

Topography and surface properties of clay minerals analyzed by atomic force microscopy

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Abstract

The specific surface area (SSA) of natural particles is an important parameter to quantify surface processes such as dissolution and adsorption. In this study, the SSA of illite and montmorillonite particles was determined by N₂ gas adsorption (BET), the EGME method and atomic force microscopy (AFM). By AFM it was possible to analyze additionally the specific basal surface area (BSA) and the specific edge surface area (ESA). For the calculation of the surface area from the AFM data we used three different approaches, which yielded similar values. Furthermore, there was a strong correlation between the specific surface area and the particles' height. For illite BET estimated a SSA of 46 m²/g, while 54 AFM images resulted in a mean SSA of 64 m²/g. For montmorillonite we found a SSA of 79 m²/g by BET and of 246 m²/g by AFM (n=42). We assume that the commonly used preparation method for AFM samples causes delamination of clay minerals, leading to particles with a thickness of only 4 to 10 unit layers.

Key Words

Montmorillonite, illite, specific surface area, specific edge surface area, AFM

Introduction

The specific surface area is an essential parameter to quantify processes at the solid/liquid interface. The gas adsorption method BET (Brunauer *et al.* 1938) is a routine method for specific surface area determination, which uses non-polar gases such as N₂ or Ar to determine the outer surface of solid materials. Unfortunately, the BET method fails to determine the complete surface area of materials featuring outer as well as inner surfaces, e.g., sheet silicates. A more successful alternative is the adsorption method introduced by Carter *et al.* (1965) using liquid ethylene glycol monomethyl ether (EGME) that penetrates into the interlayer space due to its polarity. Both the BET and the EGME method determine bulk values and do not allow quantifying distinct crystal faces. The latter is especially desirable for clay minerals, which are extremely anisotropic: Their basal (001) plane is covered by saturated surface groups, which are chemically less reactive than those on edge surfaces, which are built up of surface groups with broken bonds. Atomic force microscopy (AFM) allows creating three-dimensional height images of single clay particles and determining the edge surface and basal surface area separately. As single particles are measured, the result is not a bulk value, but a distribution of measured surface areas, which reveals information about the heterogeneity of the sample. In some publications, the specific surface area (SSA), the specific basal surface area (BSA), and the specific edge surface area (ESA) were determined with AFM, and these data were in good agreement with BET-determined SSA data (Bickmore *et al.* 2002, Tournassat *et al.* 2003, Jodin *et al.* 2004, Metz *et al.* 2004, Hassan *et al.* 2006). However, since Metz *et al.* (2004) estimated completely different SSA values with BET and AFM (BET: 34 +/- 2 m²/g versus AFM external SSA: 136 +/- 20 m²/g), it is questionable, as to whether BET and AFM really determine the identical surface area. Metz *et al.* (2004) suggested that the common AFM preparation, using highly diluted suspensions (few tens of mg sample per litre) to separate the individual clay particles, leads to the delamination of the clay minerals. Here, we present data for the specific surface area (SSA), the specific basal surface area (BSA) and the specific edge surface area (ESA) as determined by AFM for montmorillonite and illite particles. Then, we compare the AFM-SSA with SSA measurements from N₂-BET and EGME and discuss the observed differences.

Methods

Atomic force microscopy

AFM: A suspension of 0.05 g clay mineral per litre 10 M NaOH was dispersed for 2 min in an ultrasonic bath. Three droplets of this suspension were placed on a freshly cleaved mica surface and dried over night. Images were taken with a Picoforce MultiMode AFM (Veeco Instruments, USA) in contact mode under

ambient conditions. Three different approaches were used to calculate the specific surface area (SSA), the specific edge surface area (ESA) and the specific basal surface area (BSA) from AFM-height images:

1) We used the average height h , the base area a , the perimeter at the base area of the particle p and the volume V . With the known density ρ , we calculated the BSA, ESA, and SSA according to the following equations:

$$BSA_1 = 2 \cdot a / (\rho \cdot V)$$

$$ESA_1 = h \cdot p / (\rho \cdot V)$$

$$SSA_1 = BSA_1 + ESA_1$$

2) We applied the method by Bickmore *et al.* (2002). To get a more precise ESA, the particles were cut on every morphological terrace into horizontal slices. Then, the particle's ESA was determined by summing up the ESAs of the single slices:

$$BSA_2 = 2 \cdot a / (\rho \cdot V)$$

$$ESA_2 = \sum h_i \cdot p_i / (\rho \cdot V)$$

$$SSA_2 = BSA_2 + ESA_2,$$

where h_i is the height of one sheet, and p_i the perimeter of a single slice.

3) Each clay mineral is built up of a certain number of unit layers (UL). The specific surface area of one UL of a montmorillonite was determined by XRD to be $754 \text{ m}^2/\text{g}$. (McEwan 1961). We also used this value for illite, because the structures of these two minerals are very similar. With the known length of the unit cell's a-axis a_{UC} and b-axis b_{UC} (McEwan 1961) and a UL's height h_{UL} of 1 nm the SSA, BSA and ESA can be calculated:

$$BSA_3 = BSA_{UL} \cdot h_{UL} / h_{particle}$$

$$ESA_3 = ESA_{UL} \cdot p / (a_{UC} \cdot b_{UC})$$

$$SSA_3 = BSA_3 + ESA_3,$$

where BSA_{UL} is the basal surface area of one UL ($754 \text{ m}^2/\text{g}$) and ESA_{UL} the ESA of one UL.

N₂-BET

N_2 adsorption (BET) was performed with an Autosorb1 instrument (Quantachrome, Odelzhausen, Germany). The SSA was calculated according to the BET equation from 11 measurements recorded for each mineral in the relative pressure range of 0.05 to 0.3. Prior to the measurements, the samples were outgassed for at least 24 h at 313 K in a He flow to remove adsorbed water from the surfaces.

EGME method

Two replicate samples of 1 g were dried at room temperature and in vacuum using a dessicator supplied with P_2O_5 until the weight remained constant. Then, the samples were wetted with 1.5 mL ethylene glycol monomethyl ether (EGME). The excess liquid was removed by evacuating the dessicator supplied with anhydrous $CaCl_2$ until the decrease in weight was less than 1 mg/d for 3 days. The SSA was calculated using the mass of the retained EGME and assuming that a monomolecular layer of the liquid remained on the surface. The molecular coverage of $52 \times 10^{-16} \text{ cm}^2/\text{molecule}$ was adopted from Carter *et al.* (1965).

Results and discussion

Approximately 100 illite ($n=54$) and montmorillonite ($n=42$) samples have been imaged by AFM, and their SSA, BSA and ESA was estimated using the 3 presented approaches. This resulted in similar weighted mean SSA, BSA, and ESA values (Figure 1). For illite, we obtained a weighted mean SSA of $64 \text{ m}^2/\text{g}$, and for montmorillonite of $246 \text{ m}^2/\text{g}$. The weighted mean ESA was $4 \text{ m}^2/\text{g}$ for illite, and $7 \text{ m}^2/\text{g}$ for montmorillonite, resulting in an ESA-to-BSA ratio of 0.06 for illite and 0.04 for montmorillonite. A strong correlation between the particle's height and SSA, but weak correlations between the basal area and SSA as well as between the volume and SSA suggest that the SSA of these particles was mainly determined by their thickness (Figure 2). The EGME method yielded a SSA of $112 \text{ m}^2/\text{g}$ for illite and $450 \text{ m}^2/\text{g}$ for montmorillonite, while N_2 -BET measurements estimated a SSA of $46 \text{ m}^2/\text{g}$ for illite and $72 \text{ m}^2/\text{g}$ for montmorillonite. The SSA determined by the EGME method was nearly twice as high as that determined by AFM, because the EGME method includes the interlayer surface in contrast to AFM. That AFM determined for 30% of the measured montmorillonite and 10% of the illite particles a SSA higher than the EGME-SSA, can be explained due to the fact, that the EGME method estimates bulk values, whereas AFM determines distributions of measured surface areas. We assume that the observed discrepancies between BET and AFM can be due to (i) the BET preparation, namely the outgassing temperature, (ii), the destruction of the original

clay particles during AFM preparation or (iii) a non-representative selection of analyzed particles by AFM. To investigate as to whether the outgassing temperature prior to the BET measurement was responsible for the difference in AFM and BET results, we increased the outgassing temperature from 40 °C to 250 °C. For montmorillonite, the SSA increased with an increasing outgassing temperature from 70 to 77 m²/g, while a decreasing surface area from 40 to 34 m²/g was observed for illite (Table 1). We conclude that the BET SSA varied with the outgassing temperature, but this variation was not large enough to explain the discrepancy between the BET SSA and the AFM SSA.

To investigate as to whether the AFM preparation caused a delamination of the clay particles, we considered the theoretical thickness of illite and montmorillonite particles based on the measured BET and AFM surface areas. For example, to reach the measured BET SSA of 46 m²/g, an illite particle must consist of 21 ULs, while it consists of only half as much (9 ULs) to obtain a SSA of 64 m²/g as determined by AFM. Assuming an UL height of 1 nm this value fits well with the measured particle height of 10 nm. This suggests that the illite particles must have split into halves during the AFM preparation to explain the observed difference in SSA. Likewise, montmorillonites of 9 ULs (BET SSA of 79 m²/g) would have to delaminate to particles with only 4ULs to explain the AFM-SSA (246 m²/g). We therefore conclude that the AFM preparation or a non-representative selection of analyzed particles by AFM is responsible for the observed discrepancies between SSA values determined by AFM and BET.

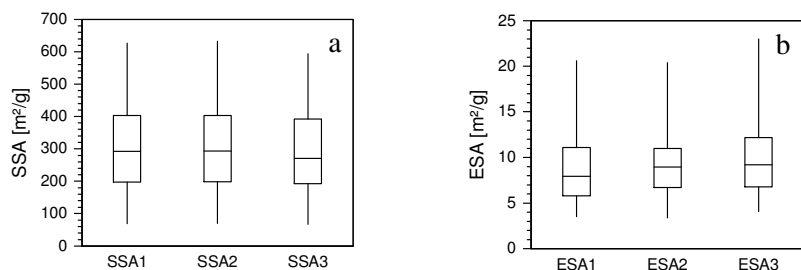


Figure 1. Boxplots of the specific surface area (SSA) a) and the specific edge surface area (ESA) b), comparing the results of the three different approaches used to calculate these values from the AFM images. Data are shown exemplary for the montmorillonite sample (n=42).

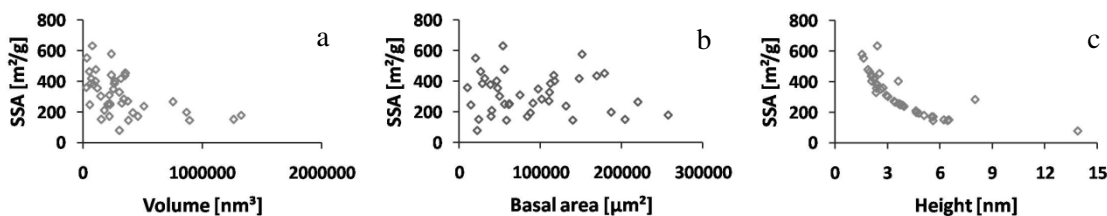


Figure 2. Correlations between the specific surface area (SSA) and the particle volume a), the basal plane b) and the particle height c). Data are shown exemplary for the montmorillonite sample (n=42).

Table 1. Specific surface area values determined by BET using different outgassing temperatures.

| Temperature | Illite | Montmorillonite |
|-------------|--------|-----------------|
| 40 °C | 40 | 70 |
| 110 °C | 35 | 73 |
| 180 °C | 35 | 76 |
| 250 °C | 34 | 77 |

Conclusion

The specific surface area, the specific basal surface area and the specific edge surface area of two clay mineral samples was determined with AFM. Three different approaches to extract the surface area from the AFM images estimated similar weighted means. It was shown that measuring only the particle height may have led to a reliable SSA calculation for clay minerals. Most AFM values were clearly lower than the EGME values but larger than the N₂-BET values. We explain the first by the fact that EGME values included the interlayer space, but AFM did not. An explanation for the latter may be (i) the different sample preparation, i.e., particle delamination during the AFM preparation or (ii) a non-representative selection of particles for AFM analysis. Currently we are testing both hypotheses: The first by performing particle size analyses (dynamic light scattering) on differently diluted suspensions and the second by taking more AFM images.

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