

SURFACE AREA OF VERMICULITE WITH NITROGEN AND CARBON DIOXIDE AS ADSORBATES

JOSEPHUS THOMAS, JR. and BRUCE F. BOHOR
Illinois State Geological Survey, Urbana, Illinois

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Abstract—Surface-area studies were made on several homoionic vermiculites with both nitrogen and carbon dioxide as adsorbates. These studies show that only very slight penetration occurs between individual vermiculite platelets. This is in contrast to an earlier investigation of montmorillonite where it was found that the degree of penetration between layers is quite high, particularly for carbon dioxide, and is governed by the size and charge of the interlayer cation. The inability of these adsorbates to penetrate substantially between vermiculite platelets is due primarily to this mineral's high surface-charge density.

The extent of penetration of nitrogen and carbon dioxide at the edges of vermiculite platelets, though slight, is influenced by the coordinated water retained within the sample at a given degassing temperature. Forces between layers are weakened with increasing water content, which permits slightly greater penetration by adsorbate gases. Thus, the surface area of vermiculite, as determined by gas adsorption, is larger than the calculated external surface area based upon particle size and shape considerations. In addition, "extra" surface is provided by the lifting and scrolling of terminal platelets. These morphological features are shown in scanning electron micrographs of a naturally occurring vermiculite.

INTRODUCTION

THE GAS adsorption method of Brunauer, Emmett and Teller (1938)—B.E.T. method—is generally regarded as the standard against which other methods are compared in the determination of the surface area of fine particles. The method has been used extensively with clay minerals. Until recently, it has been assumed that nitrogen, the most widely used adsorbate at temperatures near its boiling point ($\sim 77^\circ\text{K}$), does not penetrate between the layers (platelets)* of montmorillonite but instead is adsorbed only on the external surface. A recent study by Thomas and Bohor (1968), however, has shown that some penetration does occur, governed by the size and charge of the exchangeable cation. That is, an increase in the degree of penetration (also somewhat time dependent) by nitrogen coincides with an increase in the size of the exchangeable monovalent cation.

The use of carbon dioxide as an adsorbate at $\sim 195^\circ\text{K}$ results in a still greater degree of penetration, as it is a more energetic molecule at its appre-

ciably higher adsorption temperature than is nitrogen at its lower adsorption temperature. This difference in penetration between the two adsorbates is well known to those working with microporous substances, such as coal and molecular sieves. The validity of the B.E.T. method for microporous substances has been questioned by many workers, but a recent study by Mikhail, Brunauer and Bodor (1968) offers convincing evidence that the method does give a correct value for the entire surface accessible to the adsorbing gas. In this regard, the spaces between clay-mineral layers may be considered as micropores of a very special shape. The forces between layers of Cs-montmorillonite are weak enough to allow complete penetration by carbon dioxide.

The question arises as to what extent, if any, nitrogen and carbon dioxide are able to penetrate between the layers of vermiculite, which is structurally similar to montmorillonite but less expandable in the presence of polar vapors. A study by Raman and Mortland (1966), with nitrogen as the adsorbate, has shown that only slight differences exist among the measured surface areas of various homoionic vermiculite samples. As they pointed out, however, the values were larger than those calculated from particle-size considerations and were nearly twice as large as those obtained for

*We will restrict the use of the term "layer" throughout this paper to unbounded (except in the z-axis direction) two-dimensional extensions of unit cells, and refer to bounded individual layers or groups of several layers in clay crystals as platelets.

micaceous in the corresponding size ranges. With the assumption that only the external surface area is measured with nitrogen as the adsorbate, the higher values for vermiculite were attributed to the presence of scrolled platelet edges, described earlier by Raman and Jackson (1964), and to capillaries, cracks and crevices.

The objective of the study reported here was to determine whether or not the surface areas of various homoionic vermiculites differed significantly when carbon dioxide was used as the adsorbate. Determinations with nitrogen were made for comparative purposes. Vermiculite morphology was examined with the scanning electron microscope in order to provide visual evidence of phenomena contributing to the experimental results obtained.

EXPERIMENTAL

Sample preparation

A vermiculite from Libby, Montana, was used in this study. The sample was hand-ground in a millite mortar and then further sheared and dispersed with a blender. The $< 1\text{-}\mu$ fraction was separated from the coarser fraction by centrifugation. Homoionic samples of Li-, Na-, K-, Mg-, and Cs-vermiculite were prepared from the finer fraction by a method described by the authors (1968) in their earlier study on montmorillonite. In the present study, however, the vermiculite was left in contact with the different salt solutions for an appreciably longer time (72 hr) than was the montmorillonite. Neutron activation analysis of the Cs-vermiculite confirmed that a high degree of substitution had occurred, yielding a value for Cs of 120 mg (± 10 per cent) per gram of dried sample (~ 100 meq/100g).

Surface-area measurements

The thermal conductivity apparatus, various operational procedures, use of carbon dioxide as an adsorbate, and size of the carbon dioxide molecule have been discussed in some detail in the authors' earlier study (1968) and need little further discussion here.

Samples were degassed in a flow of helium overnight (16 hr), prior to the measurements. One series of samples was degassed at 110°C and another series at 175°C . In addition, higher temperatures were used with two samples for special comparison.

Electron microscopy

A Stereoscan II scanning electron microscope (Cambridge Scientific Instruments, Ltd.) at the Central Microscope Laboratory of the University of Illinois was used to examine and photograph samples of natural vermiculite. The $< 1\text{-}\mu$ fraction

was spray-dried (to maximize randomness of orientation) onto aluminum foil, mounted on a sample stud, and vacuum-coated with palladium and gold prior to placing it in the scope. The junior author is preparing a description of this sample preparation method for publication in the near future. Primary instrument magnifications of about 13,000X and 26,000X were used to obtain the scanning micrographs of this material.

RESULTS AND DISCUSSION

Surface-area values from nitrogen and carbon dioxide adsorption are shown in Table 1. It is immediately obvious from these values that an increase in the size of the interlayer monovalent cation is not accompanied by an increase in surface area with either nitrogen or carbon dioxide as the adsorbing gas. In fact, the highest value for each adsorbate with each suite of samples was obtained for Mg-vermiculite; the divalent magnesium cation is only slightly larger than lithium, smallest of the monovalent cations. This is in direct contrast with the effect of interlayer substitution in montmorillonite, where the surface-area values for monovalent cation substitution with carbon dioxide as the adsorbate ranged from $99\text{ m}^2/\text{g}$ for Li-montmorillonite to $315\text{ m}^2/\text{g}$ for Cs-montmorillonite. The total surface area would be twice these values minus the external surface area, because only one molecular layer of adsorbate is held between each pair of clay layers.

The forces between layers in vermiculite are not weakened sufficiently, even by intercalation of the large cesium cation, to permit appreciable penetration by carbon dioxide. Longer adsorption periods (16 hr) failed to increase the quantity of gases adsorbed on Cs-vermiculite, again in contrast with the behavior of carbon dioxide on montmorillonites. Thus, the non-polar gases are unable to overcome the energy barrier (activation energy concept implicit) that exists between vermiculite platelets. This can only be interpreted as being due to the higher charge density on individual vermiculite layers resulting from the greater degree of substitution of aluminum for silicon in the outer tetrahedral sheets. The primary source of the negative charge on montmorillonite arises from the substitution of magnesium for aluminum in the inner octahedral sheet. The interlayer cation, of course, will be held more strongly by the tetrahedral charge source than by the farther removed octahedral charge source, as predicted by Coulomb's law. This, in turn, increases the forces between layers, resulting in other recognized differences in vermiculite as compared with montmorillonite, such as the slower rate of swelling in polar vapors,

Table 1. Surface-area values from nitrogen adsorption and carbon dioxide adsorption on $< 1\mu$ fraction of homoionic vermiculites using 3-point B.E.T. plots established from half-hour adsorption periods

Replaceable cation	Pauling radius (Å)	Degassing temperature (°C)	Weight loss, (%) [*]	Surface area (m ² /g)	
				N ₂ adsorption	CO ₂ adsorption
Mg ²⁺	0.65	110	5.51	43	70
		175	5.92	37	48
		300†	7.34	38	44
Li ⁺	0.60	110	4.46	33	41
		175	4.79	36	39
Na ⁺	0.95	110	4.08	29	50
		175	5.54	33	40
K ⁺	1.33	110	2.42	40	50
		175	2.73	38	36
		500†	3.05	30	31
Cs ⁺	1.69	110	1.31	38	51
		175	2.12	36	40

^{*}Determined from the oven-dried (90°C) sample weight before and after degassing in helium.

†Same sample as that run at 175°C but held for an additional hour at temperature shown, and surface area then redetermined.

the decreased degree of hydrolysis of adsorbed cations, and the slower rate of interlayer cation diffusion.

Variations of 2–3 m²/g in the range of surface area shown in Table 1 for the differently treated samples are not particularly significant. However, it is seen that approximately 20–70 per cent more surface is available to carbon dioxide than to nitrogen for all of the samples degassed at the lower (110°C) temperature. The difference is not as great for samples degassed at 175°C, as the values from carbon dioxide adsorption on these samples are appreciably lower and more nearly equal to the relatively unchanged nitrogen adsorption values. A sample of K-vermiculite, which had been subjected to a degassing temperature of 500°C, produced essentially the same surface-area value with each adsorbate. This was the only sample subjected to such a high degassing temperature.

From the higher values obtained with carbon dioxide adsorption, it is readily apparent that some penetration occurs between the vermiculite platelets, restricted no doubt to areas near the outer edges. The marked decrease in sample surface area with increased degassing temperature, again with carbon dioxide as the adsorbate, appears to be a result of the further removal of retained water coordinated with the interlayer cation. The higher surface-area values for Mg-vermiculite appear to be associated with the greater retention of water in this sample under comparable degassing conditions. This is shown in Table 1 by the additional loss in weight of Mg-vermiculite when the same sample that had been degassed for 16 hr at 175°C was de-

gassed an additional hour at 300°C. It is seen that the additional loss in weight is greater than that for K-vermiculite treated similarly but with a final degassing temperature of 500°C rather than 300°C.

Close comparison of the absolute weight loss values for the different samples in Table 1 should not be made, because the "dried" samples before degassing were kept only in screw-cap vials, and thus were not maintained under rigorous humidity conditions during the experimentation period. However, the data reflect the fact that the magnesium cation, among those cations studied, has the highest charge-to-size ratio (ionic potential), which is associated with strong polarizing effects and increased covalent character. Thus, it would be expected – and is shown by these test results – that Mg-vermiculite would retain coordinated water more tenaciously at comparable elevated temperatures than would the other vermiculites studied.

The manner in which the retained water influences the surface area of vermiculite, as determined by the adsorption of non-polar gases, is not well defined at this time. The evidence from this study suggests that stresses are set up between clay layers at certain water concentrations (depending upon the interlayer cation), owing to surface tension differences and the imbalance of forces exerted upon the terminal platelets that cause slight platelet separation, particularly at the edges. In the extreme cases, complete lifting and scrolling of outermost platelets occurs.

Micrographs 1-a, 1-b, and 1-c of the $< 1\mu$ fraction of naturally occurring vermiculite (containing essentially Mg as the interlayer cation) are of

considerable help in this interpretation, and further substantiate the studies of Raman and Jackson (1964). The tendency of the outermost platelets to curl is rather commonplace, as is the slight separation of platelets at the edges, shown in the upper left portion of micrograph 1-a. In several instances, the outermost platelet (or packet of platelets) succeeds in peeling up from the particle, as shown in micrograph 1-b, or may completely break away from the main particle and remain scrolled, as

As stated earlier, the slightly higher surface-area values for Mg-vermiculite, at the lower degassing temperature, appear to be associated with a higher water content coordinated with the magnesium cation and the consequently weaker interlayer forces. When the sample is degassed at progressively higher temperatures, the water content decreases, and the increased interlayer forces cause the outer platelets to settle back into a more nearly parallel arrangement. The measured surface area then decreases as the degree of penetration by the adsorbate decreases. This effect is more sensitive to carbon dioxide, of course, owing to its greater penetration at its higher adsorption temperature.

It is likely that platelet separation and scrolling of terminal platelets is common with all the homoionic vermiculites, provided there is sufficient coordinated water present. This would be difficult to verify by electron microscopy, either by direct observation or with replicas prepared under high vacuum. Varying degrees of coordinated water (again depending upon the interlayer cation) will be removed under vacuum, even at relatively low temperatures. Curling should be more evident on the surface of a vermiculite particle in which the coordinated water is more difficult to remove. If the water is easily removed, as in the case with a large monovalent interlayer cation, then the curling, breaking away, and scrolling of outer platelets may occur during the high-vacuum period prior to observation. There should be ample evidence, however, of the smaller scrolled particles that had broken away from the main vermiculite flakes.

SUMMARY AND CONCLUSIONS

The main points arising from this study may be stated as follows:

(1) Increasing the size of the interlayer cation does not weaken the forces between vermiculite platelets sufficiently to permit an increasingly greater degree of penetration by non-polar adsorbates (such as nitrogen and carbon dioxide), contrary to the findings of a similar study with montmorillonite. This is attributed primarily to the higher surface-charge density in vermiculite.

(2) Significantly higher surface-area values from carbon dioxide adsorption over those from nitrogen adsorption attest that slight edge penetration of adsorbate gases does occur between vermiculite platelets.

(3) The amount of retained water, coordinated with the interlayer cation in degassed samples, appears to have considerable influence on the degree of adsorbate penetration. Mg-vermiculite, for example, yields somewhat larger surface-area values as a result of greater water retention at a given degassing temperature. This is an effect of the high charge-to-size ratio of the magnesium cation. The exact manner in which water influences the penetration is not clear, although it is thought that stresses between vermiculite layers are induced from surface-tension differences and from the imbalance of forces on the terminal platelets.

(4) The higher-than-calculated (from particle size and shape considerations) surface-area values for vermiculite by gas adsorption methods arise not only from the slight penetration between platelets but also, in agreement with Raman and Mortland (1966), from lifting and scrolling of terminal platelets. Scanning electron micrographs of these phenomena are shown, which further substantiate the studies of Raman and Jackson (1964), shown in micrograph 1-c. In this regard, the curling of the outermost platelets of vermiculite is not unlike that commonly observed in electron micrographs of montmorillonite particles, except that the latter are usually thin and this permits whole particles to scroll or curl at their edges.

Thus, surface-area values from the adsorption of non-polar gases are higher than calculated values (from particle size and shape considerations), not only because of slight penetration of the adsorbates at the platelet edges, but also because of the "extra" surface that becomes available from the lifting, breaking away, and scrolling of outermost platelets.

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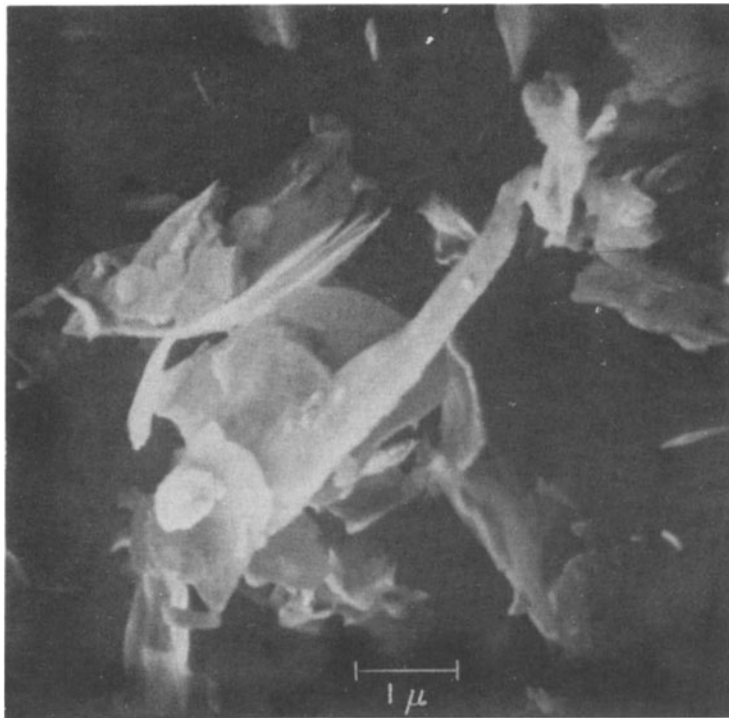


Fig. 1. Scanning electron micrographs of spray-dried natural (Mg) vermiculite from Libby, Montana.

Fig. 1-a. Lifted terminal platelets and separation at crystal edges shown by grouping in upper left center of photo. Bright spherical object on the large lath-shaped crystal in the center is a droplet of coating metal formed by sputtering during its evaporation.

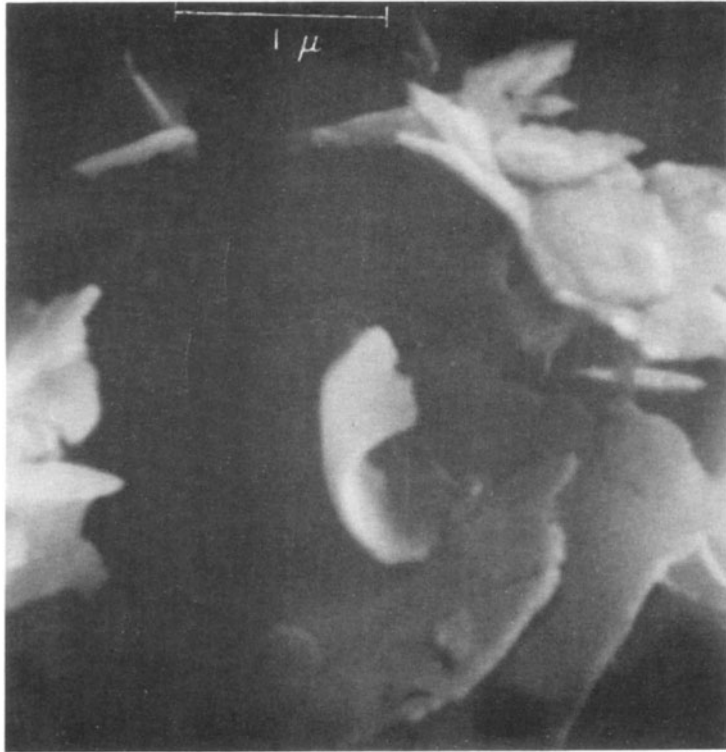


Fig. 1-b. Bright curled object at center is a partial terminal platelet peeling away from the crystal surface below.

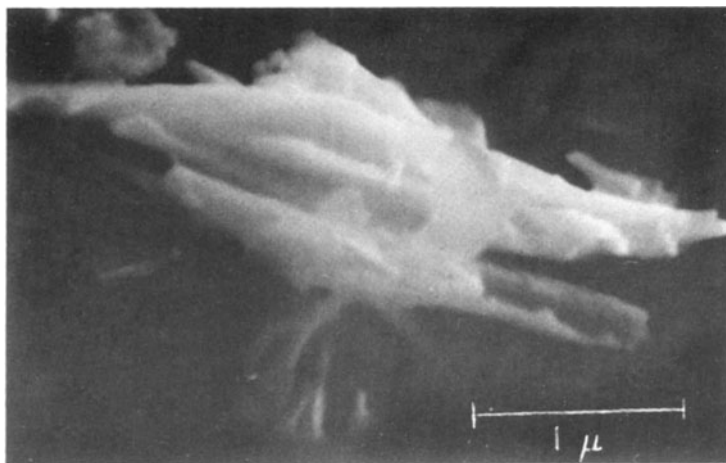


Fig. 1-c. Group of scrolled platelets. Note the spatulate shape of the lower particle.

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Résumé—Des études de zones de surface ont été effectuées sur plusieurs vermiculites homoioniques avec, en tant que produits d'adsorption, à la fois le nitrogène et l'oxyde de carbone. Ces études montrent que seule se produit une très légère pénétration entre les différentes plaquettes de vermiculite. Ceci fait contraste à une étude antérieure sur le montmorillonite où l'on avait trouvé que le degré de pénétration était assez élevé entre les couches, en particulier pour l'oxyde de carbone, et que celle-ci est contrôlée par la taille et la charge du cation de la couche intermédiaire. L'impossibilité de ces produits à pénétrer assez profondément entre les plaquettes de vermiculite est dûe premièrement à la haute densité de charge-surface de ce minéral.

Le degré de pénétration du nitrogène et de l'oxyde de carbone aux bords des plaquettes de vermiculite, bien que faible, est influencé par l'eau de coordination retenue dans le prélèvement à une température donnée de dégazification. Les forces entre les couches s'affaiblissent avec la croissance de la teneur en eau, ce qui permet une pénétration légèrement plus grande par les gaz d'adsorption. Ainsi, la zone de surface de vermiculite, telle qu'elle est déterminée par l'adsorption des gaz, est plus étendue que la zone de surface externe calculée selon la taille et la formes des particules. De plus, une surface "supplémentaire" est fournie par l'élévation et le déroulement des plaquettes terminales. Ces caractéristiques morphologiques sont démontrés en développant des micrographes d'électrons d'un vermiculite se produisant naturellement.

Kurzreferat—Es wurden Oberflächenstudien an verschiedenen homoionischen Vermiculiten und zwar mit Stickstoff und Kohlendioxyd als Adsorbaten durchgeführt. Diese Versuche zeigen, dass nur sehr geringe Penetration zwischen den einzelnen Vermiculitplättchen stattfindet. Das steht im Gegensatz zu einer früheren Untersuchung von Montmorillonit, wo man feststellte, dass das Maß der Eindringung zwischen Schichten recht hoch war, besonders für Kohlendioxyd, und dass dasselbe durch die Grösse und durch die Ladung der Zwischenschichtkationen bestimmt wird. Die Unfähigkeit dieser Adsorbate, wesentlich zwischen die Vermiculitplättchen einzudringen, ist in erster Linie der hohen Oberflächenladungsdichte dieses Minerals zuzuschreiben.

Das Ausmass der Penetration von Stickstoff und Kohlendioxyd an den Rändern der Vermiculitplättchen ist zwar gering, wird aber durch das innerhalb der Probe bei einer bestimmten Entgasungstemperatur zurückgehaltene Koordinationswasser beeinflusst. Die zwischen den Schichten wirkenden Kräfte werden schwächer mit zunehmendem Wassergehalt, wodurch etwas stärkere Penetration durch die Adsorbategase ermöglicht wird. Die durch Gasadsorption bestimmte Oberfläche des Vermiculits ist also grösser als die auf Grund der Teilchengrösse und Teilchenform berechnete äussere Oberfläche. Dazu kommt noch, dass durch Heben und Rollen der Endplättchen "extra" Oberfläche zustandekommt. Diese morphologischen Verhältnisse werden in Abtast-Elektronenmikrographien eines natürlich vorkommenden Vermiculits aufgezeigt.

Резюме—Проведено определение площади поверхности для нескольких гомоионных вермикулитов с использованием в качестве адсорбатов как азота, так и углекислоты. Показано, что только незначительное количество газа проникает между отдельными пластинками вермикулита. Полученные данные резко отличаются от данных более раннего изучения монтмориллонита; для этого минерала установлено значительное проникновение газа, особенно углекислоты, между слоями и доказано, что оно зависит от величины и заряда межслоевого катиона. Неспособность тех же адсорбатов проникать в существенных количествах между пластинками вермикулита объясняется прежде всего высокой плотностью его поверхностных зарядов.

Степень проникновения азота и углекислоты по краям пластинок вермикулита, хотя и являющаяся незначительной, зависит от количества координационной воды, содержащейся в минерале при заданной температуре дегазации. Силы, действующие между слоями, ослабевают с возрастанием содержания воды, что делает возможным несколько большее проникновение газов—адсорбатов.

Площадь поверхности вермикулита, определенная по адсорбции газов, больше, чем площадь его внешней поверхности, вычисленная по данным о величине и форме частиц. Дополнительная поверхность создается расщеплением краев частиц; об этом говорит изучение природного вермикулита с помощью сканирующего электронного микроскопа.