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A SIMPLE METHOD FOR PARTIAL PURIFICATION OF REFERENCE CLAYS

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Abstract—The influence of clay preparation procedure on sorption and hydrolysis of carbaryl (1-naphthyl, *N*-methyl carbamate) by the reference smectite SWy-2 was examined. For research purposes, reference clays are sometimes used without purification, or more commonly, the <2 μm size fraction is obtained by gravity sedimentation or low-speed centrifugation. We determined that these common methods did not remove all the inorganic carbonate impurities present in SWy-2, and that these impurities caused alkaline conditions in aqueous clay suspensions leading to the alkaline hydrolysis of carbaryl to 1-naphthol. The hydrolytic activity of homoionic K-SWy-2 disappeared once carbonates were eliminated. Two methods were evaluated for preparing K-SWy-2 devoid of inorganic carbonates. In Method A, inorganic carbonates were first removed by incremental additions of a 0.5 M sodium acetate buffer (pH 5.0) until the clay suspension reached pH 6.8, followed by low-speed centrifugation to obtain the <2 μm size fraction; in Method B, the order of these steps was reversed. Carbaryl hydrolysis was used as a probe to determine the effectiveness of the two methods in terms of the removal of carbonate accessory minerals. Homoionic K-SWy-2 obtained by Methods A and B produced near neutral pH when suspended in water and hydrolysis of carbaryl in these suspensions was not evident. In this regard, both clay preparation methods were acceptable. However, there were procedural advantages with Method B, which is therefore recommended for the partial purification of reference clays, as detailed in this paper.

Key Words—Clay Preparation, Carbaryl, Carbonate Impurities, Reference Clays, Sorption, SWy-2.

INTRODUCTION

Our previous study showed that carbaryl (1-naphthyl, *N*-methyl carbamate) hydrolysis in slurries of the reference clay SWy-2 was due to the presence of inorganic carbonate impurities (*e.g.* calcite and dolomite) (Arroyo *et al.*, 2004). Dissolution of these carbonates created alkaline conditions leading to the alkaline hydrolysis of carbaryl to 1-naphthol. Other organophosphorus and carbamate pesticides are also unstable under alkaline conditions (Fukuto, 1987). Carbonates are often present in reference clays as sparingly soluble clay-sized minerals (Grim and Guven, 1978; Mermut and Cano, 2001; van Olphen and Fripiat, 1979; Vogt *et al.*, 2002). Although such carbonates are not reliably removed by common purification procedures based on particle size separation (Arroyo *et al.*, 2004), they are subject to selective dissolution (Kunze and Dixon, 1986; Gee and Bauder, 1986; Moore and Reynolds, 1989). Treatment of clays with strong acids (*e.g.* HCl) to remove carbonates can cause destruction of the crystalline structure of clay minerals (Gee and Bauder, 1986; Loeppert and Suarez, 1996). Therefore, weak acid treatment with 0.5 M sodium acetate buffer at pH 5 is recommended for removal of carbonates from clay mineral samples (Kunze and Dixon, 1986).

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Although several methods have been published for separation and purification of clays from soils and sediments (Kunze and Dixon, 1986; Gee and Bauder, 1986; Moore and Reynolds, 1989; Jackson, 1979), and for purifying clay samples (Moore and Reynolds, 1989), it appears that there is no general recognition of the need to purify commercially available clay minerals prior to use in surface chemistry studies, and certainly no uniform experimentally validated method in use for doing so. Many previous studies of the complexation, polymerization, sorption and degradation of organic contaminants and pesticides by clays have reported some type of clay purification method based on wet sedimentation (Aguer *et al.*, 2000; Boyd *et al.*, 2001, Haderlein and Schwarzenbach, 1993; Li *et al.*, 2003; Mingelgrim *et al.*, 1977; Mortland and Halloran, 1976; Pusino *et al.*, 1988, 1995, 2000, 2003; Sawhney *et al.*, 1984; Sheng *et al.*, 2001; Soma *et al.*, 1986; Wei *et al.* 2001), whereas other studies used clay samples without prior purification (*e.g.* Forteza *et al.*, 1989; Haderlein and Schwarzenbach, 1993; Haderlein *et al.*, 1996; Li *et al.*, 2003). Experimental details regarding purification steps such as dispersal methods, sedimentation times, centrifugation forces and times, and type of membranes used for dialysis *etc.* are often different or unspecified. This situation may have been exacerbated by the commercial availability of 'standard', 'reference' or 'specimen' clays. Certainly, failure to purify clay minerals and/or utilization of non-uniform purification procedures diminish our ability to compare and reproduce results from different studies and laboratories even when

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standard clay mineral samples are used. Consequently there is a need for operational standardization of purification procedures for reference clays in applications where such purification is required or desired.

The objective of this study is to develop a convenient and reliable procedure for the partial purification of reference clays, avoiding any harsh chemical treatments that may cause alteration or destruction of the clay structures. All relevant experimental details and observations regarding such a method are described herein. The recommended method should advance the use of standard materials in surface chemistry studies utilizing clay minerals.

MATERIAL AND METHODS

The reference smectite clay (SWy-2) used in this study was obtained from the Source Clays Repository of The Clay Minerals Society (Purdue University, West Lafayette, Indiana, USA). Milli-Q deionized (d.i.) water (Millipore Corporation, Bedford, Massachusetts, USA) was used for all sample preparations.

Method A. Removal of carbonate prior to particle-size fractionation

Sample dispersion. The reference smectite clay SWy-2 was suspended in d.i. water for 24 h while stirring using a magnetic stir-bar and plate to hydrate the clay. The suspension was obtained by mixing 5.0 g of clay with 100 mL of d.i. water in a 1 L beaker.

Chemical removal of carbonate. After suspending the clay, the pH was measured (>7) and then the clay suspension was titrated with 0.5 M Na acetate buffer (pH 5.0) until the pH of the clay suspension reached 6.8 (Kunze and Dixon, 1986). During the titration, water (total volume $\approx$ 700 mL) was added to decrease the viscosity of the clay suspension, which had increased over time with the incremental addition of Na acetate buffer. After pH 6.8 was reached initially, the sample was stirred for 1 h, during which the pH increased to 8. Titration with 0.5 M Na acetate was then continued until pH 6.8 was again reached. This step was repeated three times until the pH remained constant at 6.8 for 30 min. The total volume of 0.5 M Na acetate buffer added was 39.5 mL.

Removal of soluble salts. The titrated clay suspension was poured into four 250 mL polyethylene centrifuge bottles, closed with screw-on caps, and then centrifuged for 30 min at 3295 *g* (4500 rpm) using a Sorvall GSA rotor and centrifuge (DuPont Company, Delaware, USA). The supernatant liquid was discarded. The flocced clay solids from the four bottles were combined into two bottles, then washed by resuspending the clay in 200 mL of d.i. water. The two bottles were laid on a rotary Innova 2300 Platform Shaker (New Brunswick Scientific Co., Inc., Edison, New Jersey, USA) and shaken at 120 rpm for 8 h. The bottles were then centrifuged as above and the clear supernatant liquid discarded.

Particle-size fractionation. The clay in each bottle was resuspended in 200 mL of d.i water by laying the bottles on a rotary shaker and shaking at 120 rpm for 8 h. The <2 μm clay-sized particles were obtained by separating the >2 μm particles using low-speed centrifugation (58–60 *g* for 6 min) (Costanzo, 2001). The supernatant liquids containing clay-sized particles of <2 μm particles were siphoned into separate 250 mL centrifuge bottles. The >2 μm particles (sediment) were collected, quick frozen, freeze dried and stored. The clay suspension was subjected again to high-speed centrifugation (3295 *g* for 30 min) and the clear supernatant liquid discarded. Clay-size particles were combined in one 250 mL centrifuge bottle and then subjected to K^+ saturation (see below).

Method B. Particle-size fractionation prior to removal of carbonate

Sample dispersion. The reference clay SWy-2 was suspended in d.i. water for 24 h while stirring using a magnetic stir-bar and plate to hydrate the clay. The suspension was obtained by mixing 5.0 g of clay with 100 mL of d.i. water in a 250 mL polyethylene centrifuge bottle.

Particle-size fractionation. To obtain the <2 μm clay-sized particles the clay suspension was centrifuged for 6 min at 58–60 *g* (~600 rpm) using a Sorvall GSA rotor and centrifuge (Costanzo, 2001). The supernatant liquid suspension containing the <2 μm clay-sized particles was siphoned into a 250 mL polyethylene centrifuge bottle. The pellet containing the >2 μm particles was re-suspended with 100 mL of d.i. water by mixing briefly using a Vortex mixer, and then subjected to low-speed centrifugation as before to recover additional clay-sized particles. The supernatant suspension was siphoned and added to the previously collected suspension of clay-sized materials. The >2 μm particles (sediment) were quick frozen and freeze dried.

Chemical removal of carbonate. The suspension of clay-sized particles from above was titrated with 0.5 M Na acetate buffer (pH 5.0) until a pH of 6.8 was obtained; the sample was stirred for one more hour during which the pH remained stable. The total volume of Na acetate buffer added was 6.5 mL.

Removal of soluble salts. To promote flocculation of the clay, ~1.5 g of NaCl were added to the bottle containing the clay suspension and stirred for ~5 min until the salt was dissolved, then the suspension was centrifuged for 20 min at 3295 *g* (4500 rpm). The supernatant liquid was discarded, and the clay pellet resuspended in 200 mL of d.i water by laying the centrifuge bottle on

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a rotary shaker and shaking at 120 rpm for 8 h. The clay suspension was again centrifuged at 3295 *g* (4500 rpm) for 30 min and the supernatant liquid discarded. The clay-size particles were then subjected to K^+ saturation (see below).

Preparation of homoionic K-clays (Methods A and B)

The clay pellets in the 250 mL centrifuge bottles from Methods A and B were each resuspended in 200 mL of 0.1 M KCl; the bottles were laid on a rotary shaker and shaken at 120 rpm for 8 h, then the clay suspensions were centrifuged for 20 min at 3295 *g* (4500 rpm) and the supernatant liquids discarded. This procedure was repeated four times. The clays were then resuspended in 200 mL of d.i. water by shaking at 120 rpm on a rotary shaker for 8 h, centrifuged at 3295 *g* (4500 rpm) for 30 min, and the supernatant liquids discarded. For each clay centrifuge pellet, a 50 mL portion of d.i. water was added and the whole was placed in porous membrane tubing (two 30 cm × 50 mm sections of molecular weight cut-off 6000–8000, obtained from VWR Scientific-Spectrum Medical Industries, Inc., Laguna Hills, California, USA) and dialyzed against distilled water until free of chloride as indicated by $AgNO_3$. Both samples were quick frozen, freeze dried and stored in polyethylene bottles.

Other clays

A description of materials and methods used to prepare other clay samples referred to in this paper, *i.e.* whole clay (no purification at all), clay-sed. (obtained by gravity sedimentation without carbonate removal), clay-cent. (obtained by low-speed centrifugation without carbonate removal), and light fraction (a subfraction of SWy-2 composed of the lighter-colored material), as well as characterization of mineral phases by X-ray diffraction (XRD), were detailed by Arroyo *et al*. (2004).

Scanning electron microscopy (SEM)

The K-SWy-2 samples were subjected to SEM analysis, which included qualitative analytical X-ray energy-dispersive spectroscopy (EDS) and imaging of gold/carbon-coated clay films using a JSM-6400V scanning microscope equipped with a Noran detector unit. The EDS spectra were obtained using electron-beam spot sizes of ~2–10 μm, and a lifetime of 120 s. Analyses were standardless.

Chemicals

Carbaryl (>99% purity) was obtained from ChemService (West Chesnut, Pennsylvania, USA) and 1-naphthol (>99% purity) was obtained from Sigma-Aldrich (St. Louis, Missouri, USA). Carbaryl and 1-naphthol solutions were prepared in 0.1 M KCl at pH 3.0 (adjusted with HCl) and used as standards for analysis by high-pressure liquid chromatography (HPLC). Sodium acetate trihydrate was the A.C.S. reagent and obtained from J.T. Baker (Phillisburg, New Jersey, USA) and glacial acetic acid was obtained from Mallinckrodt-Baker, Inc. (Paris, Kentucky, USA).

Sorption kinetics

Kinetics of carbaryl adsorption were measured in slurries of K-SWy-2 clays using a batch method. Solutions of 40 μg/mL of carbaryl in 0.1 M KCl at ambient pH 6.5, protected from light, were prepared and used immediately for the sorption experiments. 5 mL volumes of the 40 μg/mL carbaryl solution were pipetted into triplicate 7.4 mL borosilicate amber glass vials (Supelco, Bellefonte, Pennsylvania, USA) containing 60 mg of clay. The contents of the vials were mixed briefly using a vortex mixer, then rotated continuously for various time intervals at room temperature (23±1°C). The samples were centrifuged (~3500 *g* for 20 min) after 2, 4, 24, 48, 72 and 96 h reaction times. Aqueous concentrations of carbaryl and 1-naphthol were determined by HPLC using a Perkin Elmer system (Shelton, Connecticut, USA) consisting of a binary LC 250 pump, a UV/VIS detector set at 230 nm, and a series 200 autosampler. Chromatographic data were acquired using Turbochrom software 6.1. Reverse-phase chromatography was carried out using a 150 × 4.6 mm Supelcosil-C_{18} column, of 5 μm particle size and 120 Å pore size (Supelco). The mobile phase was an isocratic mixture of 71% methanol and 29% water at pH 3.2 (adjusted with HCl). The injection volume was 25 μL and the flow rate was 1.0 mL/min. Identification and quantification of carbaryl and 1-naphthol were achieved using analytical standards of known concentrations.

Methanol extractions of the centrifuged clay pellets were conducted to determine the amounts of adsorbed carbaryl. Vials containing clay pellets and residual water were weighed to determine the amount of water present, then 5 mL of methanol were added. Vials were mixed using a Vortex mixer, rotated continuously at room temperature for 24 h, then centrifuged at 3500 *g*. Carbaryl concentrations in the extracts were determined by HPLC. Amounts of carbaryl sorbed by clay were obtained by subtracting the calculated mass of carbaryl present in residual water from the mass of carbaryl extracted by methanol.

RESULTS

Two procedures were used to isolate carbonate-free clay-sized particles from reference smectite SWy-2. In Method A, carbonates were removed prior to separating the <2 μm particles, and in Method B, carbonates were removed after separating the <2 μm particles, using low-speed centrifugation. Clay samples prepared by these methods were compared to the reference clay (SWy-2) used as received (whole clay) and to clays where the <2 μm particles were obtained without removal of carbonates, utilizing either gravity sedimen-

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tation (clay-sed.) or low-speed centrifugation (clay-cent.); details regarding the preparation of the last two clays can be found in Arroyo *et al*. (2004).

Method A

Clay-sized particles (<2 μm) were obtained from SWy-2 after removal of carbonates. Briefly, SWy-2 was mixed with d.i. water (1:20) to form a suspension. Carbonates were removed by incremental addition of Na acetate buffer (pH 5) until the clay suspension pH reached 6.8. During this operation the viscosity of the clay suspension increased markedly. Since the clay suspension became too thick for effective mixing, addition of water was necessary, which caused a substantial increase in the total volume of suspension. By the end of the titration (pH 6.8), the volume of clay suspension had increased by about seven times. High-speed centrifugation (3295 *g*) was used to separate the clay from the aqueous phase. After washing the clay to remove soluble salts and resuspending the clay in d.i. water, the clay-sized particles were obtained by low-speed centrifugation (58−60 *g* for 6 min). The yield of clay-sized particles was ~74% (wt./wt.) of the original SWy-2. Visually, it consisted mostly of yellow material plus a small amount of brown material. The dark brown sediment (obtained during low-speed centrifugation) comprised ~10% of the original weight of the SWy-2 clay, and it was presumably free of carbonates. The mass removed during isolation of carbonate-free clay-sized particles (obtained by subtracting the mass of the neutralized-clay and neutralized-sediment from the initial amount of clay) was ~16% (wt./wt.) of the whole clay.

Method B

The reference clay was initially suspended in d.i. water, then the clay-sized particles (<2 μm) were obtained by low-speed centrifugation prior to the removal of carbonates by titration with Na acetate buffer. The volume of Na acetate buffer needed to remove inorganic carbonates from the <2 μm clay-sized fraction was only one sixth of that used in Method A where the whole clay was titrated. After titration with Na acetate buffer, the <2 μm fraction was isolated by high-speed centrifugation. Subsequent washing of the clay pellet with d.i. water caused dispersion of some clay particles, apparent from the presence of turbidity and the yellow color of the supernatant liquid. The method was

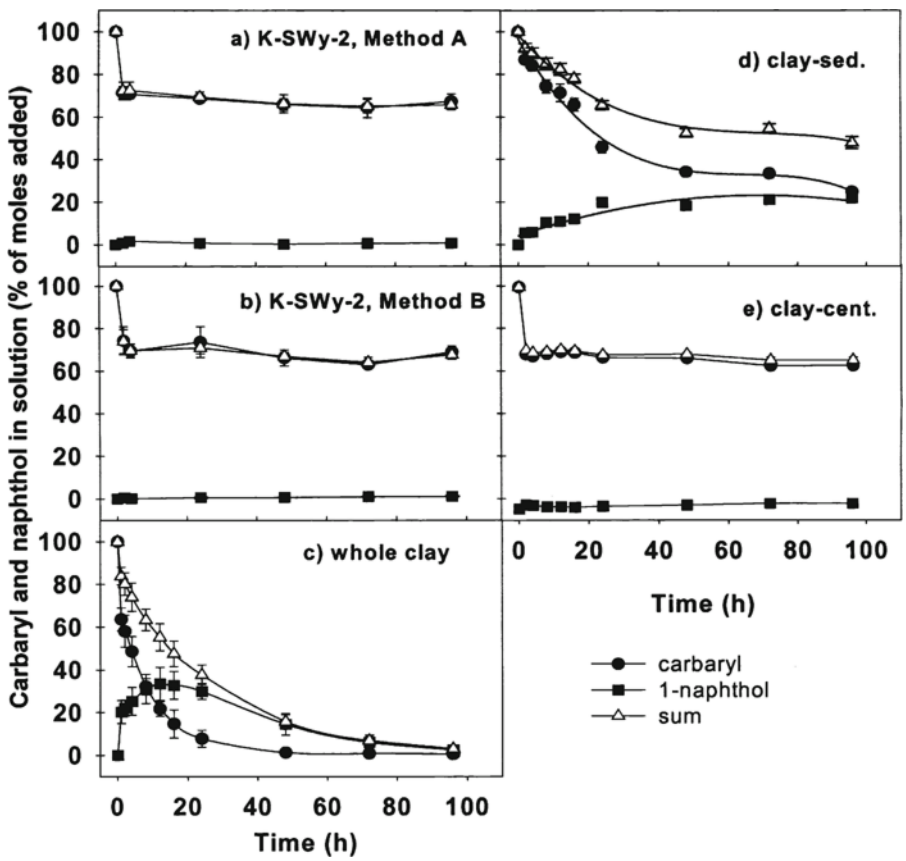


Figure 1. Sorption and hydrolysis of carbaryl by the reference smectite clay SWy-2 in the homoionic K-form: (a) carbonate-free clay, Method A, (b) carbonate-free clay, Method B, (c) whole clay, (d) clay-sed., and (e) clay-cent. Preparations c, d and e did not include carbonate dissolution (see Arroyo *et al*., 2004).

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therefore modified by increasing the ionic strength of the original <2 μm clay suspension (*i.e.* the acetate buffer-titrated clay suspension) to 0.1 M by adding NaCl prior to high-speed centrifugation. This appeared to completely flocculate the clay and allow it to be removed effectively from suspension by centrifugation as indicated by loss of turbidity and color in the supernatant liquid. The material obtained in this fashion, after K^+ saturation, corresponded to 77% (wt./wt.) of the original SWy-2 and consisted mostly of yellow material plus a very small amount of brown material. The dark brown sediment (>2 μm fraction, obtained from the original low-speed centrifugation) constituted ~18% of the total weight of clay and contained carbonates and other impurities. The mass removed by titration of the fractionated clay (obtained by difference from the initial amount of clay minus the sum of neutralized-clay and sediment) comprised ~5% (wt./wt.) of the whole clay.

Carbaryl sorption

Batch equilibrium experiments were conducted to measure the distribution of carbaryl between K-SWy-2 and water and to evaluate hydrolysis of carbaryl to 1-naphthol. Hydrolysis of carbaryl was used as an ultra-sensitive probe to detect the presence of carbonate impurities in the various clay preparations. In our previous study (Arroyo *et al*., 2004), we observed a color change in K-SWy-2 from pale yellow to gray when carbaryl was added to suspensions of the unfractionated (whole) clay or to clays fractionated based on conventional <2 μm particle size separations, but where carbonates were not removed using acetate buffer. In this study, the carbonate-free clays obtained by Methods A and B did not manifest a change of color when mixed with aqueous carbaryl solutions.

Carbaryl sorption and hydrolysis experiments were performed in batch utilizing the carbonate-free clay slurries prepared by Methods A and B, and the results compared to our previous data (Arroyo *et al*., 2004). The previous study utilized whole, unfractionated clay, clay subjected to gravity sedimentation overnight (clay-sed.), and clay subjected to low-speed centrifugation (clay-cent.); the last two methods are commonly used to obtain the <2 μm particle-size fraction. Carbaryl sorption in the carbonate-free clay slurries obtained by Methods A or B appeared to reach equilibrium within 4 h, at which point ~30% of the original carbaryl had been removed from aqueous solution (Figure 1a,b). This corresponded to an amount sorbed of ~1.0 mg/g clay. No appreciable production of 1-naphthol was noted in these slurries. This is in contrast to the fate of carbaryl in suspensions of the whole clay and clay-sed. (Arroyo *et al*., 2004), where disappearance of carbaryl from aqueous solution was continuous; 80% and 40% of carbaryl had disappeared within 48 h, respectively (Figure 1c,d). In slurries of the whole clay, 1-naphthol concentration maximized at ~24 h, then declined to nearly zero between 24 and 96 h, whereas with clay-sed., 1-naphthol concentrations were nearly constant between 24 and 96 h (Figure 1c,d). There was negligible formation of 1-naphthol in slurries of the clay-cent. reported by Arroyo *et al*. (2004) (Figure 1e), which is similar to the results obtained using the carbonate-free clay slurries prepared by Methods A and B.

Recovery of sorbed carbaryl by methanol extraction of the carbonate-free clays was ~100% (Figure 2a,b). This is in stark contrast to the very small quantities (<1%) of carbaryl and 1-naphthol that could be extracted with methanol from whole clay (Arroyo *et al*., 2004).

Scanning electron microscopy (SEM)

The >2 μm particles (sediment without carbonates removed) under Method B were examined to determine particle morphologies and semi-quantitative elemental compositions. Figure 3 shows X-ray maps of the >2 μm fraction for O, Fe, Na, Mg, Al, Si, K, Ca and Ti. Note the presence of a Ca-rich but Si-poor particle (probably a carbonate mineral) in the lower left of the Ca map. Figure 4 shows a photomicrograph of the light fraction obtained previously (Arroyo *et al*., 2004), which contained only the pale yellow material. As described previously (Arroyo *et al*., 2004), this version of fractionated smectite yields a suspension pH of 8.2 and caused carbaryl to hydrolyze to 1-naphthol. The SEM image (Figure 4) looks like a pure smectite due to its closed fine texture and honeycomb arrangement of

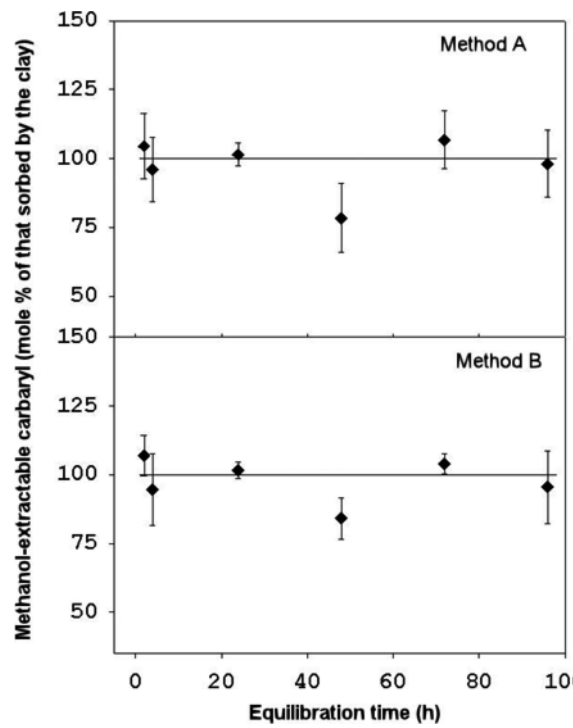


Figure 2. Amounts of sorbed carbaryl extracted by methanol from K-SWy-2 prepared by Methods A and B.

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particles, presenting no visual evidence of solid-phase carbonates. Also, EDS spectra for the whole clay show the presence of Ca and Ti (Figure 5a), but neither was detected in EDS spectra of the 'light fraction' (Figure 5b). Thus, solid-phase carbonates can be present and chemically active in preparations of SWy-2, despite not being apparent in SEM images (Figure 4), and being undetected by XRD (Arroyo *et al.*, 2004) or by EDS analysis (Figure 5b).

DISCUSSION

Since 1972, The Clay Minerals Society (CMS) has provided a common set of well characterized reference clays for research purposes through the Source Clays Project (Costanzo, 2001). The reference clays facilitate comparisons of data obtained from different studies and laboratories. However, different sample purification/preparation methods may undercut efforts to ensure the use of common standard materials in studies utilizing clay minerals, and in allowing comparison of results from different studies. It is probably most common in the fields of clay- and soil-science to purify clay mineral samples by fractionation based on particle size, although this is not performed by any uniform method. In some instances, commercially available clays, including the CMS reference clays, are used without purification. The variety of clay preparation methods utilized in the past

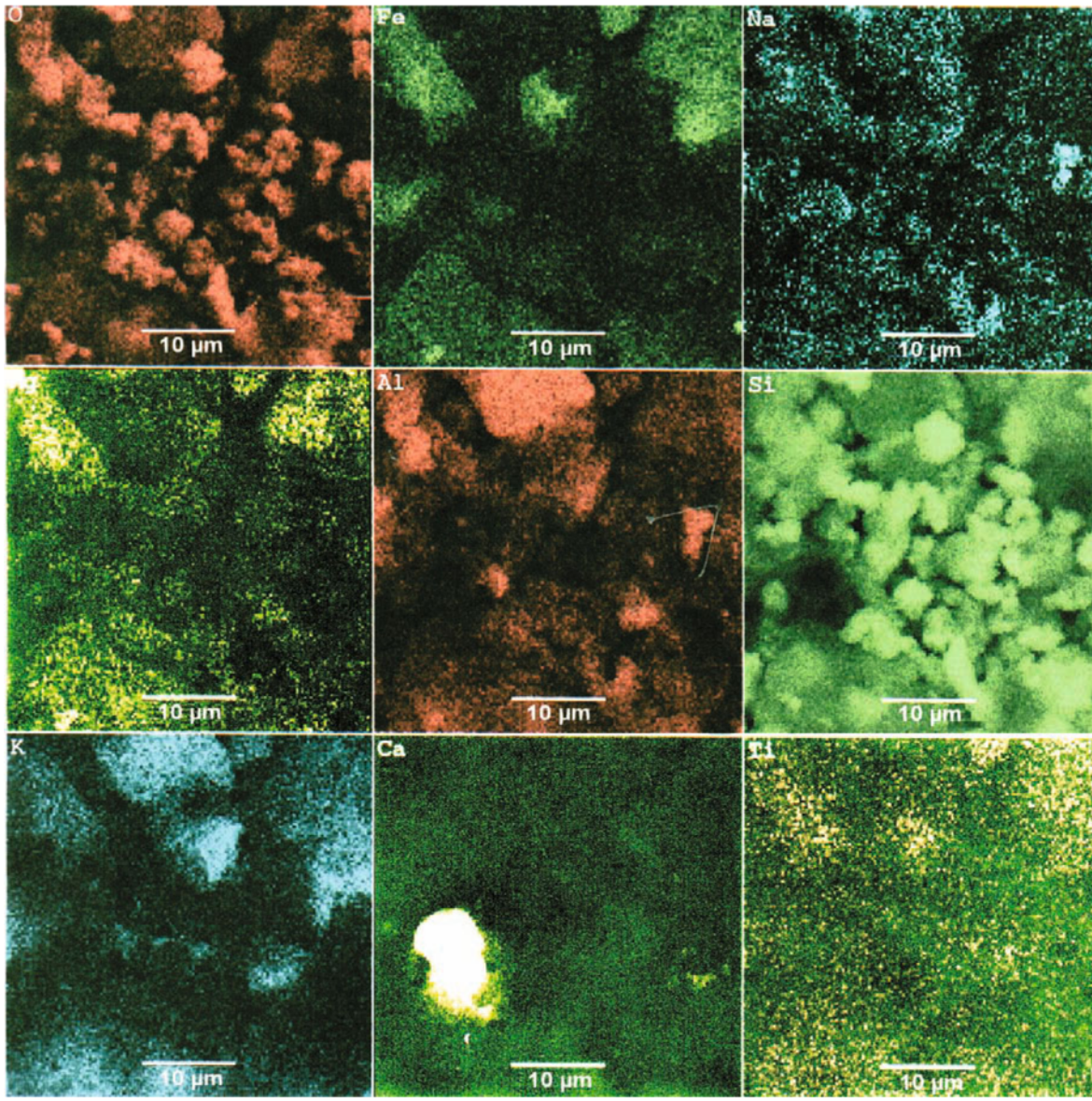


Figure 3. X-ray map of the >2 µm fraction of SWy-2. Elements determined were: O, Fe, Na, Mg, Al, Si, K, Ca and Ti. The brightness of each pixel in the X-ray map is directly proportional to the quantity of element present. Note the calcite particle in the Ca map.

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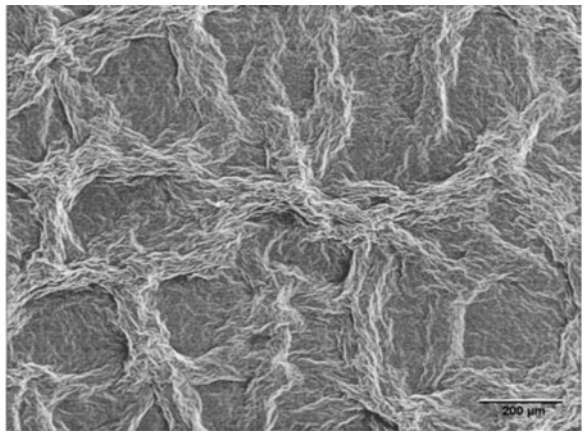


Figure 4. SEM image of the light fraction of SWy-2 (Arroyo *et al.*, 2004), which occurs in a closed fine texture showing a honeycomb arrangement of particles.

demonstrates the necessity of developing standard methods for purifying reference clays prior to their use in surface chemistry studies. Such methods would be useful to clay scientists and those in related fields such as soil science and environmental science that commonly use commercially available clay mineral samples.

It has been demonstrated that smectite clays may potentially contribute to the degradation of certain carbamates (Wei *et al.*, 2001) and other pesticides

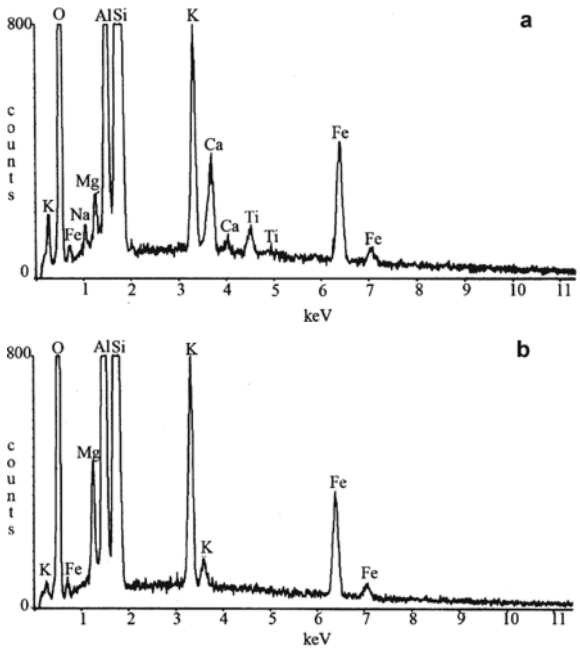


Figure 5. EDS spectra of K-SWy-2: (a) whole clay, with elemental composition of O (50.1%), Mg (0.6%), Al (4.9%), Si (35.6%), K (2.7%), Fe (3.6%), Na (0.7%), Ca (1.2%) and Ti (0.5%); and (b) the light fraction of SWy-2 (Arroyo *et al.*, 2004) with elemental composition of O (51.5%), Mg (1.7%), Al (11.5%), Si (28.3%), K (3.5%) and Fe (3.4%).

(Pusino *et al.*, 2000). In our previous study (Arroyo *et al.*, 2004), we observed both the apparent sorption and hydrolysis of carbaryl in slurries of the reference smectite K-SWy-2. The extent of carbaryl disappearance from solution and appearance of its hydrolytic product 1-naphthol varied depending on the clay preparation and purification method. We reported that several common methodological approaches used to isolate clay-sized particles did not reliably remove carbonate impurities, and that such carbonate impurities may influence or even control sorption and degradation processes. We concluded that even trace quantities of carbonates in SWy-2 could, through dissolution, cause an alkaline pH leading to the alkaline hydrolysis of carbaryl. Such hydrolytic activity, present even in partially purified clays (*e.g.* after overnight gravity sedimentation), could be mistakenly attributed to the clay mineral itself or to some other reactive mineral component. Other reference clays obtained from natural deposits may contain even greater amounts of carbonate impurities (*e.g.* hectorite, SHCa-1) where commonly used purification approaches based on sedimentation or low-speed centrifugation would be even less proficient at removing carbonates. In fact, when we collected the <2 µm particle size of the hectorite SHCa-1 clay by gravity sedimentation and low-speed centrifugation methods, both caused alkaline pH after stirring the clay in water for a few minutes. It therefore seems apparent that particulate carbonate impurities as well as carbonate cementing materials should be removed by selective acid dissolution as these materials may be reactive or cause chemically reactive conditions.

Particle-size separations are commonly recommended prior to mineralogical analyses of mineral components present in soils and other geosolids. Other methods are used to remove carbonates, organic matter and Fe oxides from soil samples (Jackson, 1979; Kunze and Dixon, 1986; Gee and Bauder, 1986; Moore and Reynolds, 1989). The need for use of such treatments when dealing with soil samples is widely recognized. Specimen clays or reference clays, like soils, are natural materials that may require pretreatment to remove impurities. In a previous study (Arroyo *et al.*, 2004), the use of the carbamate pesticide carbaryl, which is subject to alkaline hydrolysis, provided an excellent case-in-point that reference clays should be chemically treated to remove carbonates which might otherwise dissolve and cause alkaline conditions leading to unexpected chemical reactivity. For carbonate removal, the method of Kunze and Dixon (1986) was modified to avoid subjecting the clay to high temperatures or to large volumes of buffer at low pH, and yet ensure that reference clays are free of carbonates. Dissolution of carbonates in clay suspensions, and removal of CO_2 (g), was reliably achieved by constant stirring in an open beaker accompanied by the slow addition of Na acetate acid buffer (pH 5). The clay suspensions titrated to

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stable pH of 6.8 in this manner minimized the potential for silicate dissolution.

CONCLUSIONS

We found it more convenient to obtain first the <2 μm particles by low-speed centrifugation, then remove carbonate impurities using Na acetate buffer. In comparison, removal of carbonate impurities from the SWy-2 clay suspension by titration with Na acetate buffer prior to particle size separation (Method A) was laborious and required considerably more time. Carbonates dissolved by the buffer (prior to particle-size fractionation) caused an increase in suspension viscosity. The addition of water to decrease viscosity and allow effective stirring caused a large increase in volume of clay suspension and consequently an increase in the time spent for centrifuging. It was also more difficult to obtain a stable pH of 6.8 when titrating the clay with Na acetate buffer was the initial purification step. In Method B, after the initial clay-water mixing period, the clay-sized particles were separated by low-speed centrifugation. Carbonate impurities present in the resultant fractionated SWy-2 clay suspension were easily eliminated by titration with Na acetate buffer, *i.e.* much less buffer was required and the pH in the titrated sample was more stable. When preparing larger amounts of clays, the practical advantages of Method B (more stable pH and much less volume enhancement) are particularly attractive. The washing process to eliminate soluble salts, and the homoionic cation saturation step, are similar in complexity in both methods A and B. Likewise, similar yields of carbonate-free clay-sized materials are afforded by Methods A and B. Both methods achieved removal of carbonates and eliminated the hydrolytic activity associated with SWy-2. Method B is recommended due to its convenience.

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