MEASUREMENT OF CLAY SURFACE AREAS BY POLYVINYLPYRROLIDONE (PVP) SORPTION AND ITS USE FOR QUANTIFYING ILLITE AND SMECTITE ABUNDANCE

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Abstract—A new method has been developed for quantifying smectite abundance by sorbing polyvinylpyrrolidone (PVP) on smectite particles dispersed in aqueous solution. The sorption density of PVP-55K on a wide range of smectites, illites and kaolinites is ~0.99 mg/m^2, which corresponds to ~0.72 g of PVP-55K per gram of montmorillonite. Polyvinylpyrrolidone sorption on smectites is independent of layer charge and solution pH. PVP sorption on SiO_2, Fe_2O_3 and ZnO normalized to the BET surface area is similar to the sorption densities on smectites. γ-Al_2O_3, amorphous $Al(OH)_3$ and gibbsite have no PVP sorption over a wide range of pH, and sorption of PVP by organics is minimal. The insensitivity of PVP sorption densities to mineral layer charge, solution pH and mineral surface charge indicates that PVP sorption is not localized at charged sites, but is controlled by more broadly distributed sorption mechanisms such as Van der Waals' interactions and/or hydrogen bonding. Smectites have very large surface areas when dispersed as single unit-cell-thick particles (~725 m^2/g) and usually dominate the total surface areas of natural samples in which smectites are present. In this case, smectite abundance is directly proportional to PVP sorption. In some cases, however, the accurate quantification of smectite abundance by PVP sorption may require minor corrections for PVP uptake by other phases, principally illite and kaolinite. Quantitative XRD can be combined with PVP uptake measurements to uniquely determine the smectite concentration in such samples.

Key Words—Clay, Illite, Intercalation, Montmorillonite, Polyvinylpyrrolidone, PVP, Quantitative Mineralogy, Smectite, Surface Area.

INTRODUCTION

Smectitic minerals may have a strong, sometimes dominant, effect on the physical and chemical properties of soils and sediments because of their large surface areas, large cation exchange capacities (CEC) and swelling properties. However, the quantification of smectite minerals in sediments has remained problematic (Środoń *et al.*, 2001). The first fundamental question in such studies is "What is a smectite?" This question has been a popular philosophical topic among clay mineralogists. A traditional mineralogical definition, based on chemistry and structure, is difficult to apply both because smectite has a wide range of possible compositions and a variable structure that depends on hydration state, and because of the practical difficulty of isolating a single pure clay phase from a mixture for accurate chemical analysis. In fact, compositional variability between and within individual smectite particles may mean that smectitic minerals actually defy the strict definition of a phase (May *et al.*, 1986). Before the work of Nadeau *et al.* (1984) and Nadeau (1985) and those who followed, a practical working definition of smectites was any 2:1 clay mineral with an interlayer that swells to 17 Å when exposed to ethylene glycol vapor. However, this functional definition has become increasingly problematic as additional work has shown that illite-smectite mixed-layer clays can be dispersed into fundamental particles (Drits *et al.*, 1998). When in a dispersed state, the illite particles display only a 10 Å XRD peak (Eberl *et al.*, 1998). However, when dried, the interfaces between the reassembled illite particles can be X-ray coherent, and yield layers that expand to 17 Å with ethylene glycol. This leads to an ambiguity in distinguishing between interparticle diffraction within an illite sample, and the presence of a discrete smectite phase.

We suggest that a more practical working definition of a 'smectite' is a 2:1 clay which, when Na saturated, can be dispersed into single unit-cell-thick particles in aqueous solution. This is the definition of a 'smectite' used in this work. As will be shown, the ability to separate the unit-cell layers of a clay largely correlates with chemistries found within the more traditional definition of 'smectite' group minerals. Whereas the dispersion criterion is a useful and a practical definition of smectite, it should be noted that the ability to disperse smectite fundamental particles in the laboratory does not necessarily imply anything about the smectite-to-illite reaction mechanism or the presence or absence of larger authigenic smectite/illite aggregates in sedimentary rocks.

Na-saturated smectite particles can be dispersed as single-unit-cell thick (~1 nm) particles in solution. It is the surface area of these particles which will be easily accessible to solution and which will control the

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physical and chemical properties of smectites in saturated environments. However, we found X-ray diffraction (XRD) to be an inappropriate method for quantifying the amount of these smectite particles. Completely dispersed smectite particles have no 00*l* XRD peak, because the single unit-cells do not have a repeat distance in the *c* direction (Eberl *et al*., 1998). The *a-b* plane of smectites generate XRD peaks (particularly the 060 reflection), but these peaks closely overlap with illites and micas, which are nearly ubiquitous in natural samples. When smectites and illites are dried, the particles are easily deformed by strong surface interactions to form highly oriented and coherent aggregates of illite-smectite crystals (Blum, 1994) which generate the commonly observed 00*l* diffraction peaks by interparticle diffraction (Nadeau *et al*., 1984). However, in complex mixtures containing minerals in addition to smectite, both the 'stacking' efficiency and the crystal orientation relative to the X-ray beam become highly variable, making quantification of smectites using the 00*l* XRD peaks inaccurate (Figure 1).

During sorption of inert gases in a dry environment, (*i.e.* using N_2, Kr or various organic vapors by the Brunauer, Emmett and Teller (BET) method) the gas does not access the 'internal' surface between coherently stacked crystals, and therefore grossly underestimates the smectite surface area that is exposed to solution (Alymore and Quirk, 1967). Smectites may also be quantified by measurement of the CEC though for smectites this can vary by a factor of two, leading to a similar error in using it to quantify smectite abundance. In addition, other minerals and organic matter may also contribute to the CEC in an unquantifiable manner.

The sorption of ethylene glycol monoethyl ether (EGME) has been suggested as a technique to quantify smectite abundance (Cihacek and Bremer, 1975; Chiou and Rutherford, 1997; Quirk and Murray, 1999;

Kennedy *et al*., 2002). However, recent work (Chiou and Rutherford, 1997; Rutherford *et al*., 1997) has shown that sorption of EGME is highly dependent on the EGME partial pressure, exchangeable cation and layer charge, as well as on void sizes and organic carbon content. We argue that the determination of smectite abundance by the sorption of PVP avoids many of the problems discussed above.

Polyvinylpyrrolidone (PVP, CA#9003-39-8) is a widely used industrial surfactant, emulsifier and adhesive, with applications including hair spray, textile dye stripping, extender for blood plasma, ink-jet printing, tablet binder in pharmaceuticals, and the adhesive at both ends of toilet paper rolls. Polyvinylpyrrolidone polymers are synthesized from the monomer shown in Figure 2. Polyvinylpyrrolidone is available in a variety of chain lengths with molecular weights (MW) ranging from 10 K to 1200 K, which corresponds to chains of ~90 to 11,000 monomers.

Polyvinylpyrrolidone has been widely investigated as a surfactant. Frances (1973) and Levy and Frances (1975a) first studied the sorption behavior of PVP on montmorillonites, and Levy and Frances (1975b) proposed using an XRD technique utilizing intercalated PVP to quantify the amount of montmorillonite in a sample in the presence of other swelling clays, such as vermiculite. The nature of PVP binding to montmorillonite surfaces has also been studied by Gultek *et al*. (2001) and by Séquaris *et al*. (2000, 2002). There have been studies of PVP sorption on silica by Cohen Stuart *et al*. (1984), Esumi and Oyama (1993), Gun'ko *et al*. (2002) and Thibaut *et al*. (2000), on alumina by Otsuka and Esumi (1994) and by Esumi *et al*. (1994, 2000) and on kaolinite by Israel *et al*. (2001), and on zirconium by Rovira-Bru *et al*. (2001). There have also been more general studies of the binding configuration and structure of PVP both on surfaces and in solution
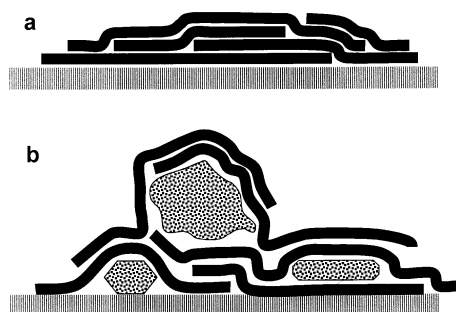

Figure 1. The planar faces of smectite particles in dried samples have strong attractive forces with most silicate minerals, which easily deform the crystals to the underlying surface. A good analogy is 'vacuum packing' the sample. Figure 1 illustrates (a) the high degree of smectite conformation and orientation in samples with large smectite contents, and (b) the lower and variable degree of coherent smectite stacking and orientation in mixtures containing other minerals in addition to smectites.
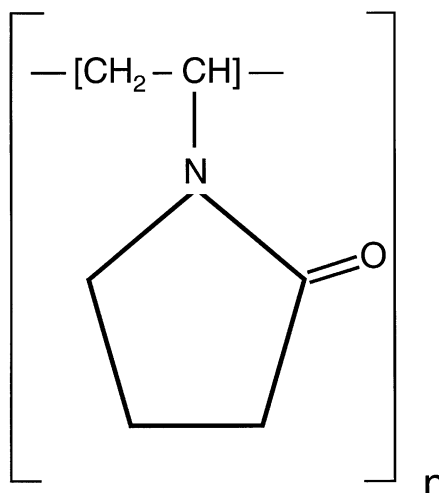

Figure 2. Chemical structure of the polyvinylpyrrolidone (PVP) monomer.

(Barnett *et al*. (1981); Gargallo *et al*. (1993); Misselyn-Bauduin *et al*. (2001); Smith *et al*. (1996); and Sun and King (1996)). Most of these studies were broadly aimed at understanding how PVP sorption can be used to modify colloid particle surfaces for better dispersion during industrial applications. Recently PVP 10K has been used to intercalate illite fundamental particles for XRD analysis (Eberl *et al*., 1996, 1998; Uhlík *et al*., 2000). When the PVP/clay suspension is evaporated, the PVP widely separates the illite particles, eliminating interparticle diffraction, and allowing the quantification of illite particle thicknesses from the broadening of the 001 peak.

METHODS

For surface-area determination by PVP, the sample is typically Na (or Li) saturated with 1 M NaCl twice to assure complete saturation and dispersion of smectite particles, and then washed to remove all soluble salts which might interfere with measurement of PVP concentration by weight. Dialysis bags with a molecular-weight pore size of 10K are effective for both removing residual NaCl and any other low-molecular weight-soluble material which might be present in the sample, while retaining all the clay particles.

Procedure

(1) A 15 mL centrifuge tube with lid is weighed, and then ~50 mg of dry smectitic clay (or other material with an equivalent surface area of ~40 m^2) is weighed into the centrifuge tube. A replicate determination is routinely made with a sample ~½ the mass of the first determination.

(2) About 5 mL of water are added, and the sample is thoroughly dispersed with an ultrasonic probe. The tube is then weighed, ~2 mL of ~10% PVP 55K are added, and the tube is reweighed.

(3) The sample is then shaken overnight, and centrifuged until the solids are completely separated from the solution. We usually use ~4 h at 10,000 rpm.

(4) A sample vial is weighed with the lid, solution is decanted from the centrifuge tube into the vial, closed and weighed. The vial is then dried at 85ºC overnight, capped immediately after being removed from the oven, and reweighed when cool.

The mass of PVP sorbed on the sample is then calculated as the difference between the mass of PVP added to the centrifuge tube and the mass of PVP remaining in solution after the sorption reaction, as calculated from the measured PVP concentration, and the original amount of solution in the tube (determined by mass). All masses are determined ±0.0001 g.

Procedure comments

There is considerable latitude in the amount of sample that can be used, but it is difficult to suspend effectively 40 m^2 of surface area when analyzing small-surface-area (<50 m^2/g) samples such as kaolinite or silica. A sample size of 1 g per 5 mL of water seems like a practical limit for fine material (<2_μm), but larger masses of high silt or sand samples can be accommodated. The amount of PVP solution added can be adjusted for small- or large-surface-area samples to maintain a nearly constant final PVP concentration in solution. This precaution retains sensitivity in the analysis while remaining on the flat portion of the sorption isotherm. The PVP uptake on the Wyoming and Belle Fourche low-charge smectites and the RM30 illite was measured both with and without overnight shaking. Samples with immediate centrifugation (*i.e.* no shaking) sorbed >90% of the PVP sorbed overnight, so the PVP sorption kinetics are fast. However, sorption kinetics were not investigated for a wide spectrum of materials, and samples were routinely shaken overnight to assure complete sorption.

Settling of single unit-cell-thick smectite particles is difficult, and requires considerable centrifugation time. However, PVP sorbed on the clay surfaces prevents flocculation by traditional techniques such as adding methanol or acetone, increasing the ionic strength or manipulation of solution pH. As a result, we relied on high-speed centrifugation to remove the clays from solution. Undoubtedly, some small clay particles will remain suspended in solution. However, the error introduced is proportional to the fraction of clay remaining in solution. By using different centrifuge times up to 48 h, we concluded that as long as the solutions appeared completely clear to the eye, the error introduced by any incomplete settling of a few fine particles was <<1% of the PVP sorbed. Many previous studies have used UV sorption to measure the PVP concentrations in solution, which would be much simpler than gravimetric analysis. However, we found that the UV sorption spectra were extremely sensitive to residual colloids in solution. Because of the difficulty in removing all the smectite particles, we found this analytical method did not produce reliable and reproducible PVP concentrations for samples containing smectite.

Another practical problem is that PVP will hydrate after it is removed from the oven, gaining several wt.% of water over ~5 days, which can lead to a large uncertainty in the calculation of the mass of PVP sorbed. The rate of PVP weight gain by hydration is initially rapid, decreasing dramatically after ~1 h, but continuing for days at a slow rate. Therefore, it is important to keep the samples isolated from the atmosphere, and measure the mass soon after the vials cool. We also found that polystyrene vials had the smallest change in mass with heating and cooling, smaller than glass or polyethylene, and yielded more reproducible results. It may also take longer than expected to dehydrate the PVP in the oven, and it is necessary to heat the samples for at least several hours after they appear dry.

Preparation of PVP reagent

Typically, ~50 g of 55K PVP reagent are dissolved in ~400 mL of distilled water. The PVP has a nearly infinite solubility in water, but the dissolution kinetics can be very slow. The beaker is usually stirred and heated gently on a hot plate for several hours. The PVP of all molecular weights seemed stable up to at least 120ºC, and the reported melting point of PVP-55K is >300ºC. The solution is then transferred to a volumetric flask, cooled to room temperature, and diluted to 500 mL. The PVP solutions are stable indefinitely if sterile, but are subject to biodegradation. Therefore, solutions were usually refrigerated to retard colonization if they were stored for more then a few days. Each batch of PVP reagent must be individually calibrated, typically by evaporating multiple aliquots of 1 to 10 mL of solution at 85ºC as in step 4 of the sample procedure. Reproducibility is generally <±0.2%, and yields a final solution of between 9.4 and 9.5 wt.% PVP, indicating the initial reagent is ~5 wt.% water.

Determination of sample-specific surface areas

In examining the behavior of PVP sorbed on minerals, and in the development and validation of the PVP sorption method, it is critical to have some independent measure of the mineral surface area in order to evaluate the sorption density. As mentioned in the introduction, there is no other reliable technique for determination of smectite surface area. However, because we know the geometry of the smectite crystals, we can calculate a theoretical surface area. Elementary smectite crystals are 1 nm thick, and from transmission electron microscopy (TEM) (Nadeau, 1985) and atomic force microscopy (AFM) (Blum, 1994) observations, they have diameters from ~0.1 to 2 μm. Using the lower value of 0.1 μm for the diameter, the edges are calculated to contribute <2% of the surface area. Therefore, we can treat smectite as an infinitely large sheet 1 nm thick for the calculation of surface area. Although the chemistry of smectites may vary greatly, the structure is always very similar to that of muscovite, and consequently we can use the molar volume (V_{mol}) of muscovite (140.71 cm^3/mol (Robie *et al.*, 1979)) as V_{mol} for all smectites. This volume ignores interlayer swelling by hydration, but this is appropriate because we consistently exclude the interlayer water in both the chemistry and the volume assumptions. The surface area of a smectite therefore is:

$$SA = \frac{2V_{mol}}{hF_{wt}} \quad (1)$$

where *SA* is the specific surface area (defined as surface area/mass), *h* is the thickness of the crystal (for muscovite and smectites *h* = 1 nm), and F_{wt} is the formula weight of the mineral (~373 g/mol for the Belle Fourche smectite). For a typical montmorillonite, this

formula yields a specific surface area of ~755 m^2/g. However, this *SA* is calculated for dehydrated smectite. Montmorillonite which is oven dried at 105ºC still retains ~4.0 wt.% interlayer water (determined by heating at 300ºC overnight) but the effective *SA* remains the same. This additional water reduces the specific surface area of a smectite sample weighed in air by ~4%, to ~725 m^2/g for a typical montmorillonite. The latter surface area, measured F_{wt} and equation 1 are used to calculate the *SA* of many of the smectites shown in Table 1.

For pure illite, surface areas are also calculated using equation 1, except that *h* is taken as the mean crystallite thickness determined using the MudMaster program (Eberl *et al.*, 1996), which analyzes XRD peak shapes to determine crystal-size distributions. For all the minerals except smectite and illite, the BET surface area was used to check the PVP method. The BET surface area was measured by sorbing and desorbing N_2 from the surface. These samples all have a more blocky morphology without significant coherent stacking and interparticle diffraction. Consequently, it is assumed that in the dried samples, N_2 which has a diameter similar to that of a water molecule, has access to the same surfaces which are accessed by solution after aqueous dispersion.

RESULTS

Sorption on smectites

A sorption isotherm for the Belle Fourche bentonite (a low-charge smectite) is shown in Figure 3 for PVP-10K and -55K. The general shapes of the isotherms are consistent with the sorption of PVP on the clay surface, with a well defined surface saturation plateau at 0.61 g and 0.72 g of PVP sorbed per gram of clay (g/g) for PVP-10K and PVP-55K, respectively. The sorption isotherms are not fitted well by either a theoretical Langmuir or Freundlich isotherm, as is evident from the non-linearity of either a reciprocal or log-log plot,
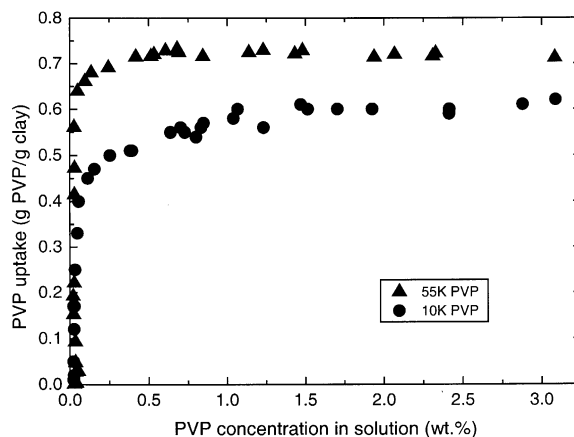

Figure 3. Sorption isotherm of 55K and 10K PVP on Belle Fourche smectite.

Table 1. PVP-uptake measurement of various minerals.

Sample	Mineral	PVP-55K uptake (g/g)	Surface area (m^2/g)	PVP surface area (m^2/g)	PVP-55K uptake (mg/m^2)
Belle Fourche	montmorillonite	0.72[a]	725[b]	725	0.99
Belle Fourche (Ca-sat.)	montmorillonite	0.44	725[b]	443	0.61
Wyoming 'B'	montmorillonite	0.71	725[b]	715	0.98
Wyoming B (Ca-sat.)	montmorillonite	0.46	725[b]	463	0.63
Kinney	high-charge smectite	0.71	752[b]	715	0.98
SAz-1 (Cheto)	high-charge smectite	0.71	717b	715	0.99
SAz-1 (Cheto) (Ca-sat.)	high-charge smectite	0.33	717[b]	332	0.46
Hectorite	Li smectite	0.72	725[c]	725	0.99
Camp Berteau	montmorillonite	0.71	725[c]	715	0.98
Red Hill	montmorillonite	0.72	725[c]	725	0.99
Bates Park Montana	montmorillonite	0.64	725[c]	644	0.88
Glen Silver Pit, Idaho	montmorillonite	0.50	725[c]	503	0.69
Fe smectite	nontronite	0.64	654[d]	644	0.98
Saute Loupe	nontronite	0.65	654[d]	655	0.99
Amargosa	sepiolite	0.34		342	
IMV	sepiolite	0.23		232	
Arkansas	rectorite	0.36	363[c]	363	0.99
Slovakia	K-rectorite	0.35	363[c]	352	0.96
Wyoming 'C'	montmorillonite	0.71	725[c]	715	0.98
Dry Branch	kaolinite	0.012	14.0[e]	12	0.86
KGa-1	kaolinite	0.0089	10.0[e]	9	0.89
KGa-2	kaolinite	0.018	22.6[e]	18	0.82
Libby	vermiculite	0.00	5		small
SG4	illite	0.034	35[f]	34	0.97
RM30 (Na sat)	illite	0.071	63[f]	71	1.13
RM30 (Ca sat)	illite	0.073	63[f]	74	1.16
Marblehead	illite	0.105	117[f]	106	0.90
Fithian, Illinois	illite	0.074	176[f]	75	0.42 or 8%[h]
3M3	illite	0.51	201[g]	514	61% smectite[h]
IM5	illite	0.31	148[g]	312	29% smectite[h]
Activated carbon	reagent	0.11	883[e]	111	0.12
Florida peat	humic standard	−0.017			
Fe_2O_3	hematite	0.0103	10.5[e]	10	0.98
Fumed SiO_2	amorphous	0.13	280[e]	131	0.46
$Al(OH)_3$	amorphous	0.0014			~0
$Al(OH)_3$	synthetic gibbsite	−0.003	0.09[e]		~0
γ-Al_2O_3	reagent	0.0016	175[e]		~0
ZnO	reagent	0.0025	3.83[e]		0.65

[a] The uptake of PVP-10K, 40K and 360K are ~0.61, ~0.68 and ~0.76 g/g, respectively.
[b] Calculated based on measured chemistry, the molar volume of muscovite and 1 nm thick crystals.
[c] Estimated surface area (see text).
[d] Calculated assuming a composition of $NaFe_4Si_{7.34}Al_{0.66}O_{20}(OH)_4$, an ideal nontronite.
[e] N_2 BET surface area.
[f] Computed from illite particle thickness distributions based on MudMaster XRD measurements.
[g] Surface areas measured by MudMaster (XRD). However, these samples are very thin illites which probably contain single unit cell smectite particles which are not detected by XRD.
[h] The % smectite is computed based on measured PVP uptake and the MudMaster surface area for the illite component.

respectively (not shown). Nevertheless, there is a wide range of solution PVP concentrations at which the amount of PVP sorption is nearly constant. Throughout this range of solution PVP concentration, the amount of PVP sorbed is proportional to the amount of clay present, but independent of the solution composition.

There is also a trend of slightly greater PVP sorption with increasing polymer chain length which is observed over a range of PVP molecular weights from 10K

(0.61 g/g) to 360K (0.76 g/g). The mass of PVP sorbed per unit mass (or *SA*) increases only slightly (~20%) as the polymer chain length increases by a factor of 36, indicating that the area per polymer unit (Figure 2) remains nearly constant. This observation is consistent with a conceptual model in which the PVP chains are lying on the surface, and not analogous to detergent molecules which are arranged perpendicular to the surface.

The unbonded electron pairs on either the amine or the carbonyl groups located on the five-member ring might be expected to act as weak Lewis bases. However, PVP does not appear to protonate significantly in the near-neutral pH region. A solution of 1% PVP-10K was titrated with HCL and NaOH. The solution neutralized 92 µeq of charge per g of PVP-10K between pH 5 and pH 9, which corresponds to ~1 charge per polymer chain. In practice, the PVP does not significantly buffer the solution pH. The pH of a 1 wt.% PVP solution is ~8.5, but the pH of the final suspension is controlled primarily by the surface chemistry of the sample, which in turn often reflects the last solution to which the sample was exposed.

Shifting the solution pH (by the addition of NH_4OH or HCl, which should be lost in the vapor phase when evaporated) had no discernible effect on the amount of PVP sorbed on smectites, at least in the pH range from 6 to 10 (Figure 4). There does appear to be some effect of low pH on PVP sorption, but this is probably an experimental artifact. As hydrochloric acid is added to the suspension, protons substitute for Na^+ on the smectite exchange sites, releasing Na^+ to solution. When the solution is evaporated the Na^+ is retained as NaCl. This salt gives the appearance of a greater mass of PVP in solution, and therefore less PVP is calculated as sorbed on the clay. Differences in the fixed charge of the smectite (Table 1) also had no discernible effect on the PVP sorption density in the range from 0.3 to 0.8 charges per half formula unit, nor does it appear to be affected by whether or not the charge is in tetrahedral or octahedral sheets. This insensitivity to layer charge is highlighted in particular by the similar PVP uptake of the Wyoming and Belle Fourche low-charge smectites, and by the Cheto, Kinney and Otay high-charge smectites (Table 1).

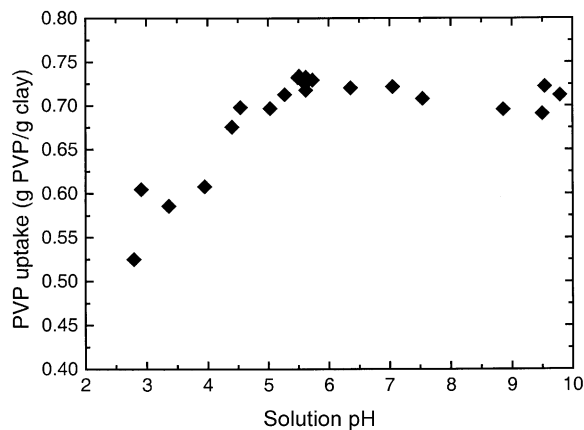A major issue in designing a technique using PVP to measure smectite surface areas was the effect of the suspension density (g clay/mL water). The higher the solid-to-solution ratio (SSR), the greater the sensitivity of the technique, since a greater proportion of the PVP in solution is sorbed. Low-charge smectites, such as the Belle Fourche and Wyoming bentonites had very little dependence on the suspension density (Figure 5). However, high-charge smectites such as the Cheto and Kinney displayed a strong dependence on suspension density. The cause of this SSR effect is not understood, but is generally consistent with the higher-charge smectites having a greater tendency to form aggregates in solution before the PVP is added. However, the PVP sorption of the high-charge smectites is very reproducible, and is not strongly dependent on the time the solution sits between ultrasonic dispersion and addition of the PVP. This observation would suggest that it is a subpopulation of particles which tends to aggregate quickly, rather than a highly time-dependent phenomenon.

The abundance of low-charge *vs*. high-charge smectites in most natural environments is not known, because this is a quantity which can only be determined accurately on pure samples, usually from bentonites or hydrothermal veins. These environments, although economically important, are not representative of most natural sediments. Differences in dispersion caused by charge-density differences could lead to considerable uncertainty in the surface-area determination of unknown samples by PVP sorption. However, it was found that mixtures of low- and high-charge smectites do not vary their sorption properties in a simple linear mixing (Figure 5) as might be expected. The addition of 50% low-charge smectite to 50% high-charge smectite results in PVP sorption behavior nearly identical to that of a pure low-charge sample. Thus, the solution density should not be a significant effect for samples that contain <50% high-charge smectite. This assumption can be tested by measuring two different sample masses which should yield the same PVP sorption density, and this procedure is recommended for samples of unknown composition.
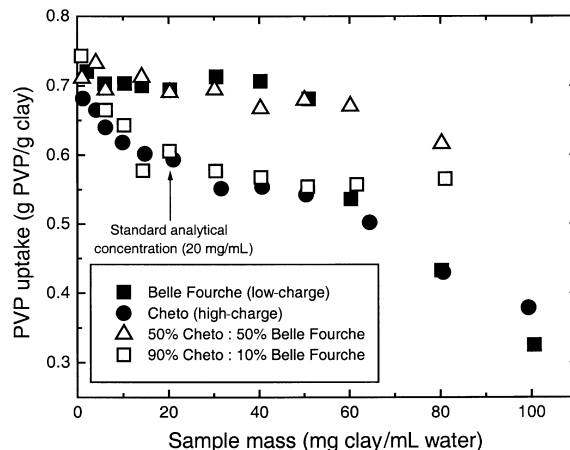

Figure 4. The effect of solution pH on the sorption of PVP-K55 on Belle Fourche smectite.

Figure 5. The effect of solid-to-solution ratio on PVP-K55 uptake.

XRD evidence for the thickness of sorbed PVP

The XRD patterns for smectite solutions with different SSRs (Figure 6) give some insight into the difference in behavior of low-charge and high-charge smectites. It is important to remember that Figure 6 reflects smectite orientations after evaporation, and not in solution. All smectites dispersed in PVP solutions with a small SSR had no XRD 00*l* diffraction peaks. Such XRD patterns show only the smectite structure factor and weak and broad reflections from the PVP matrix. This is consistent with the observations of Eberl *et al.* (1998) for a dilute suspension of Kinney smectite in PVP. The lack of diffraction peaks in dilute solutions indicates that the smectites are dispersed as single-unit-cell crystals with enough excess PVP between the particles after evaporation to completely eliminate interparticle diffraction. However, as the SSR increases, the low-charge and high-charge smectites display different behaviors. For example, the Belle Fourche has no XRD peaks until a SSR of ~14 mg/mL, at which point a peak appears at ~34.5 Å along with its higher orders. At such low angles, the Lorentz polarization factor (L_p) has a significant effect on peak shapes and positions. All *d* spacings were determined after L_p removal, although Figure 6 shows the uncorrected XRD patterns. The peak at 34.5 Å increases in intensity

with increasing SSR until ~50 mg/mL, beyond which the intensity continues to increase, but the peak position also moves to larger angles, reaching 27 Å at a SSR of 100 mg/mL, and the higher-angle reflections become less rational.

In contrast to the Belle Fourche sample, the Cheto high-charge smectite has a very weak peak at ~23.5 Å at the lowest SSR of 1 mg/mL, which is detectable only at a greatly expanded scale from that used in Figure 6b. The 23.5 Å peak increases in intensity with increasing SSR, and shifts to slightly higher angles, approaching 22 Å at a SSR of 100 mg/mL. The Kinney, also a high-charge smectite, has a behavior intermediate between the Belle Fourche and Cheto (not shown in Figure 6). At a low SSR, the Kinney smectite has a weak peak at ~34.5 Å, which increases in intensity as the SSR increases. At an SSR of 30 mg/mL the peak begins to shift to a progressively lower *d* spacing, finally reaching ~23 Å at a SSR of 100 mg/mL. The multiples of the high-angle peaks initially become more irrational as the peak position moves away from 34.5 Å, and then become more rational again as the peak position approaches 23 Å.

These XRD observations can be explained by a simple structure, with stacking of 12.5 Å smectite crystals (10 Å 2:1 silicate layer + 2.5 Å due to hydration of the surface) with either one or two 11 Å thick PVP
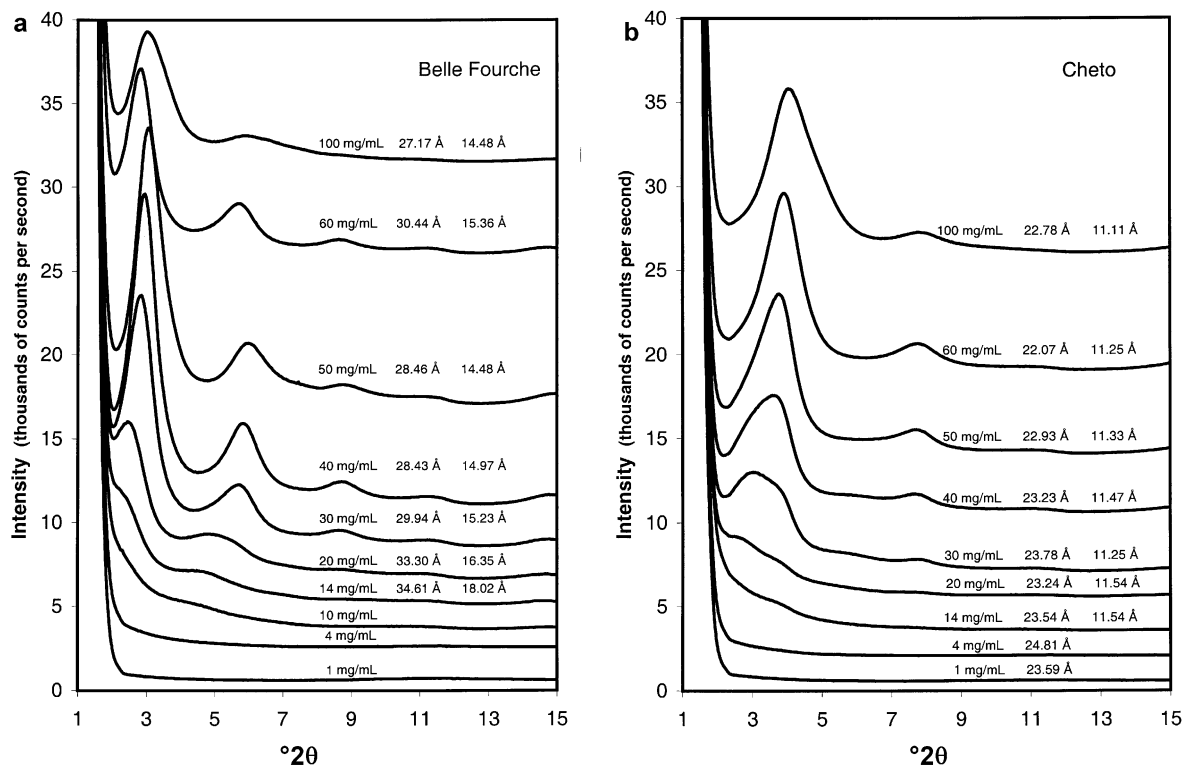

Figure 6. XRD patterns of (a) Belle Fourche low-charge montmorillonite, and (b) Cheto high-charge montmorillonite. Each trace is labeled with the solid-to-solution ratio, followed by the positions of the first and second peaks as determined from L_p-corrected traces (not shown). Baselines of the patterns have been offset to add clarity.

interlayers. The conceptual model is shown in Figure 7. At low SSR values, all the clays have a tightly bound 11 Å layer of PVP sorbed on their surfaces, but there is sufficient unbound PVP in solution to widely separate the clay crystals, yielding no XRD peak (*i.e.* only the structure factor is visible) when dried. In the case of Belle Fourche, as the SSR increases and the clay particles become more closely packed, some crystals begin to align, creating interparticle diffraction with a 34.5 Å periodicity. Basically, as the number of particles increases and the amount of PVP in solution stays nearly constant, there is less PVP between each particle to disrupt interparticle diffraction. Since the amount of PVP sorption on each surface remains at 11 Å, these interparticle associations, if present in solution, would not effect the amount of PVP taken up from solution. This picture is consistent with the observation that the PVP sorption on Belle Fourche is not changed by SSRs below ~50 mg/mL (Figure 5). We can also compare this uptake to the computed thickness of the sorbed PVP layer based on the observed uptake from solution (Figure 3). Assuming the smectite particles have a density of 2.5 g/cm³ and a thickness of 12.5 Å, and the PVP layer has a density of 1.1 g/cm³, the PVP surface layer is calculated from the PVP uptake of 0.73 g/g to have a thickness of 10.2 Å, in good agreement with the XRD data of 11 Å.

As the SSR of the Belle Fourche increases to >~50 mg/mL, some interlayers have only one layer of PVP between smectite 2:1 layers. This uptake produces a spacing of 23.5 Å, causing the shift of the 34.5 Å peak to smaller apparent spacings with a loss in rationality of
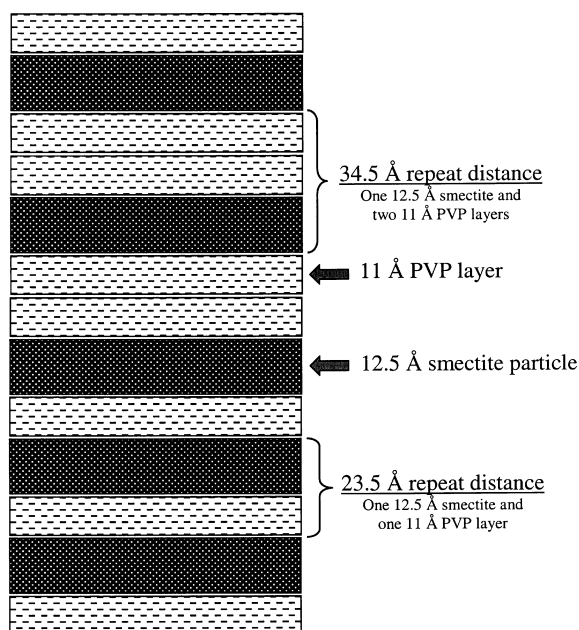

Figure 7. Proposed structure for generating the 34.5 Å and 23.5 Å repeat distances observed in XRD patterns (Figure 6).

the multiple *d* spacings, typical behavior of randomly interstratified mixed-layer clays (Moore and Reynolds, 1989). Formation of 23.5 Å aggregates in solution would produce a reduced PVP uptake, because two surfaces share one PVP layer, with each surface being effectively only 50% covered. This model is consistent with the reduced PVP uptake by Belle Fourche at SSRs >~50 mg/mL (Figure 5).

In contrast to the Belle Fourche, the Cheto starts with a few 23.5 Å aggregates even at an SSR of 1 mg/mL, and the number of aggregates increases quickly with increasing SSR. This behavior is consistent with the formation of 23.5 Å aggregates in solution, which explains why the uptake of PVP on the Cheto appears to be strongly dependent on the SSR even at low SSR values. The shift of peak positions to <23.5 Å at the highest SSRs may indicate the interstratification of 12.5 Å interlayers with no intercalated PVP at the highest clay concentrations. The Kinney at first forms 34.5 Å aggregates, but progressively moves toward 23.5 Å at higher SSRs much more quickly than the Belle Fourche, with a randomly interstratified structure during the transition.

Thus, the uptake of PVP from solution as a function of SSR (Figure 5) is consistent with the XRD evidence, and it appears that the XRD patterns reflect aggregates of clay crystals which formed in solution. We propose an explanation for these observations, based on the relative rates of PVP sorption *vs.* particle aggregation. The clay particles are dispersed in solution prior to the addition of PVP, as shown by all smectites being nearly completely dispersed at low SSRs. Once the PVP solution is added, the PVP must sorb to all the clay surfaces before the particles aggregate. If this occurs, then there is an 11 Å PVP layer on all the surfaces, and the PVP uptake from solution is independent of the SSR. However, if the smectite particles associate before completion of the PVP sorption, then some clay particles may end up sharing a PVP layer with an adjacent particle, forming the 23.5 Å structure. As the SSR of the suspension increases, the mean distance between particles in solution decreases, increasing the likelihood of particles associating before PVP sorption is complete, and favoring the formation of the 23.5 Å structure. It seems reasonable that high-charge smectites would have a greater propensity to aggregate than low-charge smectites, and would be more sensitive to the SSR.

Illite and vermiculite

Natural sediments usually contain a complex mixture of clay minerals; therefore it is important to investigate the effects of a broader spectrum of minerals on PVP uptake. Illites are the other clay minerals with a large surface area present in many soils and sediments. Illites have a structure very similar to smectites, except that the fundamental particles are ⩾2 unit-cells thick, and interior 00*l* interfaces are fixed by K⁺ ions that cannot

be readily cation exchanged or expanded by ultrasonic dispersion, ethylene glycol or EGME. The exterior 00*l* surfaces of the illites should behave in a similar manner to smectites, and the exterior unit-cells of illites are thought to have a chemistry and fixed charge that are similar to low-charge smectites (Środoń *et al.*, 1992). Sorption of PVP on a range of different illites (Table 1) is consistent with this conceptual model. When normalized to illite surface area determined by MudMaster (Eberl *et al.*, 1996), illites have the same PVP sorption density and behavior as low-charge smectites.

The specific surface areas (m^2/g) of illites can at most be 50% that of smectite (assuming all the illite crystals are two unit-cells thick, *e.g.* a rectorite), and the surface area decreases rapidly as the illite particles increase in thickness ($SA \propto 1/T$). The PVP sorption on two different rectorites, in which most of the particles are 2 nm thick, is shown in Table 1, and is about half the value of smectites on g/g basis, as would be expected if the particles are two unit-cells thick. When illite particles reach a mean thickness of 12 nm, they will have a specific surface area ~8.3% that of smectites. Thus, if illite is abundant, it may contribute significantly to the amount of PVP sorbed by a sample, and in samples with a small abundance of smectite mixed with a large amount of thin illites, illite may dominate the PVP sorption. Therefore, it is necessary to correct PVP-based measurements of smectite abundance for illite in samples where significant illite is present, as will be discussed later.

The behavior of vermiculites is intermediate between the behavior of illite and smectite. The interlayer cations in vermiculites are exchangeable, but are not swollen by ethylene glycol, and vermiculite is not dispersed into 'fundamental' particles. Rather, vermiculites maintain 'large' crystals with a small external surface area, but with the interlayers accessible for cation exchange. It appears that PVP does not enter the vermiculite interlayers, and that vermiculites are not a significant source of PVP sorption.

Oxides

Sorption of PVP on amorphous (fumed) silica is shown in Figure 8a, and has a similar sorption density to that of smectite and illite surfaces (Table 1). These data are consistent with the PVP sorption data of Thibaut *et al.* (2000) and Cohen Stuart *et al.* (1984). We did not measure quartz, because grinding to a sufficiently fine grain size to detect PVP sorption produced abundant amorphous material. Presumably quartz would act in manner similar to that of amorphous silica, as the local surface chemistry of amorphous SiO_2 and quartz are similar, and PVP sorption appears insensitive to the detailed surface structure. In natural samples, quartz may be high in abundance but with low surface area, and even highly pitted quartz will contribute insignificantly to the surface area in comparison to smectite.

In contrast to amorphous silica, γ-Al_2O_3 sorbed no PVP (Figure 8b). The point of zero charge (PZC) of γ-Al_2O_3 is near pH 8.5 (Huang and Stumm, 1973). Changing the solution pH on either side of the PZC to create positively and negatively charged γ-Al_2O_3 surfaces had no effect on the lack of PVP sorption. The apparent increasingly negative values for γ-Al_2O_3 PVP uptake at low and high pH are thought to be an artifact, the result of Al_2O_3 dissolution which increases the mass of solids in solution. Minimal PVP sorption to alumina surface has also been reported by Otsuka and Esumi (1994) and Esumi *et al.* (2000). Similar to γ-Al_2O_3, gibbsite and amorphous $Al(OH)_3$ showed no PVP sorption, and it appears that aluminum oxyhydroxides do not contribute significantly to PVP uptake. However, hematite (Fe_2O_3) showed PVP uptake equivalent to the silicates on a per surface area basis (Table 1).

Kaolinite

Kaolinite presents a somewhat different situation from smectite and illite. For any kaolinite crystal, one surface should be an octahedral Al-OH surface and the other side a tetrahedral Si-O-Si surface. Based on the oxide analysis, we would expect that PVP would sorb on the tetrahedral side and not on the octahedral side, producing a PVP sorption per unit surface area (g PVP/m^2) that is one half that of smectites and illite. Kaolinite uptake of PVP (Figure 9) is near the detection limit for this technique, but it appears that kaolinite sorbs PVP in a similar manner and at the same surface density as smectites and other minerals, contrary to our expectation. Bonding between kaolinite layers is weak, and previous AFM observations have shown that vigorous ultrasonic treatment can generate some 7 Å thick kaolinite crystallites (Blum and Eberl, 1992). Qualitatively, these single-layer crystals appeared to be a very small fraction of the total sample, but, there was concern that our experimental procedure could be increasing the amount of kaolinite surface area present in the sample. If ultrasonic dispersion doubled the
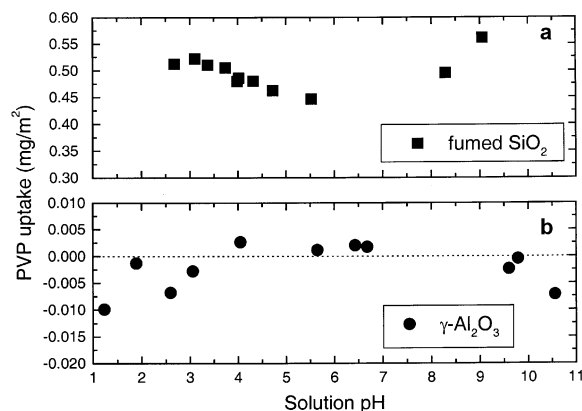

Figure 8. PVP uptake by SiO_2 and γ-Al_2O_3 as a function of solution pH.

kaolinite surface area, then the apparent sorption of PVP on both surfaces of the kaolinite based on the BET surface area could be explained. Figure 10 shows that increasing the duration of ultrasonic treatment of the kaolinite had no impact on the amount of PVP sorbed, and that this procedure does not distort the results. However, grinding the kaolinite in a McCrone mill (a variety of vibrating rod mill) does systematically increase the PVP uptake by the sample, presumably by grinding of the kaolinite to a finer grain size, and thus, increasing the surface area.

Organic matter

A final consideration for natural samples is the effect of organic matter on PVP sorption. One end-member for organic carbon is activated carbon, which has a very large and reactive surface area (883 m^2/g). The PVP did sorb on activated carbon with an average density of 0.12 mg/m^2, significant but much smaller than the value of ~1 mg/m^2 for silicates. The most likely explanation is that PVP sorbed to activated carbon at about the same density as on silicates. However, a large portion of the activated carbon surface area is internal, as is obvious from its silt size particles which have a surface area actually greater than those of smectites. Apparently, many of these pores are small enough that PVP-55K cannot access the interior. However, the internal porosity would be accessed by N$_2$, and thus, the sorption density based on N$_2$ BET surface areas appears low.

Consequently, organic carbon has the potential to uptake PVP. However, shales and sediments are rarely more than a few wt.% organic carbon, and natural organic material typically has surface areas that are orders of magnitude smaller than activated carbon. For example, a Florida (Pahokee) peat (an International Humic Substances Society source material), is a highly reactive natural organic material with a large surface area, but it has a small, apparently negative uptake of PVP. The dissolved organic matter imparted a d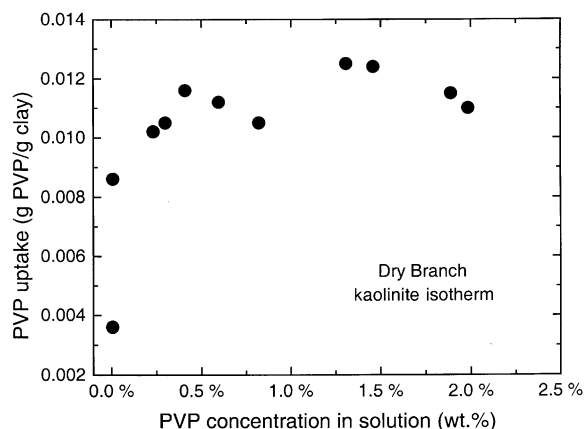ark yellow-brown color to the PVP solution, consistent with an increase in dissolved organic matter (DOC) in solution, and with the apparent negative PVP uptake. This experiment indicates that even with a thoroughly water-washed sample, the PVP in solution solubilized (presumably by complexation) more organic matter than PVP was sorbed on the organic surfaces. We have also observed that some organic-rich shales impart a dark brown color to the PVP solution, indicating the solubilization of organic matter. It appears that the major caveat for organic-rich samples may not be the uptake of PVP by the organics, but the potential solubilization of DOC by the PVP measurement procedure. It may, therefore, be advantageous to wash organic-rich samples with an organic solvent or destroy reactive organic matter with peroxide before the PVP analysis of organic-rich samples, but this approach was not thoroughly investigated. An advantage of PVP uptake by organic carbon may be that organics sorbed to the clay surfaces will not greatly effect the measured surface areas of the clays, and should not interfere with smectite abundance measurements.

DISCUSSION

The nature of PVP sorption

The conceptual model for PVP sorption on silicates can be constrained based on the observations reported earlier. The insensitivity of the absolute mass of PVP sorbed on the chain length indicates the PVP chains are lying parallel to the silicate surface, so that the area covered per polymer is approximately proportional to the polymer length. The large area covered by each PVP polymer, coupled with the apparent lack of sensitivity of PVP sorption to the details of surface chemistry, layer charge or solution pH, suggest the interaction between adjacent PVP chains is a major factor in the formation of the surface layer. However, there is no indication of the addition of more than an ~11 Å thick layer of PVP to the

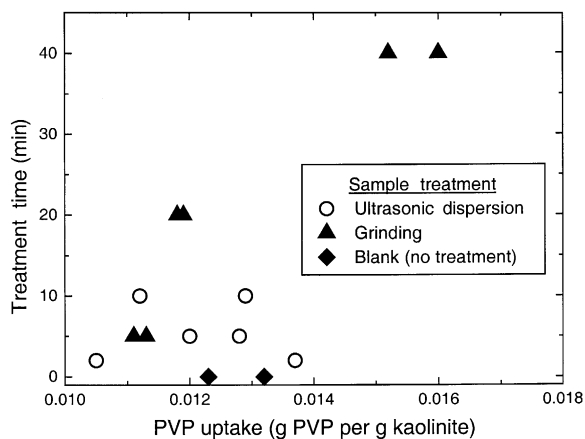Figure 9. PVP sorption isotherm for Dry Branch kaolinite.

Figure 10. The effect of ultrasonic dispersion and grinding (methanol in McCrone mill) pretreatments on the amount of PVP uptake on Dry Branch kaolinite.

surface, suggesting that the surface also plays an important role in the formation of the PVP layer, and that this is not a surface-precipitation-type process. The XRD peaks at 23.5 and 34.5 Å (Figure 6) also suggest that the sorbed layer is relatively uniform in thickness, because a variability in the thickness of the PVP layer between particles would not produce a coherent XRD peak. The observations are all consistent with the sorption of a monolayer of PVP chains on the surface, although we have no direct evidence as to the organization of PVP within the sorbed layer. The reason why the Si-OH surface of fumed silica sorbs PVP but the Al-OH surface of gibbsite (or γ-Al$_2$O$_3$) does not is still unknown.

Accuracy of PVP uptake as a measure of surface area

The results have already illustrated some of the difficulties in constraining the accuracy of a PVP-uptake measurement as a measure of surface area. Table 1 presents data from a wide range of materials. However, the only parameter directly describing PVP sorption is grams of PVP sorbed per gram of sample. The repeatability of measurement is generally (with several caveats discussed below) very good, and almost always better than ±5% for smectite-rich samples. However, this quantity is difficult to evaluate independently. In looking at the sorption per unit surface area, we can easily compare values, but these quantities incorporate errors in the surface-area determinations which are potentially numerous and significant. We certainly can compare the results of different smectites. At least theoretically, the only difference in the specific surface areas of the different smectites is the difference in density resulting from variations in the chemical composition of the unit-cell. In general, the smectites shown in Table 1 are in good agreement, clustering around 0.72 g/g. However, the purity of any smectite sample which has not been extensively characterized is always suspect, and 'impurities' can usually be invoked as an explanation for PVP-uptake numbers below 0.72 g/g. For example, the Glen Silver Pit smectite in Table 1 has a PVP uptake of 0.50 g/g, which could easily be explained by contamination with a small amount of amorphous material, illite or another silicate. One encouraging aspect of the smectite data in Table 1 is that no samples yielded a PVP uptake significantly greater than 0.72 g/g.

The determination of illite surface areas are all dependent upon the MudMaster analysis. The use of MudMaster as a technique for determining illite surface areas appears to be valid (Eberl *et al*., 1998; Dudek *et al*., 2002), but the accuracy is still difficult to constrain. The question of the illite sample 'purity' also introduces an uncertainty for many illite samples. Finally, the use of N$_2$ surface areas for the non-clays for comparison with PVP surface areas is justifiable, but as suggested by the measurements of activated carbon, the surface area

accessible to N$_2$ with a MW of 28 and PVP with a MW of 55,000 are not necessarily equivalent, especially if there is considerable internal microporosity. Despite all these caveats, we see a relatively consistent result of ~0.99 mg of PVP 55K sorbed per m^2 of surface area on a range of smectites, illites, silica and other materials (Table 1). This consistency gives confidence that PVP uptake can be used to accurately quantify silicate mineral surface area.

Quantitative measurement of smectite abundance

To quantify the amount of smectite in a complex mixture, it is necessary to know how much PVP has been sorbed by other phases, such as illite, kaolinite, quartz and feldspars. However, non-phyllosilicate minerals rarely make up a significant portion of the <2 μm fraction of natural samples and their surface areas are very small. Therefore, non-clays contribute very little to the total sample surface area. For example, in a sample which is 1 wt.% smectite and 99 wt.% 2 μm diameter spheres ($\rho = 2.8$ g/cm^3), the smectite would account for 88% of the total surface area. If the spheres are 5 μm, 1 wt.% smectite would account for >95% of the surface area. Even in fine-grained natural samples, the non-clays will rarely contribute significantly to the total surface area if smectite is present, and can be ignored. An exception may be ferrihydrite, which may occur in abundance near active redox interfaces, such as outflows from sulfide-rich tailings piles. Ferrihydrite has a highly variable surface area, initially up to several hundred m^2/g, but decreases rapidly with recrystallization over a period of days to weeks. The presence of ferrihydrite could therefore complicate any PVP analysis, and may require removal by selective dissolution before a meaningful PVP uptake measurement can be performed.

Illite and kaolinite generally have surface areas that are only a fraction of that of smectites, but they may still contribute a significant proportion of the surface area and PVP uptake if smectite is present in only small proportions. Thus, the surface area attributable to smectite in a sample can be calculated as:

$$SA^*_{sample} = (SA^*_{kaolinite})(M_{kaolinite}) + \\ (SA^*_{illite})(M_{illite}) + (SA^*_{smectite})(M_{smectite}) \quad (2)$$

where M is mass fraction of the mineral in the sample, and $SA*$ is the specific surface area. Equation 2 must then be solved for $M_{smectite}$.

SA_{total} is determined experimentally as:

$$SA^*_{sample}\left[\frac{m^2}{g}\right] = \frac{\text{mass of PVP uptake [g/g]}}{0.99[g/m^2]} \quad (3)$$

The $SA*$ of smectite was calculated earlier from the molar volume and formula weight to be ~725 m^2/g. The wt.% kaolinite in the sample can be determined using the quantitative XRD techniques of Środoń *et al*. (2001). The specific surface area of the kaolinite in the sample is

unknown and must be estimated. The surface areas of kaolinites do not vary as greatly as illites and are generally near 25 m^2/g for poorly crystallized kaolinites, with well ordered kaolinites slightly lower, as low as 10 m^2/g. Thus, SA_{total} is ~30 times more sensitive to the abundance of smectite than kaolinite. In most cases the total kaolinite correction is small and the uncertainties in the kaolinite surface areas are not significant.

SA^*_{illite} can be calculated from the crystal size distribution obtained from the 001 XRD peak shape using MudMaster measurements, as described earlier. The wt.% of illite in the sample can not be determined separately from smectite using the quantitative XRD techniques of Środoń *et al.* (2001), but the wt.% of illite plus smectite ($M_{ill+smec}$) can be determined (from the from the integrated intensity of the 060 reflection of a randomly oriented sample in comparison with an internal standard). Thus, one can substitute $[M_{ill+smec} - M_{smec}]$ for $[M_{ill}]$ in equation 2, and solve for M_{smec}:

$$M_{smec} = \frac{SA^*_{total} - SA^*_{kaol}M^*_{kaol} - SA^*_{ill}M^*_{ill+smec}}{755 - SA_{ill}} \quad (4)$$

Thus, equation 4 can be used to determine the mass of smectite in a sample, even in the presence of significant amounts of illite and kaolinite.

Analyses of several artificial mixtures are shown in Figure 11. Mixtures were made by combining measured amounts of Belle Fourche smectite (montmorillonite, SA = 725 m^2/g), Dry Branch kaolinite (SA = 14.0 m^2/g by BET), RM30 illite (mean particle thickness of 11.6 nm and surface area of 63 m^2/g by MudMaster) and quartz (ground in a shatter box; assumed $SA \ll 1$ m^2/g). The mixtures were divided into five series, with smectite varying between 5% and 80% in each series. We can calculate the specific surface area of each mixture by using the surface areas of the components in the proper proportions. We then used the measured PVP uptake and equation 3 to calculate a sample-specific surface area, and used equation 4 to determine the smectite content of the sample. As would be expected, the non-smectite components had the largest relative impact on the specific surface area when samples had small smectite concentrations and/or large illite content. Both Figures 11a and 11b show good linear correlations between measured and predicted values, with a slope of ~1. The components all appear to act independently in suspension, with no interaction or aggregation which impacts the PVP uptake. These experiments indicate both the validity and sensitivity of the approach outlined in equations 1 and 2 which uses PVP uptake by complex mixtures to determine the smectite content of samples. However, we used purified components which can be dispersed easily. Cements in natural samples might affect the ability to disperse clays and possibly impact the PVP uptake. This is not an issue we have investigated, but chemical treatments described by

Jackson (1985) can be used to remove cements prior to PVP analysis.

Applications of the PVP technique

Because smectites have a significant influence on the properties of many natural and synthetic materials, both as a major phase and a minor contaminant, there is a large number of potential problems for which the ability to quantitatively measure smectite abundance would be helpful. Several applications that are immediately apparent include; (1) the characterization of petroleum reservoirs and cap rocks, and reaction paths within sedimentary basins; (2) prediction of the geotechnical properties of soils and rocks, particularly the detection of swelling potential in soils; (3) the characterization of bentonites and other clays for application in ceramics, paper, drilling fluids and liners; and (4) determining the provenance of sediments in fluvial and lacustrine systems.
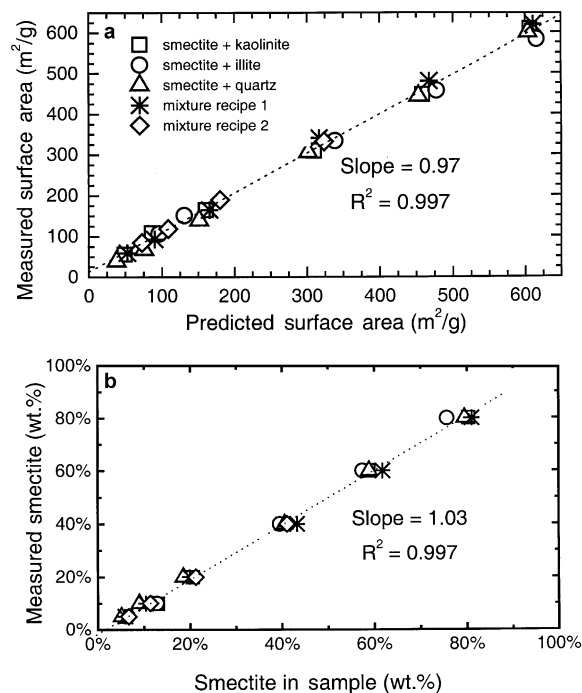

Figure 11. (a) The surface area measured by PVP uptake *vs.* the surface area predicted from the composition of the sample and the independently determined surface areas of the components. (b) The composition of the smectite measured in the samples by PVP uptake as a function of the amount of smectite mass added to the sample. The first three mixtures are variable amounts of smectite with the remaining portion of the sample containing a single additional phase. Recipe 1 is variable amounts of smectite with the remainder divided equally between kaolinite and illite. Recipe 2 is smectite plus 20% each of kaolinite and illite with the remainder quartz, except 80% smectite, which has 10% each of kaolinite and illite.

CONCLUSIONS

The uptake of polyvinylpyrrolidone (PVP) dispersed in solution yields an accurate measure of the surface area of silicate minerals. The sorbed PVP layer is ~11 Å thick, and corresponds to ~0.99 g 55K PVP per m^2 of surface area. Na-saturated smectites can be dispersed readily as single-unit-cell crystals and they tend to dominate sample surface areas. Therefore, PVP uptake (0.72 g PVP per g smectite) can be used to quantify the abundance of smectitic minerals in a sample. Quantitative XRD techniques can be used to refine further the measurement of smectite abundance by correcting the sample for illite and kaolinite surface areas.

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