layer)

A regular mixed-layer special clay, rectorite (RAR-1), was found at Jeffrey Quarry, North Little Rock, Pulaski County, Arkansas, USA, by Miser and Milton (1964). The RAR-1 rectorite has an average BET value of 7.6 m<sup>2</sup>/g. Guo *et al.* (2004) used rectorite as a matrix and prepared mesoporous solid superacid in the form of pillared clay and characterized its structure using BET. Guo and Chen (2005) prepared La-containing sulfated Zr-pillared clay solid acids with rectorite as the matrix and characterized by nitrogen adsorption-desorption and showed that regularity for the layer structure of the catalysts formed is significantly improved with greater SSA. Du *et al.* (2005) characterized Al-pillared rectorite. Microwave irradiation of the rectorite produced a large SSA of 180 m<sup>2</sup>/g.

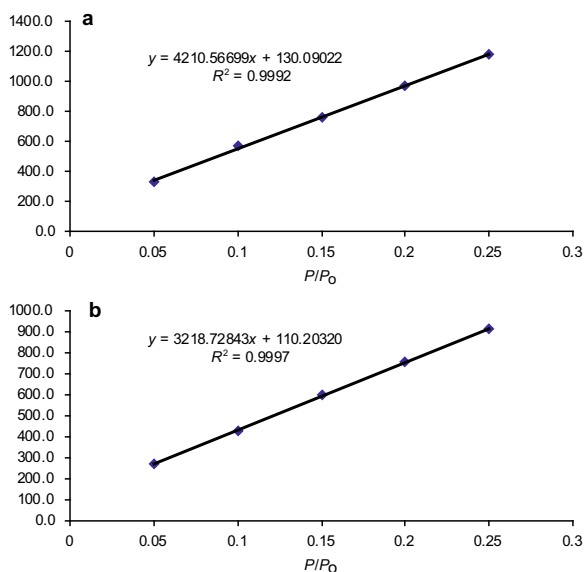


Figure 1. BET SSA measurement of The Clay Minerals Society Special Clay, CAR-1, cookeite, from Arkansas, USA: (a) the first BET plot and (b) the second BET plot.



*Illite-smectite mixed-layer clays (60/40 and 70/30 ordered)*

The 60-40 ordered illite-smectite mixed-layer special clay ISMt-1, ( $K_{0.84}Ca_{0.21}Mg_{0.05}Na_{0.01}$ ) ( $Al_{3.37}Mg_{0.45}Fe_{0.16}^{3+}Ti_{0.02}Fe_{0.01}^{2+}$ )( $Si_{7.08}Al_{0.92}$ ) $O_{20}(OH)_4$  was originally found in Cretaceous Mancos shale, USA; the 70-30 ordered illite-smectite mixed-layer special clay ISCz-1, ( $Ca_{1.00}K_{0.95}Na_{0.09}Mg_{0.03}$ ) ( $Al_{3.39}Mg_{0.48}Fe_{0.12}^{3+}Fe_{0.01}^{2+}$ )( $Si_{7.19}Al_{0.81}$ ) $O_{20}(OH)_4$  was originally found in Czechoslovakia. It is important to note that there are major differences between the 60-40 and 70-30 ordered illite-smectite mixed-layer special clays. The ISMt-1 has a very small average BET SSA value of 0.4 m<sup>2</sup>/g; ISCz-1 has an average BET SSA value of 34.3 m<sup>2</sup>/g, almost 80 times greater. The BET SSAs of mixed-layer clays deserve to be investigated in detail. Rajec *et al.* (1999) investigated samples containing illite and illite-smectite having different crystal shapes of plates, barrels and filaments for sorption experiments with cesium. They observed a positive correlation between total surface area and Cs-sorption capacity. Srasra and Trabelsi-Ayedi (2001) investigated the change in the pore structure and the adsorption properties of interstratified illite-smectite from Tunisia and observed that with the increase in treatment time, the total pore volume increased, while the maximum value of the SSA was attained by treating the sample with 3M HCl.

*Results of the BET SSAs of the special clays*

The overall results of the BET SSAs of these special clays are reported in Table 2. The BET SSA measurements for all 16 special clays are available from the corresponding author. Sample-to-sample reproducibility was very good, as all pair values were within 5% of each

other. This would be expected given the high coefficients of determination for the BET plots ( $R^2 \geq 0.998$ ).

It is interesting to note that the synthetic clays have very large SSAs compared to the other clays in this study. The reason is unknown. However, it is likely that the procedures used for the synthesis resulted in differences in the number of pores, the mean pore size, and the pore-size distribution.

## CONCLUSIONS

Previously reported SSAs of the special clays and clay-derived materials were determined by different authors using different techniques and different sample pretreatment conditions. This has led, in some cases, to quite different results for the same material, and substantial uncertainty with regard to how the materials compare with each other. The systematic approach and comprehensive comparisons made in this paper will allow better comparisons to be made.

In this study, the 'special clay' minerals from The Clay Minerals Society are classified under three groups based on their BET SSA values

Group-I special clays, with BET SSA values of 0.1 to 10 m<sup>2</sup>/g include ISMt-1 illite-smectite (60/40 ordered): 0.4 m<sup>2</sup>/g, CAr-1 cookeite 0.9 m<sup>2</sup>/g, CCA-2 ripidolite 1.3 m<sup>2</sup>/g and RAr-1 rectorite (regular mixed-layer) 7.6 m<sup>2</sup>/g.

Group-II special clays, with BET SSA values of 10–100 m<sup>2</sup>/g include: NAu-2 nontronite (brown): 10.6 m<sup>2</sup>/g, SBId-1 beidellite: 12.7 m<sup>2</sup>/g, NG-1 nontronite: 13.9 m<sup>2</sup>/g, IMt-2 illite: 17.5 m<sup>2</sup>/g, IMt-1 illite: 20.5 m<sup>2</sup>/g, ISCz-1 illite-smectite (70/30 ordered): 34.3 m<sup>2</sup>/g, SAz-2 Ca-montmorillonite: 41.0 m<sup>2</sup>/g, SCA-3 montmorillonite (white): 43.2 m<sup>2</sup>/g, NAU-1

Table 2. Specific surface areas (the first measurement, SSA<sub>1</sub> and the second measurement, SSA<sub>2</sub>) and average specific surface areas, SSA<sub>av</sub> with standard deviations, SD, and RSD% of the special clays from The Clay Minerals Society.

Sample	SSA <sub>1</sub> (m <sup>2</sup> /g)	SSA <sub>2</sub> (m <sup>2</sup> /g)	SSA <sub>av</sub> (m <sup>2</sup> /g)	SD	RSD (%)
SCa-3 (white)	44.85	41.49	43.2	2.38	5.5
SCa-3 (purple)	65.40	65.25	65.3	0.10	0.2
SAz-2	39.51	42.39	41.0	2.04	5.0
SBId-1	12.76	12.68	12.7	0.05	0.4
NAu-1 (green)	53.57	52.07	52.8	1.06	2.0
NAu-2 (brown)	10.43	10.79	10.6	0.30	2.4
NG-1	13.38	14.39	13.9	0.71	5.1
SYnH-1	242.5	246.2	244	2.56	1.0
SYnL-1	269.6	289.3	279	13.95	5.0
IMt-1	20.40	20.60	20.5	0.14	0.7
IMt-2	17.73	17.34	17.5	0.27	1.5
CAr-1	0.82	0.87	0.9	0.04	4.7
CCA-2	1.29	1.23	1.3	0.04	3.4
RAr-1	7.44	7.74	7.6	0.21	2.8
ISMt-1	0.47	0.37	0.4	0.07	16.0
ISCz-1	35.48	33.14	34.3	1.76	5.1

nontronite (green): 52.8 m<sup>2</sup>/g and SCa-3 montmorillonite (purple): 65.3 m<sup>2</sup>/g.

Group-III special clays, with BET SSA values >100 m<sup>2</sup>/g include: SYNH-1 synthetic hectorite: 244 m<sup>2</sup>/g and SYNL-1 synthetic Laponite: 279 m<sup>2</sup>/g.

There was no information in the literature about a BET SSA for cookeite. Thus, the BET SSA of cookeite is reported here for the first time.

Observations of special interest relate to the mixed-layer and synthetic clays. At this time, it is not understood why the mixed-layer clays should exhibit such variability from clay to clay, and this should be further investigated. Similarly, it is not clear why the SSAs of the synthetic clays should be so large. It is possible that the synthetic procedures lead to differences in the number of pores, the mean pore size, and the pore-size distribution.

#### ACKNOWLEDGMENTS

We acknowledge Prof. Robert L. Brenner of the Department of Geoscience and Prof. Douglas Flanagan of the College of Pharmacy, the University of Iowa, for reviewing an earlier version of the manuscript. We also acknowledge support from the Center for Advanced Drug Development, and the Central Microscopy Research Facility at the University of Iowa, USA. We appreciate constructive critiques and comments from three anonymous reviewers and Associate Editor Prof. Warren Huff.

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(Received 2 October 2006; revised 6 August 2007; Ms. 1223; A.E. Warren D. Huff)