

Degradation of Polydimethylsiloxanes (Silicones) as Influenced by Clay Minerals

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To better understand the environmental fate of organopolysiloxanes (silicones), this study investigated the degradation of a ^{14}C -labeled poly(dimethylsiloxane) (PDMS) on 12 Ca-saturated clay minerals. The rates and products of PDMS degradation were determined at 22 °C and 32% relative humidity, via sequential extraction and high-performance size exclusion chromatography (HPSEC). The results showed that all of the clays tested were catalysts for PDMS degradation. However, clay minerals varied substantially in their catalytic activity: kaolinite, beidellite, and nontronite were the most active; goethite and allophane were least active. In addition, PDMS degradation products bound more strongly to goethite and smectites. These results demonstrated that soil factors such as clay content and clay type are very important in determining the degradation rates of PDMS in soil.

Introduction

Silicone polymers such as poly(dimethylsiloxane) (PDMS) fluids are widely used in industrial applications and consumer products. They are essentially nonreactive, except when exposed to strong acids, bases, or oxidants. The resistance to oxidation, ozone, and UV exposure in addition to other unique properties of these materials (low surface tension, high gas permeability, thermal stability, water repellence, and high dielectric constant) are major reasons for their widespread use.

A major pathway for PDMS to enter the soil environment is via land application of PDMS-containing sewage sludge. The chemical stability of PDMS could suggest that this compound may be persistent and accumulated in various environmental compartments. Buch and Ingebrigtsen (1) demonstrated, however, that when added to air-dried soils or clay minerals, PDMS undergoes extensive hydrolytic degradation. This extensive PDMS degradation in soil was verified by Lehmann et al. (2-4) using seven soils with different geographical origins and chemical compositions. In addition, Fendinger et al. (5) found that organosilicon concentrations of sludge-amended soils were lower than expected based on PDMS loading, indicating the degradative removal of PDMS from the soil.

This degradation process is moisture sensitive and in moist soil proceeds at a slow rate (2). As the soil gradually dries from moist to air-dry, the siloxane polymers rapidly hydrolyze to oligomeric silanols and eventually to a water-soluble monomer: dimethylsilanediol (DMSD) (3, 4, 6). In open

systems such as field soils, the DMSD produced by PDMS degradation is dissipated via three pathways. Some DMSD remains bound to soil particles, some undergoes complete oxidation to CO_2 (biologically) (3, 7, 8), and some is lost via volatilization (3) and is expected to be oxidized in the atmosphere (9, 10).

Although much progress has been made in understanding the environmental fate of PDMS, we cannot yet predict the rates of PDMS degradation in various soils. Our inability to predict PDMS degradation in the environment is due partially to insufficient knowledge of the catalytic mechanisms of soil. We know that clay minerals are very reactive constituents in soil environments (8) and may be responsible for the catalytic activity of soil in PDMS degradation (1). However, we do not yet know exactly which soil mineral or minerals are responsible for catalyzing PDMS degradation. Although soil moisture was identified as the most important factor influencing PDMS degradation rates (1, 4), other soil factors may also play an important role. This is suggested by the fact that PDMS degradation rates vary significantly in different soils under the same air-dried conditions (4). These soil factors and their exact influence on PDMS degradation rates have yet to be identified.

In this study, we determined the rates of PDMS degradation and examined the degradation products in the presence of 12 different clay minerals. The objectives were to (a) evaluate the catalytic activity of various clay minerals in PDMS degradation and (b) determine the influence of clay type on the sorption of the degradation products. The minerals examined represent various soil types and different surface functional groups that PDMS would encounter in soil. The clay type effects on degradation rates, therefore, will provide the basis for elucidating PDMS degradation mechanisms and for building a widely applicable environmental fate model for silicone.

Experimental Section

The degradation of PDMS in the presence of different clay minerals was determined in four steps. First, the clay minerals were purified, converted to homoionic clays, and then characterized by X-ray diffraction and N_2 adsorption. Second, the clay samples were spiked with ^{14}C -labeled PDMS (350 cs) under controlled moisture conditions and incubated at room temperature. Third, the incubated clays were extracted at different time intervals to monitor the PDMS degradation process. Finally, the molecular weight distribution of the residual polymer was determined to see how PDMS was degraded.

Clay Minerals: Preparation and Characterization. Most of the clay minerals were from the Source Clay Minerals Repository and Ward's Earth Science Establishment (Table 1). For each smectite (montmorillonites, nontronite, and beidellite), 25 g of clay powder was weighed into a 2-L glass beaker. One liter of a mixture containing 100 mL of 32% H_2O_2 and 900 mL of 1 M NaCl solution with pH adjusted to 3.0 using dilute HCl (referred to as NaCl- H_2O_2 washing solution hereafter) was added into each beaker to remove natural organic matter and amorphous impurities, respectively. The clay suspension was allowed to react 2 days at room temperature, then transferred into four 250-mL polypropylene centrifuge bottles, and centrifuged at 3000 rpm (RCF = 2060g) for 25 min. The supernatant was decanted, and the clay was redispersed into the beaker using 1 L of NaCl- H_2O_2 washing solution. The above washing procedure was repeated twice, and the clay was then washed

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TABLE 1. Origins, Compositions, and Specific Surface Areas of Clay Minerals

clay minerals	abbreviation	origin	sources	mineral composition ^a	specific surf. area (m ² g ⁻¹)
Wyoming montmorillonite	Ca-SWY-2	Cook County, WY	Source Clay	montmorillonite (M), quartz (T)	13.3
Arizona montmorillonite	Ca-SAZ-1	Apache County, AZ	Source Clay	montmorillonite (M)	90.1
beidellite	Ca-BAZ	Cameron, AZ	Ward's	beidellite (M), quartz (T)	25.0
nontronite	Ca-NWA	Cheney, WA	Ward's	nontronite (M)	78.5
chlorite	Ca-CCA	El Dorado County, CA	Source Clay	chlorite (M)	2.9
illite	Ca-IMT-1	Silver Hill, MT	Source Clay	illite (M), quartz (T)	51.2
kaolinite	Ca-KGA-2	Warren County, GA	Source Clay	kaolinite (M)	21.7
talc	TA		Ward's	talc (M), dolomite (M)	28.3
pyrophyllite	PH		Ward's	pyrophyllite (M), muscovite (M), nactonite (T)	3.4
allophane	Ca-AAZ		Ward's	allophane (M), hollloysite (M), quartz (T)	92.0
goethite	Fe-OX		Mineral Unlimited	goethite (M)	1.5
gibbsite	Al-OX		AlCoA	gibbsite (M)	3.3

^a M, major; T, trace.

with Milli-Q water three times to remove excess H₂O₂ and NaCl.

The washed clay was dispersed in a beaker with 2 L of Milli-Q water for particle size separation by sedimentation. The dispersed clay was allowed to stand undisturbed for 24 h, and the upper 10 cm of clay suspension was then collected. The rest of the clay suspension was redispersed by stirring. This clay sedimentation/collection procedure was repeated several times to obtain a sufficient amount of clay minerals from the upper 10 cm.

To make homoionic clay, a fraction of the collected clay suspension was transferred into two polypropylene centrifuge bottles and washed four times with 250 mL of 0.1 M CaCl₂. The clay minerals were then washed three times with Milli-Q water to remove the excess salts. The resulting clay was dried using a VirTis freeze-dryer (VirTis Freezemobile).

The procedure for preparing nonsmectite minerals was essentially the same, except that the sedimentation time in size fractionation was modified to collect a larger particle size. The purity of the clay minerals was checked by powder X-ray diffraction (Table 1). The BET surface area of the minerals (Table 1) was determined by Quantachrome Corporation (Boynton Beach, FL) using a standard N₂ adsorption procedure.

Clay Spiking. Homoionic clay (0.1 g) was weighed into 25-mL glass tubes, and the open tubes were placed in the upper compartment of a desiccator containing saturated aqueous CaCl₂ solution in its bottom compartment. The moisture of the clay samples in the tubes was allowed to equilibrate with the CaCl₂ solution for 3–7 days. The pre-equilibrated clays were spiked with 0.1 mL of THF (all the THF used in this study was HPLC grade from Fisher Scientific) containing ~2 mg g⁻¹ of ¹⁴C-labeled 350 cs PDMS (38 300 Bq mL⁻¹). The tubes containing spiked clays were hooked up to a moisture-controlled flushing setup and flushed with moisture-adjusted air for 15 min to evaporate the THF. The 15-min flushing time was chosen based on a preliminary experiment showing that PDMS was not volatile and that 0.1 mL of THF (but no PDMS) was completely evaporated from a tube containing the same amount of clay after 10 min of flushing under the same conditions. The PDMS-spiked clay samples were then closed with Teflon-lined caps and incubated at room temperature (22 ± 2 °C) in the dark.

Silicone Extraction and Sample Combustion. After the spiked clay was incubated for a specified time (e.g., 1, 3, 13, 21, and 30 days for most clay minerals), the clay was

sequentially extracted first with 0.01 M CaCl₂ solution, next THF, and finally 0.1 M HCl to separate the different silicone species using a protocol obtained by modifying a published procedure (4). The CaCl₂ solution was used to obtain water-extractable, monomeric, and small oligomeric silanols. The THF extracted the remaining water-insoluble polymer residue, and the HCl solution extracted the bound silanols (4). The extracted clay was then combusted to determine (by release of ¹⁴CO₂) the amount of any nonextractable organosilicon species.

CaCl₂ solution extraction was a two-step procedure. First, 6 mL of 0.01 M CaCl₂ was added into each tube. After the sample tubes were shaken for 3 h, they were centrifuged at 3000 rpm for 25 min. The supernatant from each tube was transferred into three glass vials, and the radioactivity was analyzed by a liquid scintillation counter (LSC) (Tri-Carb 2500 TR, Packard Instrument Co., Meriden, CT) using external standards for quench correction. The clay residue was then subjected to the second extraction. The procedure for the second extraction was essentially the same, except that 20 mL of 0.01 M CaCl₂ solution was added into each tube, and only three 2-mL fractions were sampled from the supernatant and analyzed by LSC.

THF extraction consisted of three repeating steps. In each, 20 mL of THF was added into each tube containing the clay from the last CaCl₂ extraction. The sample was vortexed for 2 min, shaken for 1 h, and then centrifuged at 3000 rpm for 15 min. The supernatant was transferred into four glass vials and analyzed by LSC.

HCl extraction was a one-step procedure. A 20 mL sample of 0.1 M HCl solution was added into each tube containing clay residual from the last THF extraction. The sample was vortexed 2 min and then shaken overnight. The clay suspension was centrifuged at 3000 rpm for 25 min, and three 2-mL aliquots of the supernatant were sampled and analyzed by LSC as described above.

Combustion of the clay was done after the HCl extraction. The clay residual was first air-dried and then combusted in a biological oxidizer (OX 500, R. J. Harvey Instrument Corp., Hillsdale, NJ). The released ¹⁴CO₂ was trapped by an alkaline cocktail (C-14 Cocktail for Biological Oxidizer, R. J. Harvey Instrument Corp., Hillsdale, NJ) and analyzed using LSC.

High-Performance Size Exclusion Chromatography (HPSEC) Analysis. The extracts from the first THF extraction were also analyzed by HPSEC and an off-line LSC. The size

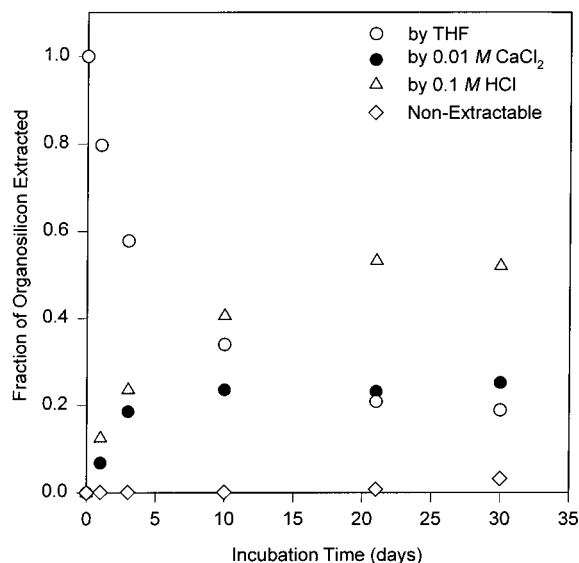
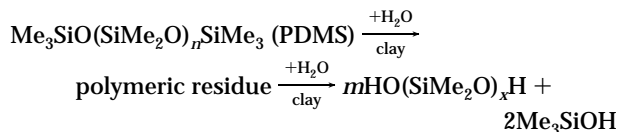


FIGURE 1. Time dependence of the THF-extractable polymeric residue, water- and HCl-extractable silanols, and nonextractable PDMS degradation products for Ca-chlorite at 32% RH.

exclusion column used was a PLgel column (3 μ m) with a 7.5 mm i.d. The HPLC (HP 1050, Hewlett-Packard) had a 1 mL sample loop, and the injection volume was 0.9 mL. The mobile phase was HPLC grade THF; the flow rate was 0.5 mL/min. Effluent from the HPSEC was sampled every half minute using a fraction collector (Retriever IV, Isco, Lincoln, NE). All samples collected were analyzed by LSC.

Results and Discussion

In the absence of clay minerals, PDMS is stable under mild environmental conditions (e.g., at ambient temperature, pH 5–9, lack of strong oxidants). However, once in contact with clay minerals, it does degrade (Figure 1):



where Me is the methyl group; $n > 100$; $m < n - 3x$; with $x = 1-3$, mainly 1. A typical degradation profile is characterized by a decrease in the THF-extractable polymeric residue with incubation time and the concomitant increases in water and HCl-extractable degradation products (Figure 1). The rates of PDMS degradation and the distribution of the degradation products strongly depend on the type of clay minerals. These are complex issues and will be examined in three steps. First, the influence of clay type on the amount and molecular weights of polymeric residue will be evaluated. Next, the effects of clay type on distribution and extractability of the degradation products will be determined. Finally, the environmental implications of these findings will be discussed.

Reduction in PDMS Molecular Weights. The polymeric residue extracted by THF included PDMS species of various molecular weight distribution (MWD), depending on reaction time and type of clay minerals (Figures 2, 3). The peak of the original PDMS was at 10.75 min, corresponding to a molecular size of ~ 195 Si–O [i.e., $-\text{Si}(\text{Me}_2)\text{O}-$] units. As the degradation proceeded, the peaks of the polymeric residue in THF extracts shifted toward longer retention time (lower molecular weight), increasing with incubation time but seldom extending beyond 16.5 min (Figure 2).

The smallest silanols (< 4 Si–O units), which eluted between 16.5 and 18 min, had already been removed by aqueous extraction and thus did not appear in the GPC curves for most clay minerals. Only nontronite at late degradation stages had a distinct peak between 17 and 18 min (Figure 2), probably arising from DMSD. The exact reason for this exception is unknown.

Most importantly, the type of clay mineral influenced the rates of GPC peak shifting and the peak widths. The rates of peak shifting were consistent with the effectiveness of the clay minerals in catalyzing PDMS degradation. The minerals effective in catalyzing PDMS degradation were distinguished from the less-effective ones by faster peak shifting to longer retention times, i.e., toward low molecular weight.

For example, it took only 0.5 h for Ca-kaolinite (one of the most effective minerals) to break down PDMS chains from initially ~ 195 $[-\text{Si}(\text{Me}_2)\text{O}-]$ units to 10–22 units (Figure 3). For Ca-illite, a less-effective aluminosilicate, shifting to the same position took about 30 days (data not shown). For oxides such as goethite and gibbsite, the major peak remained at a retention time of 11.75 min over a time period of 21 days, corresponding to ~ 100 $[-\text{Si}(\text{Me}_2)\text{O}-]$ units (Figure 3b). For chlorite and noncharged layer silicates such as talc and pyrophyllite, the GPC peaks were broader than for the rest of the clay minerals, judging by the peak area/height ratio. This was especially true for pyrophyllite (Figure 3c). The broader MWD implied a more heterogeneous nature of those mineral surfaces.

PDMS Degradation Kinetics. Besides the reduction in molecular size, lower amounts of the THF-extracted polymeric residue over time was another indication of PDMS degradation. On all clay minerals except allophane, the amount of polymeric residue decreased via two distinct phases: an initially rapid degradation followed by a slow degradation phase (Figure 4). The decrease in the amount of polymeric residue was slow on allophane, with no second phase observable within a 30-day period (Figure 4).

The clay minerals chosen represent the major clay types found in most soils around the world (17). Despite a wide variety in their chemical composition and structure, they all promoted PDMS degradation (Figure 4). Such widespread catalytic activity toward PDMS hydrolysis is consistent with previous studies reporting that PDMS undergoes significant degradation in a wide range of soils (1–4, 6).

Equally important, however, clay minerals varied substantially in their catalytic effectiveness. Among the Ca-saturated clays, Ca-kaolinite, Ca-beidellite, and Ca-nontronite were the most effective clay minerals for promoting PDMS degradation, as shown by the rapid and large extent of the decrease in polymeric residue in the initial phase (Figure 4). Gibbsite and goethite were less-effective clay minerals because they rapidly approached the slow degradation phase (Figure 4). Ca-saturated allophane was the least-effective clay mineral for catalyzing degradation due to its slow rate in the initial phase.

The variation in PDMS degradation rates among Ca-saturated clays may partially arise from the difference in surface area of the clay particles. Kaolinite, beidellite, and nontronite have higher surface areas than oxides (Table 1). As a result, not only was more PDMS degraded in the initial phase on kaolinite, beidellite, and nontronite than on oxides, but the process was also faster (Figure 4). When the rate constant of the initial PDMS degradation was normalized to the specific surface area of the mineral, the above trend changed (Table 2). On a unit-surface-area basis, gibbsite and kaolinite became the most effective catalysts, and goethite became much more effective than nontronite and montmorillonites (Table 2), suggesting a critical role for clay surface area.

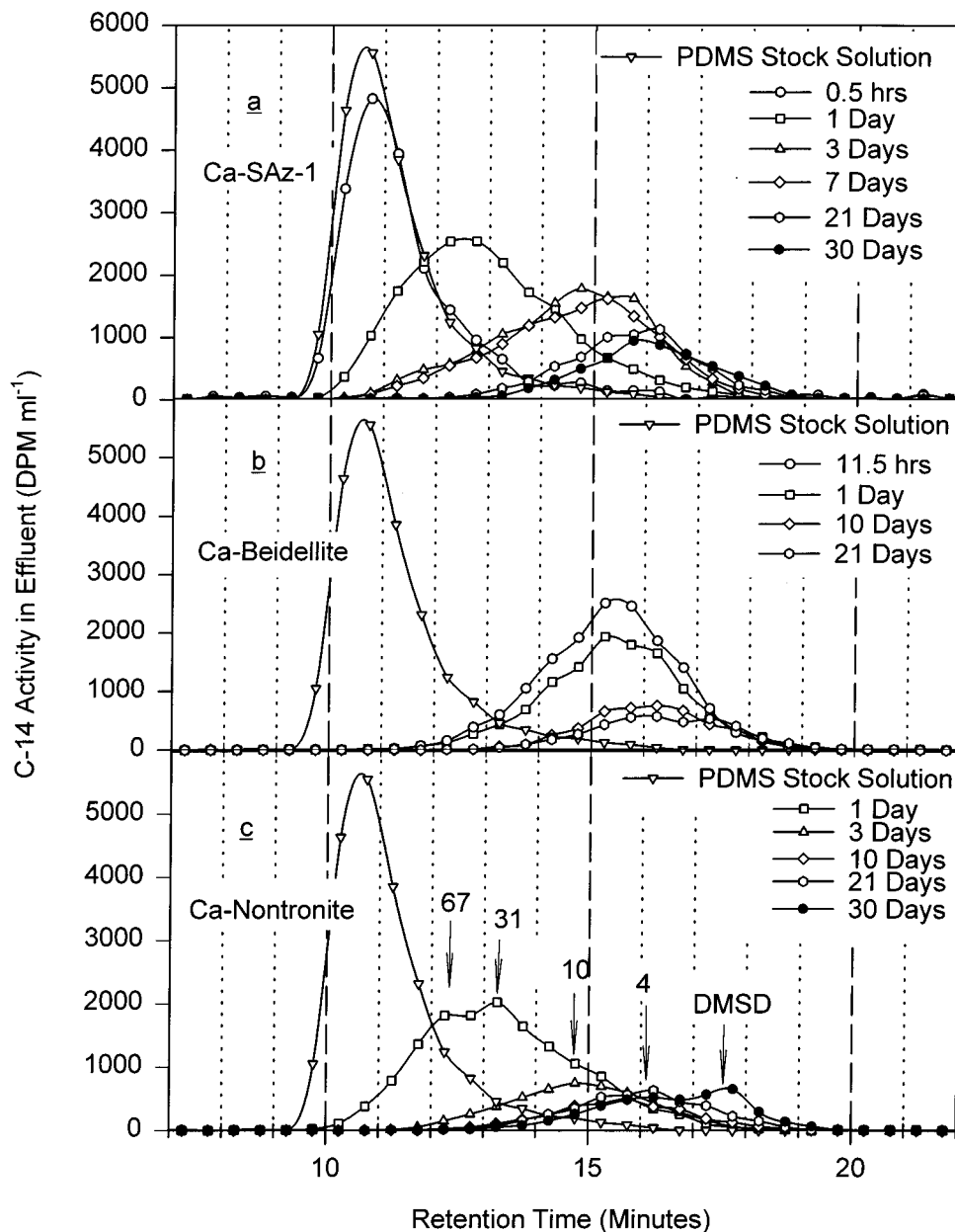


FIGURE 2. HPLC/GPC chromatograms of the polymeric residue after PDMS was incubated with three different smectites for different times. Numbers indicate the average molecular size in Si-O units.

However, surface area cannot be the only factor influencing the degradation rates. Kaolinite ($21.66 \text{ m}^2 \text{ g}^{-1}$), beidellite ($24.97 \text{ m}^2 \text{ g}^{-1}$), and talc ($28.31 \text{ m}^2 \text{ g}^{-1}$) have similar surface areas (Table 1), but their degradation rates were substantially different: kaolinite \gg beidellite \gg talc (Figures 2 and 3), an inverse trend as compared to their BET surface areas. In addition, allophane has the second largest surface area (Table 1) but was one of the less-effective clay minerals in catalyzing PDMS degradation. The discrepancy between PDMS degradation rates and mineral surface area strongly suggests that other properties were also important in determining the catalytic activities of the minerals.

The surface properties which are especially relevant to PDMS hydrolysis are the surface Brønsted and Lewis acidities. Many hydrolytic reactions are catalyzed by strong acids in homogeneous systems and surface Brønsted and Lewis acidities in heterogeneous systems (12–16). Likewise, hydrolytic degradation of PDMS can be catalyzed by both types of surface acidities. The Brønsted acidity on soil clay minerals is generated by the polarizing power of exchangeable

cations and structural metal cations (17) and thus directly depends on the type of exchangeable cations and moisture content (18). In a parallel study, Xu (19) observed a 50% to 120-fold increase when exchanging the exchangeable cations from Na^+ to Ca^{2+} or to Al^{3+} . Similarly, increases in degradation rate by factors of 2–285 were observed when humidity decreased from 100% to 32% (19). Those results strongly suggest the involvement of surface Brønsted acidity in catalyzing PDMS degradation.

The involvement of Lewis acid sites in PDMS degradation on mineral surfaces was demonstrated by the high surface-area-normalized rate constants for PDMS degradation on kaolinite, oxides, pyrophyllite, and talc (Table 2). Gibbsite has only aluminols on its surface, and kaolinite has both aluminols and siloxane oxygens on platelet surfaces, with Si-O-Al- on edge sites. Both clay minerals have very few exchangeable cations under normal pH (6.5–7.0). The high rate constants for both minerals (Table 2) suggest that aluminol Al or structural Al on edge sites provides very effective catalytic opportunities. Although they have a layer

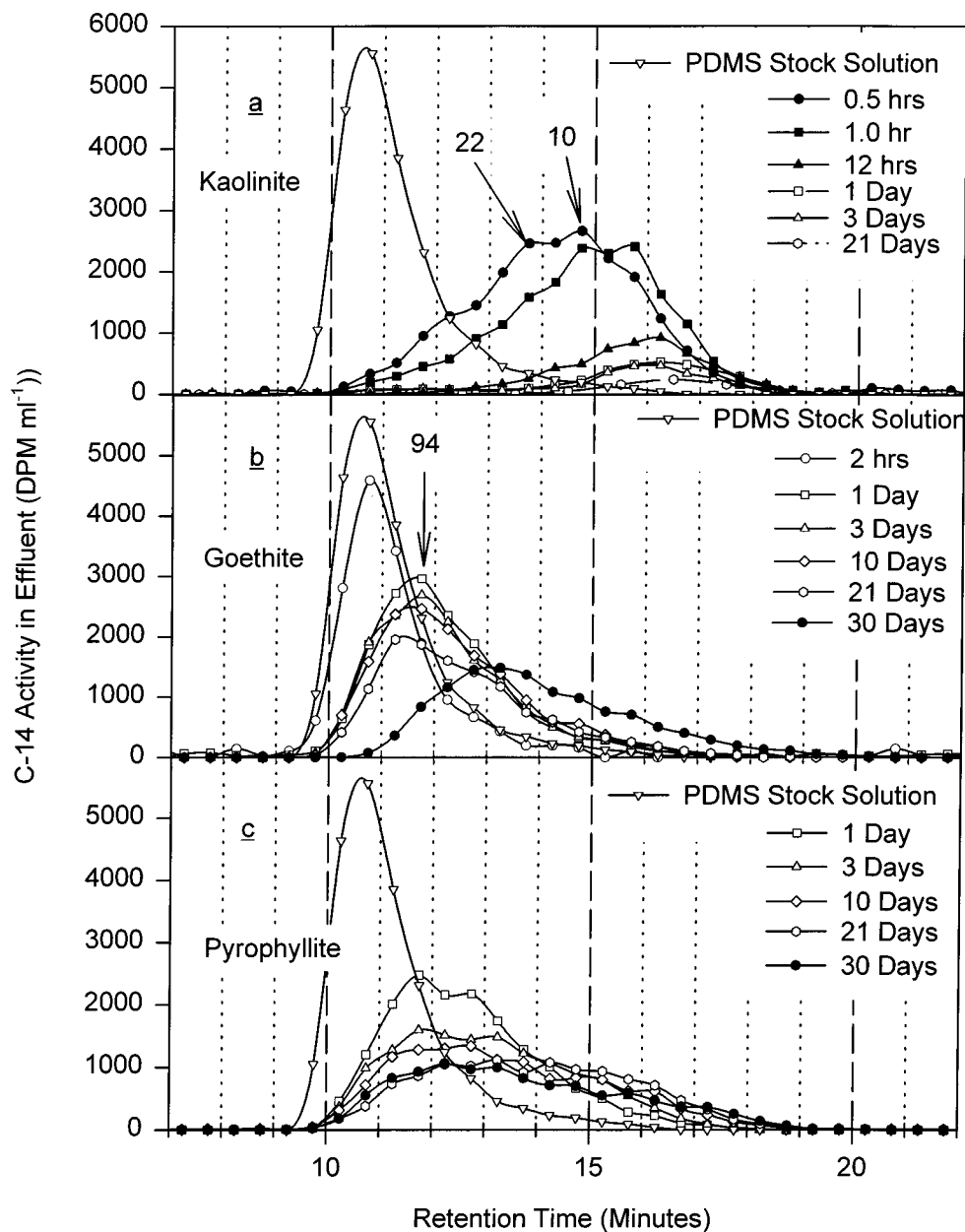


FIGURE 3. HPLC/GPC chromatograms of the polymeric residue after PDMS was incubated with kaolinite, goethite, and pyrophyllite for different times. Numbers indicate the average molecular size in Si-O units.

structure similar to montmorillonite and illite, talc and pyrophyllite have no structural charge and therefore few exchangeable cations. Even so, they promoted PDMS degradation more effectively than montmorillonites and illite (Table 2). Their ability to catalyze the hydrolytic degradation of PDMS must arise from Lewis acid sites such as the structural Mg and Si in talc and Al and Si in pyrophyllite. The higher ($\sim 9\times$) degradation rate constant for pyrophyllite than talc implies the greater effectiveness of structural Al in catalyzing PDMS degradation than Mg and Si.

Lewis acid sites are responsible for catalyzing the degradation of many organic compounds (20). The catalytic reactions involve the coordination of polar organic functional groups with structural cations on Lewis acid sites. Similarly, the hydrolytic reaction of PDMS on clay surfaces may also involve the coordination of Si-O in the PDMS backbone with the exposed metal cations on these sites. The stability of the Si-O-Si bond with respect to hydrolysis in aqueous solution is partially due to the shielding from H₂O attack by

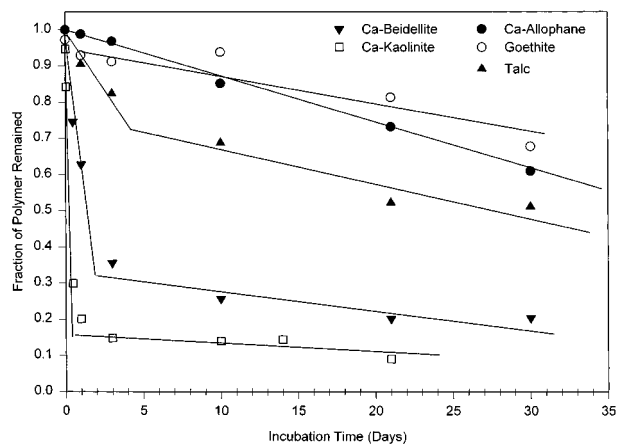


FIGURE 4. Polymeric residue remaining as a function of incubation time and clay type.

TABLE 2. Initial PDMS Degradation Rates for Different Clay Minerals

clay minerals	length of initial phase (day)	amount of PDMS degraded (mg g ⁻¹)	rate constant of initial phase (μg day ⁻¹)	normalized rate constant (μg m ⁻² day ⁻¹)
gibbsite	1.0	0.40	400	120.2
Ca-kaolinite	0.71	1.83	1299	118.7
Ca-chlorite	3.0	0.79	263	90.4
pyrophyllite	3.0	0.51	170	49.7
Ca-beidellite	3.0	1.43	477	19.1
goethite	1.0	0.18	180	11.8
talc	4.3	0.62	144	5.1
Ca-nontronite	5	1.50	300	3.8
Ca-SWy-2	16.8	0.73	43	3.3
Ca-SAZ-1	7	0.68	97	1.1
Ca-illite	22.0	1.32	60	1.2
Ca-allophane	30.0	0.82	27	0.3

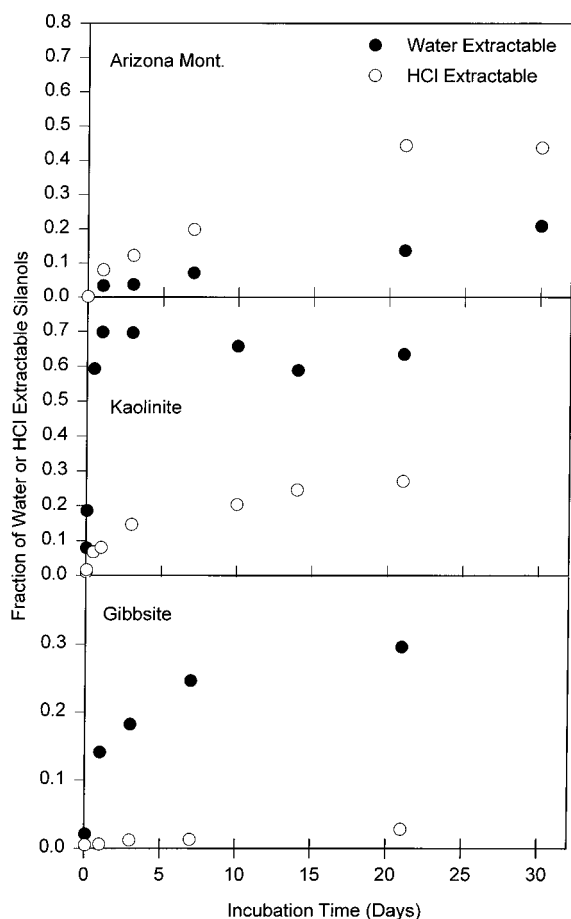


FIGURE 5. Dynamics of water- and HCl-extractable degradation products for three representative minerals.

methyl groups on Si atoms. The coordination of the Si-O-Si to any structural cations may weaken the Si-O-Si bond and expose it to water attack.

Water-Extractable, HCl-Extractable and Nonextractable Degradation Products. Two trends were observed regarding the oligomeric and monomeric degradation products. First, the HCl-extractable silanols increased with incubation time in most cases (Figure 5), while the dynamics of water-soluble organosilicon species did not follow any simple trend, instead depending strongly on the type of mineral involved (Figure 5). The water-soluble silanols consisted of monomer, dimer, and trimer diols with the general expression HO(Me₂SiO)_nH (n = 1-3) (3, 4, 6). The exact nature of the HCl-extractable organosilicon species is unknown, although it has been

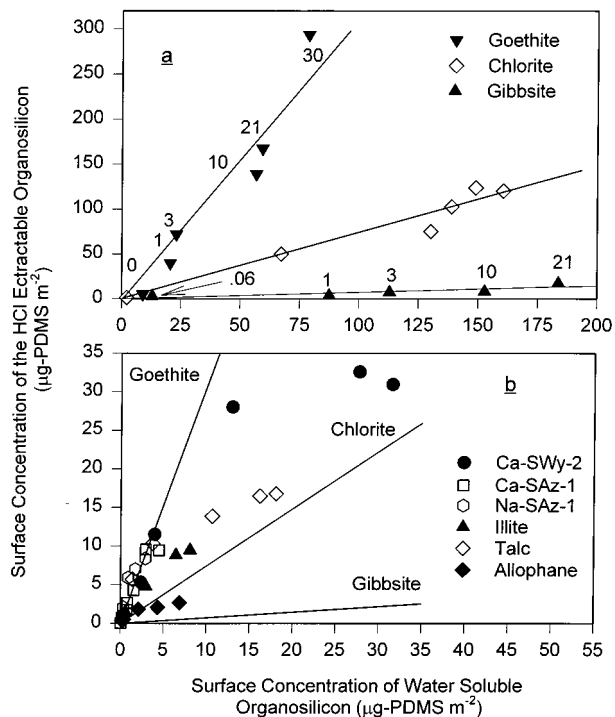


FIGURE 6. Relationship between the water-extractable and HCl-extractable organosilicon species for minerals with low to intermediate catalytic activity. The number above each data point for goethite and gibbsite indicates the incubation time in days.

proposed that they are small silanols bound to clay mineral surfaces (3).

In general, the small silanols formed by hydrolysis of PDMS can either dissolve in the water film surrounding the clay mineral particles or adsorb onto clay surfaces. We propose that the concentration of adsorbed and water-soluble silanols is determined by the rate of PDMS degradation relative to the rate of surface bonding reactions. For some minerals such as goethite, gibbsite, and chlorite, the PDMS hydrolysis was slow enough to allow development of an equilibrium between the water-soluble and HCl-extractable silanols. As a result, the surface concentrations of HCl-extractable silanols were a linear function of the water-soluble values (Figure 6).

Goethite and gibbsite defined the upper and lower limits (Figure 6a), indicating that the bonding of the silanols to ferrols (Fe-OH) is stronger than to aluminols (Al-OH). For most of the aluminosilicates, the surface concentrations of either HCl-extractable or water-soluble silanols were very small due to the high surface area of these minerals. On these minerals, silanol bonding initially followed the goethite line and then leveled off toward the chlorite line as surface concentration of HCl-extractable organosilicon increased (Figure 6b).

Most of the aluminosilicates contained small amounts of Fe in their octahedral positions and thus had limited surface density of ferrols. These ferrols may be responsible for the level of HCl-extractable silanols at low surface concentrations. It follows that the leveling off of the HCl-extractable silanols at higher surface loadings may be due to saturation of the ferrol sites. For allophane, however, the exposed surface functional groups are mainly aluminols. The slightly higher HCl-extractable organosilicon in relation to gibbsite (with aluminols only on the surface) may be caused by a small amount of hematite as a mineral impurity.

For clay minerals with fast degradation reactions, PDMS hydrolysis was rapid enough to allow silanols to accumulate in the water phase, resulting in a deviation from the

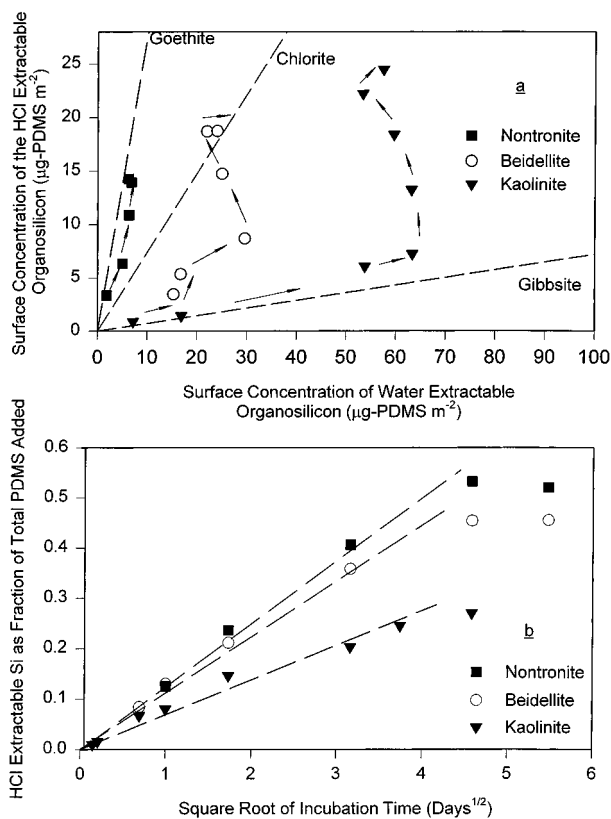


FIGURE 7. Relationship between the water-extractable and HCl-extractable organosilicon species for minerals with high catalytic activity (a) and the time dependence of HCl-extractable degradation products for those minerals (b). The arrows indicate the direction of increasing incubation times.

equilibrium position defined by other layer silicates (Figure 7a). The concentration of the HCl-extractable silanols initially showed a linear relation to the square root of incubation time (Figure 7b), suggesting a diffusion-controlled bonding process. As the bonding reaction proceeded and the rate of silanol production decreased, the HCl-extractable silanols gradually approached equilibrium with water-soluble silanols (Figure 7a). This resulted in a decrease or leveling off of water-soluble silanols with incubation time (Figure 5), clearly demonstrating the conversion of a kinetically controlled process into an equilibrium-controlled process as the reaction slowed and the reaction time increased.

In addition, the silicon species nonextractable from clay minerals by dilute CaCl₂ and HCl solutions were less than 5% of the total amount of PDMS added. The average ranged from 0 to 2.2% (data not shown), suggesting limited significance of this fraction in clay systems. These results are different from incubations of [¹⁴C]-DMSD in moist soils using a similar extraction scheme (7), in which 10–30% organosilicon species were found nonextractable by dilute CaCl₂ and HCl solutions. This discrepancy suggests that minerals were not involved in forming the nonextractable organosilicon fraction in soil.

Environmental Implications. These results have three important implications. First, PDMS degradation catalyzed by clay minerals is the rule rather than the exception. This is extremely important considering the global distribution of soils into which PDMS may potentially be introduced. Due to the tremendous diversity of soils, it is impossible to test PDMS degradation in all soils. Instead, we limited testing to a small number of soils. Our ability to extrapolate results from a few samples to thousands of untested ones depends on our knowledge of the basic soil constituents responsible

for catalyzing PDMS degradation. The widespread occurrence of these catalysts, therefore, ensures that PDMS in any soil will undergo rapid degradation as long as critical soil factors such as moisture contents are favorable.

Second, soil conditions are important in determining the rates of PDMS degradation because soil is a complex and dynamic system, with many factors that can influence the rate of such chemical processes. The previous studies (1, 2) have demonstrated that soil moisture is the single-most important factor in determining the degradation rates. This study revealed a large variation in the degradation rates of PDMS samples incubated with various clays under a constant water activity (~30% RH). The general trend for catalytic activity after normalization to surface area followed roughly the degree of mineral weathering: gibbsite ~ kaolinite > chlorite > smectites, illite, allophane.

This trend is a key in understanding the effects of soil weathering on PDMS degradation rates. Lehmann et al. (4) determined PDMS degradation rates in seven soils, including one Oxisol, one Ultisol, three Mollisols, and two Alfisols. The PDMS degradation rates after being normalized to the water contents followed the order: Oxisol >> Ultisol > Mollisols ~ Alfisols. This is consistent with the mineralogical compositions of the soils, since the dominant mineral types in Oxisol (21) and Ultisol are kaolinite, gibbsite, and iron oxide. In Mollisols and Alfisols, illite, smectites, and vermiculites dominate (22).

Third, clay minerals influence the fate of degradation products differently, arising from their different interaction strengths. Goethite interacts most strongly with the degradation products, as indicated by the steep slope of the HCl-extractable/water-extractable line in Figure 6, and thus will be more effective than other minerals in immobilizing these products. Smectites interact more strongly with the degradation products at low concentrations (Figure 6). Although the bonding strength of degradation products on these minerals may not be as strong as on goethite, their huge surface area raises their efficacy in immobilizing the degradation products.

Acknowledgments

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