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INTERLAMELLAR ADSORPTION OF CARBON DIOXIDE BY SMECTITES

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Abstract—The adsorption of CO_2 at low temperature ($\sim -70°C$) on thin films of homoionic smectites was studied by X-ray diffraction and by i.r. absorption. An increase in the d_{001} spacings of these clay films upon adsorption of CO_2 was observed. In addition, a dichroic effect was readily discernible by comparing the i.r. spectra at two different orientations of the smectite films; i.e. with the film normal and tilted 35° with respect to the i.r. beam. The CO_2 stretching vibration at 2350 cm^{-1} was used for the i.r. study. These observations conclusively show that CO_2 intercalates the smectite structure rather than being adsorbed only in pores between clay tactoids—the limiting process proposed by other investigators.

Adsorption isotherm data from earlier surface area studies are re-examined here through application of the Dubinin equation. Again, intercalation is demonstrated by convergence of the plotted experimental data for smectites containing large monovalent interlayer cations toward a pore volume that is near the calculated theoretical value for a monolayer of intercalated CO_2.

Scanning electron photomicrographs of Li- and Cs- smectites provide additional evidence that aggregation differences are not responsible for the large observed difference in BET surface areas obtained for these smectites with CO_2 as the adsorbate. At low magnification, visual differences in macro-aggregates are apparent, but at high magnification no significant differences are observed in the micro-structure of individual aggregates where the major amount of gas adsorption really occurs.

INTRODUCTION

From gas adsorption studies on homoionic smectites, Thomas and Bohor (1968) recently concluded that CO_2 and, to a lesser extent, nitrogen penetrate the interlamellar space. They reported that the extent of penetration is governed primarily by the size and charge of the replaceable interlayer cation. Complete penetration of Cs–smectite by CO_2 (at $-78°C$) was indicated. Their results were criticized by Aylmore, Sills and Quirk (1970) who believed that these gases are adsorbed in the pores between clay tactoids—their 'quasicrystalline domains'. These authors also found it difficult to accept that CO_2 can penetrate the interlamellar space, while nitrogen, a smaller molecule, is unable to do so to the same extent. Thomas *et al.* (1970) replied that the Arrhenius factor in the diffusion coefficient favors the penetration of CO_2 at $-78°C$ over nitrogen at $-196°C$ into pores of molecular dimensions. Moreover, since CO_2 is more polarizable than nitrogen, the van der Waals contribution to the adsorption energy should be higher for CO_2.

To help confirm whether or not adsorbed CO_2 is actually located between the clay lamellae, the i.r. spectra and the X-ray diffraction characteristics of clay films exposed to gaseous CO_2 at about $-70°C$ were studied. The d_{001} spacing of the clay would be expected to increase upon CO_2 adsorption. Additionally, the CO_2 stretching vibration at 2350 cm^{-1}, observed both for the clay film at normal incidence with respect to the i.r. beam, and tilted at some acute angle to the beam, should possibly show a dichroic effect if the adsorption sites are inside the interlamellar space and if the adsorbed species are oriented in such a way that the transition moment is tilted with respect to the *a–b* plane. It would be difficult to maintain that adsorption in micropores between tactoids would result in an ordered arrangement of the adsorbed species. Moreover, since it was shown by Thomas and Bohor (1968) that Ca– and Li–smectites adsorb CO_2 to a lesser extent than do K– and Cs–smectites, the dichroic effect, if any, should be more pronounced for the latter pair.

EXPERIMENTAL

Thin films of the $<2\,\mu m$ fraction of Li–, K– and Cs–smectite were produced in the usual way and mounted for study in the low temperature i.r. cell described by Fripiat and Helsen (1966). The films were outgassed at room temperature for several hours under a residual pressure of 10^{-6} torr. Pure CO_2, obtained from dry ice, was introduced into the cell at pressures between

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20 and 120 torr. The clay was that used by Thomas and Bohor (1968).

The i.r. spectra were recorded with the film either at room temperature or cooled to −78°C by a mixture of dry ice and ethanol. Spectra were obtained with the film at normal incidence and tilted 35° to the i.r. beam. It must be emphasized that the actual film temperature is not known accurately because of the absorption of radiant energy.

In the 2350 cm^{-1} region where the ν_3 stretching band of CO_2 is recorded, the contribution of atmospheric CO_2 appreciably decreases the energy received by the detector of the double-beam instrument, thereby greatly reducing the instrument sensitivity. At room temperature, however, where the amount of CO_2 adsorbed by the clay is negligible, it was observed that the Beer–Lambert law applies satisfactorily.

The same oriented films also were mounted for study in a modified version of a high temperature X-ray goniometer (Van Niekerk, 1960), which permitted the samples to be cooled to approx. −70°C. At this temperature, the amount of adsorbed CO_2 should be large enough to produce some change in the basal spacing if the adsorption process causes swelling of the clay.

The procedure in obtaining the diffraction data was as follows: The sample was outgassed under a residual pressure of 10^{-2} torr for 1 hr and the camera was then filled with CO_2 to a pressure of 700 torr. The temperature was then progressively decreased by flowing cooled oxygen through the sample holder. X-ray diffractograms (Cu Kα radiation) were obtained not only immediately after outgassing, but also at different temperatures during the cooling and rewarming cycles. Since the beryllium windows of the camera appreciably decreased the intensity of the diffracted beam, a high gain of the detector amplifier was required. This, unfortunately, decreases the signal to noise ratio. Na-, Cs- and Ca-saturated smectites were used for the X-ray experiments.

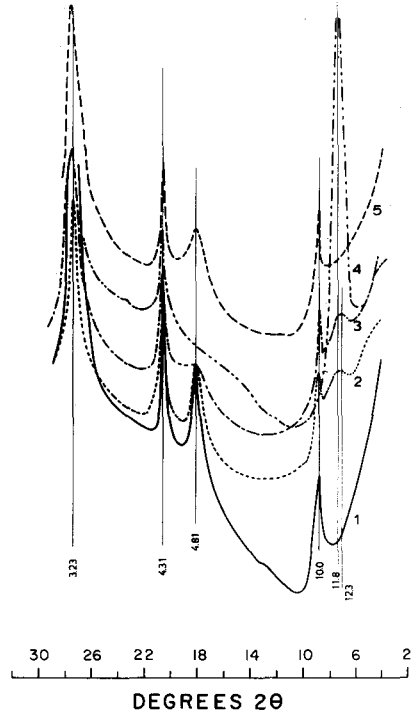


Fig. 1(a). Adsorption of CO_2 by Na–smectite. X-ray (CuKα) diagrams obtained at different stages. (1) Outgassed overnight at room temperature; (2) cooled in presence of 700 torr CO_2 at −48°C; (3) as (2), but at −62°C; (5) as (3), but rewarmed in presence of CO_2 at room temperature. Spectrum (4) has been obtained before the outgassing procedure for the air dried sample. Spacings for the main reflections are indicated.

RESULTS AND DISCUSSION

The most significant changes in the d_{001} spacings were observed for the Na–smectite as shown in Fig. 1a. In the dehydrated sample, the 001, 002 and 003 reflections were observed at 10·0, 4·81 and 3·23 Å, respectively, indicating a complete collapse of the interlamellar spacing. As the sample is cooled in the CO_2 atmosphere, these reflections decrease in intensity, with the 002 reflection disappearing almost completely at the lowest temperature. Simultaneously, a broad reflection appears at approximately 12·3 Å. As the sample is warmed in the presence of CO_2, the initial reflections are restored. For comparison, Fig. 1(a) also shows the diffractogram of the air-dried Na–smectite before outgassing. Obviously, the broad band at 12·3 Å is due to the CO_2 adsorption. It cannot be assigned to the adsorption of water impurity in the gas since this spacing is not maintained after the sample is rewarmed to 20°C. If adsorbed water were responsible for this spacing, there is no reason why it would be removed during the rewarming cycle. In absence of CO_2, the X-ray diffraction pattern of the Na sample outgassed in vacuum was not altered by lowering the temperature.

The results are much less obvious for the Ca–smectite (Fig. 1b). In the sample outgassed for 2 hr at room temperature, the long spacing is observed at 13·2 Å and a second reflection at 6·3 Å. At the lowest temperature, the first reflection increases in intensity and shifts to 14·2 Å. Accordingly, the second reflection is observed at 6·6 Å. Again, as with the Na–smectite, the diffraction pattern obtained after the sample has been rewarmed at room temperature is nearly identical to that of the initially outgassed sample. The shifts in the spacings to higher values, though not as great as with Na–

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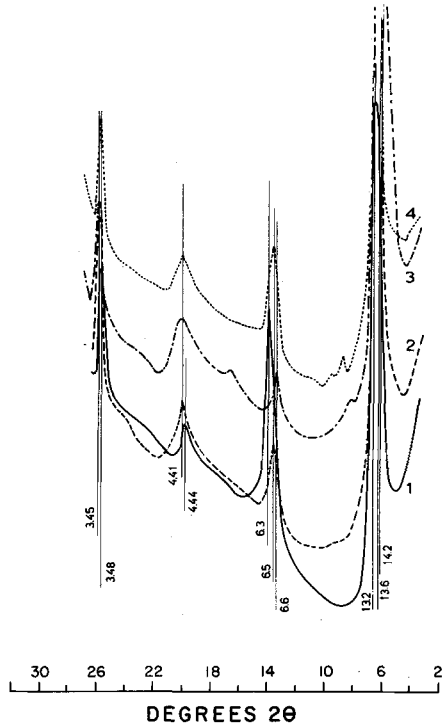


Fig. 1(b). Adsorption of CO_2 by Ca–smectite. X-ray (CuKα) diagrams obtained at different stages. (1) Outgassed for 2 hr at room temperature; (2) cooled in presence of 700 torr CO_2 at −20°C; (3) as (2), but at −63°C; (4) as (3), but rewarmed in presence of CO_2 at room temperature. Spacings for the main reflections are indicated.

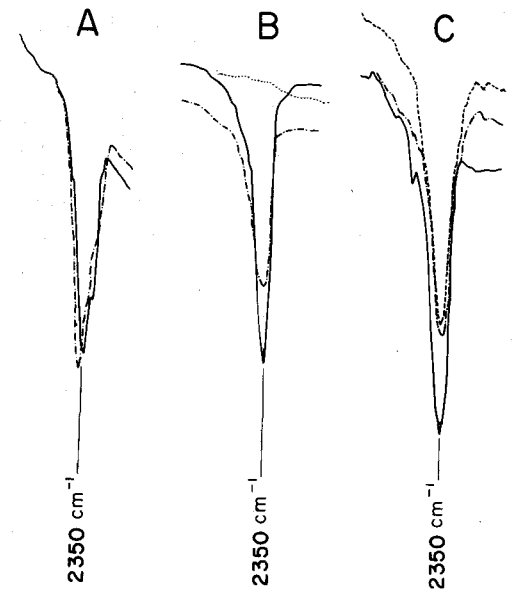


Fig. 2. I.R. transmission spectra of A: Li–smectite; B; K–smectite and C: Cs–smectite. Low temperature and notmal incidence (——); low temperature and tilted by 35° (—·—), room temperature and normal incidence (– – –). Background in absence of CO_2 (.....).

smectite, nevertheless suggest that some CO_2 also is adsorbed within the interlamellar space of the Ca–smectite.

For Cs–smectite, the first reflection observed after outgassing is at 11·8 Å, in agreement with Mamy (1968) who observed this spacing after sample dehydration at 130°C. This spacing does not change noticeably in the course of carbon dioxide adsorption. In this case, the large Cs^+ cation insures a sufficiently large spacing for intercalation of CO_2 and, therefore, its value does not change perceptibly upon adsorption. Slight swelling no doubt occurs but the detection of a few tenths of an Å unit change in *d*-spacing is difficult with broad, low-angle diffraction peaks.

At room temperature, the i.r. transmission at 2350 cm^{-1} was almost unaffected by the orientation of the clay film with respect to the i.r. beam. This result was expected because of the negligible CO_2 adsorption at this temperature. At low temperature, however, as shown in Fig. 2, a pronounced dichroic effect was observed for the Cs– and K–smectites, while for Li–smectite the absorbance at 2350 cm^{-1} was only very slightly orientation-dependent. Table 1 shows the effect of the orientation on the i.r. absorbance at the maximum of the 2350 cm^{-1} band.

The strongest dichroic effect is observed for the Cs–smectite and the weakest for the Li–smectite; that for K– smectite is intermediate. According to the intensity of the water deformation band at 1630 cm^{-1}, the Li–smectite is still appreciably hydrated after the outgassing procedure used in this work, while the K– and Cs–smectites contain much less hydration water. This hydration is also clearly noticeable in the OH^- stretching region of the spectrum. To what extent residual water allows CO_2 to penetrate the interlamellar space is not known, but obviously the suggestion that strong hydration could prevent adsorption of CO_2 between layers seems reasonable.

Table 1. Ratio of the maximum absorbance for the film tilted 35° to the i.r. beam to the maximum absorbance for the film normal to the beam, at 2350 cm^{-1}

Sample	Pressure (torr)	Low temperature (~ −70°C)	Room temperature (~ 25°C)
Cs^+	37	0·41	1·1
	77	0·51	0·98
K^+	22	0·74	0·90
	74	0·70	0·87
Li^+	70	0·86	0·95
	150	0·81	0·97

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Carbon dioxide is a linear molecule in which the transition moment associated with the ν_3 asymmetric stretching is parallel to the molecular axis. If the molecule is oriented between the layers in such a way that the transition moment is tilted to the *a–b* plane, the absorbance of the 2350 cm^{-1} band should decrease when the film is rotated in such a way that the *c*-axis is no longer parallel to the beam. Since the refractive index of the clay film loaded with CO_2 is not known, it is impossible to be more explicit about the real orientation, but it is certain that a significant fraction of the absorbed species is ordered with respect to the clay lattice.

Again, such an effect should not be conceivable for CO_2 adsorbed in the micropores between tactoids, which should be randomly distributed. If, according to the X-ray and i.r. results, an important fraction of the adsorbed CO_2 is really between the layers, the application of the Dubinin equation to the CO_2 adsorption isotherms should yield a pore volume close to that which may be calculated theoretically. The Dubinin equation is as follows:

$$\log V_s = \log V_t - k(\log P_0/P)^2$$

where k is a function of the temperature and of the adsorbent heterogeneity, P_0 and P the vapor pressure and the equilibrium pressure respectively, V_s the adsorbed volume and V_t the pore volume.

Assuming an internal specific surface area of 800 m^2 g^{-1} and a van der Waals radius for CO_2 (normal to the long axis) of approximately 3 Å, the interlamellar pore volume should be 0·12 cm^3 g^{-1}. Figure 3 shows clearly that for the K–, NH_4–, Rb– and Cs–smectites the plots of the experimental adsorption data obtained previously by Thomas and Bohor (1968) converge towards this value, assuming for CO_2 a density of 0·78 g/cm^3*. For Li–, Ba– and Ca–smectites, V_t is much smaller. Na–smectite occupies an intermediate position.

These results are in agreement with the X-ray and i.r. data which suggest that in the smectites saturated by the larger monovalent cations, CO_2 has access to the interlamellar space, while for the partially hydrated Li- and divalent cation-substituted smectites this access is more restricted.

In the study by Thomas and Bohor (1968), nitrogen penetration of smectite also was indicated, although to a much lesser extent than penetration by CO_2. Although such limited penetration by nitrogen was likely, proof of its occurrence had not yet been unequivocal for obvious reasons. In this regard, however, attention is drawn to a recent study by Knudson (1972), who reported that complete penetration by nitrogen was indicated with a smectite in which the interlayer cation had been substituted with the large organic molecule tris (ethylenediamine)–cobalt(III). This molecule gave a plate separation distance of 4·8 Å, which was apparently enough to allow complete interlamellar penetration by nitrogen molecules. Because only partial penetration with nitrogen was achieved when cesium was the exchange cation (2·6 Å separation), it seems that 4–4·5 Å separation is necessary to overcome the energy and steric effects of the nitrogen molecule and allow it to penetrate completely the smectite interlayer region.

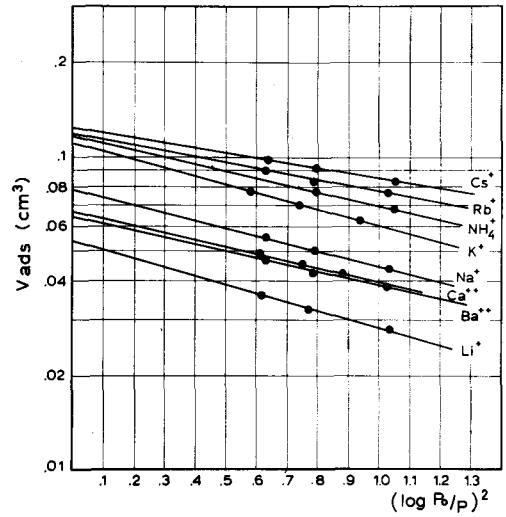


Fig. 3. Dubinin plots (see text).

Knudson (1972) maintained that the increase in surface area with increasing size of exchangeable cation, as measured by Thomas and Bohor (1968) with both CO_2 and N_2, was merely a function of the lower degree of ordering imparted to the clay platelets stacked in aggregate structures. It should be instructive to examine cation-substituted smectites directly in the scanning electron microscope (SEM) to see if this alleged stacking disorder actually occurs. Figure 4 shows low and high magnification pairs of photomicrographs of smectites saturated with Li^+ (4a,b) and Cs^+ (4c,d). At low power, there are obvious differences in the gross aspects of the smectite macro-aggregates formed with these different-sized cations, as has been observed by many workers in the past. However, at high magnification it is equally obvious that no differences are apparent in the surface microstructure of the individual aggregates (the SEM cannot resolve dimensions on the order of individual clay layers, so that we are still not

* This value corresponds to the surface packing of 22·1 $Å^2$ $molecule^{-1}$ used by Thomas and Bohor (1968) and by Aylmore *et al.* (1970).

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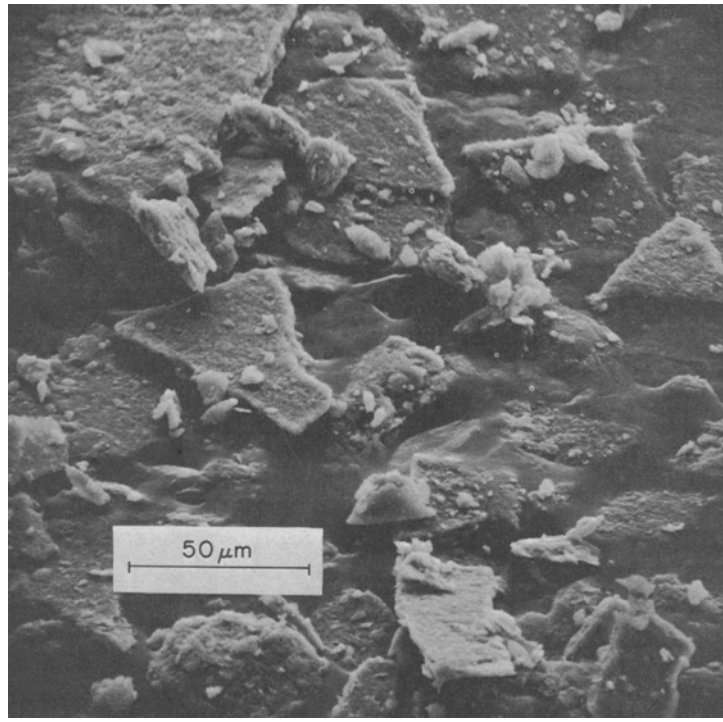


Fig. 4(a). Low magnification SEM photograph of Li-saturated smectite. Smooth substrate is aluminum paint used as adhesive on sample stub. Clay particles are platy aggregates.

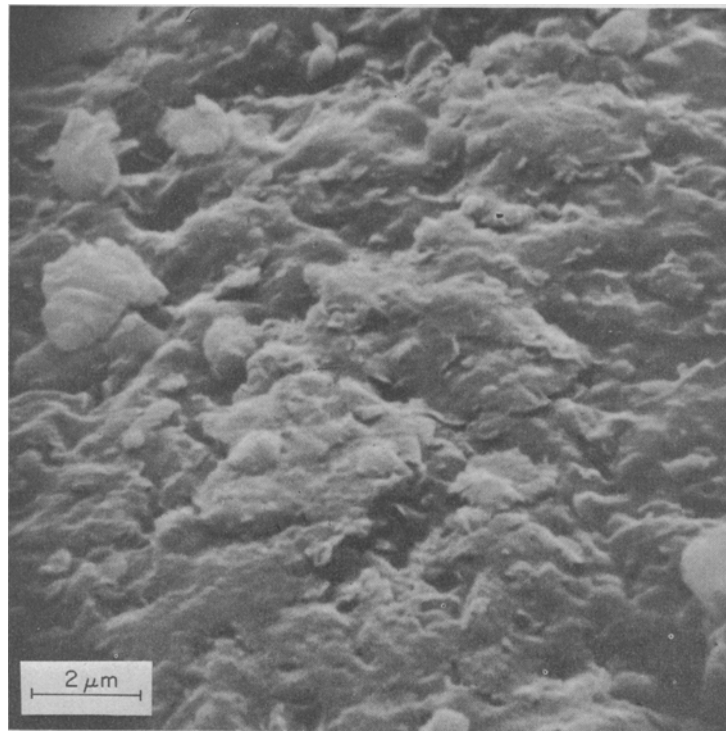


Fig. 4(b). High magnification SEM photograph of Li-saturated smectite. Surface of platy aggregate from Fig. 4(a). Face–face orientation of crystallites.

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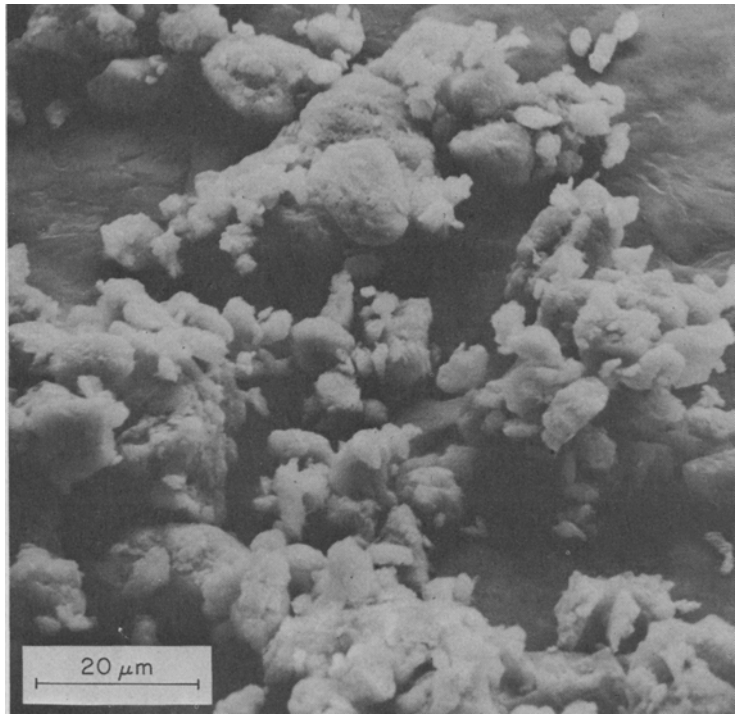


Fig. 4(c). Low magnification SEM photograph of Cs-saturated smectite. Smooth substrate is Al paint. Clay particles are rounded granular aggregates.

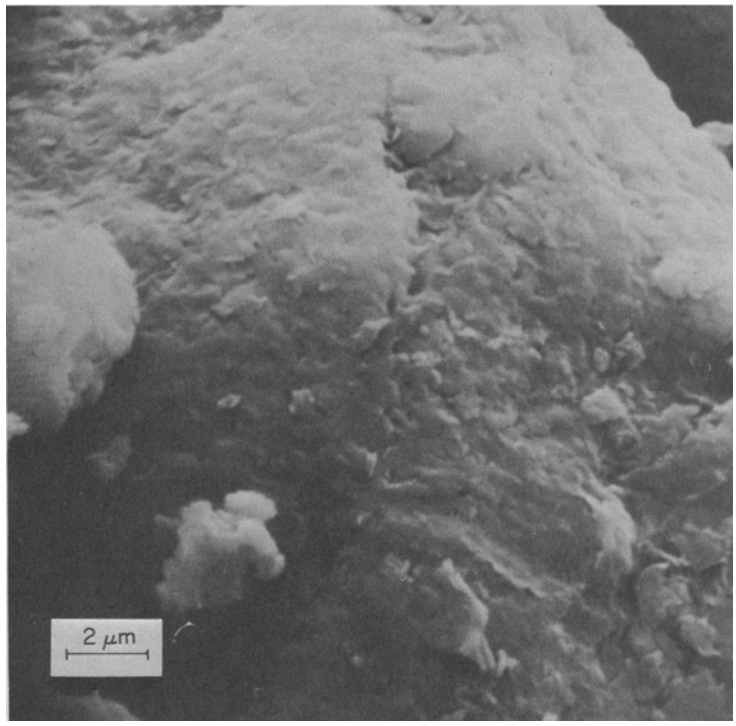


Fig. 4(d). High magnification SEM photograph of Cs-saturated smectite. Surface of granular aggregate from Fig. 4(c). Face–face orientation of individual crystallites, similar to that in Fig. 4(b).

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seeing the ultimate structure in these micrographs). Regardless of cation size, the platelets exhibit the same face-to-face arrangements, and the same order of surface roughness. Thus, on the micro-scale where molecular adsorption really takes place, there seems to be no evidence for any appreciable surface area generated by mechanical stacking differences between small and large cation-substituted smectites.

CONCLUSIONS

Although some investigators hold the view that the low-temperature adsorption of CO_2 occurs only in the pores between clay tactoids, the evidence presented in this study clearly shows that CO_2 at about $-70°C$ penetrates (intercalates) the smectite structure to a degree dependent upon the nature of the replaceable interlayer cation. This result substantiates conclusions reached in an earlier study (Thomas and Bohor, 1968) in which CO_2 was used as the adsorbate for surface area measurements. The wide range of surface areas that are obtained for various homoionic smectites thus are due mainly to the degree of intercalation of the gas molecules rather than to aggregation differences of the clay particulate structure.

Acknowledgements—It is particularly fitting that this study appears in the William F. Bradley commemorative issue. All of us were good friends of Bill's and we placed a high value on his counsel in scientific matters.

Thomas and Bohor often discussed with Bill the concept of penetration of nonpolar gases into the interlamellar space of montmorillonites (now smectites) during his annual summer tenures at the Illinois Geological Survey. Initially, he favored the classical belief that only external adsorption occurs with nonpolar gases. However, when he fully examined our experimental data—particularly the data from CO_2 adsorption—he agreed that our concept was 'a reasonable explanation of the experimental data', as he would have said in his own inimitable fashion.

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Résumé—L'adsorption à basse température ($\sim -70°C$) du CO_2 sur des films fins de smectites homoioniques a été étudiée par diffraction X et par absorption infrarouge. On a observé une augmentation des espacements d_{001} de ces films d'argile lors de l'adsorption du CO_2. De plus, un effet dichroïque est facilement discernable en comparant les spectres infrarouges pour deux orientations différentes des films de smectite, à savoir l'incidence normale et une incidence oblique pour laquelle le plan du film fait un angle de 35° avec le faisceau infrarouge. La vibration d'élongation du CO_2 à 2350 cm^{-1} a été utilisée lors de l'étude infrarouge. Ces observations montrent d'une façon concluante que le CO_2 s'intercale dans la structure de la smectite au lieu de s'adsorber seulement dans les pores existant entre les tactoïdes d'argile—ce que d'autres auteurs ont considéré comme un phénomène limitant.

Les clichés obtenus au microscope électronique à balayage pour les smectites Li- et Cs-fournissent une face sont réexaminées en appliquant l'equation de Dubinin. Ici à nouveau, on démontre l'intercalation en observant la convergence des données expérimentales recueillies pour les smectites contenant entre les feuillets de gros cations monovalents, avec la valeur d'un volume poreux qui est voisine de la valeur théorique calculée pour l'intercalation d'une monocouche de CO_2.

Les clichés obtenus au microscope électronique à balayage pour les smectites Li- et Cs-fournissent une preuve supplémentaire que les différences d'agrégation ne sont pas la cause des grandes différences observées lors de la mesure de la surface BET de ces argiles avec le CO_2 comme adsorbat. Aux faibles grossissements des différences visuelles dans les macro agrégats sont apparentes, mais aux forts grossissements aucune différence significative ne peut être observée dans la microstructure des agrégats individuels où la majeure partie de l'adsorption du gaz se passe réellement.

Kurzreferat—Die Adsorption von Kohlendioxid wurde bei geringen Temperaturen ($\sim -70°C$) an dünnen Filmen homoionischer Smectite durch Röntgenbeugung und Infrarotyabsorption untersucht. Ein Anstieg der d_{001}-Abstände dieser Tonfilme wurde als Folge der Adsorption von Kohlendioxid beobachtet.

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Zusätzlich war ein dichroischer Effekt leicht nachweisbar, wenn die bei zwei verschiedenen Orientierungen des Smectitfilmes erhaltenen Infrarotspektren—mit dem Film senkrecht und um 35° zum Infrarotstrahl gedreht—verglichen wurden. Für die Infrarotuntersuchung wurde die Kohlendioxid–Valenzschwingung bei 2350 cm^{-1} benutzt. Diese Beobachtungen zeigen schlüssig, daß das Kohlendioxid in die Smectitstruktur eindringt und nicht nur—wie es als begrenzender Vorgang von anderen Forschern vorgeschlagen wurde —in den Poren zwischen den Tontactoiden adsorbiert wird.

Adsorptionsisothermen von früheren Oberflächenuntersuchungen wurden unter Anwendung der Dubinin-Gleichung nachgeprüft. Wiederum wurde Intercalation dadurch nachgewiesen, daß die für große einwertige Kationen enthaltende Smectite aufgetragenen experimentellen Daten mit einem Porenvolumen zusammenfallen, das nahe dem für eine Einzelschicht von intercaliertem Kohlendioxid berechneten theoretischen Wert liegt.

Rasterelektronenmikroskopische Aufnahmen von Li- und Cs–Smectiten vermitteln weiteres Beweismaterial dafür, daß Unterschiede in der Aggregierung nicht für die großen beobachteten Unterschiede in den BET-Oberflächen verantwortlich sind, die für diese Smectite mit Kohlendioxid als Adsorbat erhalten werden. Bei geringer Vergrößerung sind sichtbare Unterschiede in den Makroaggregaten deutlich. Bei starker Vergrößerung werden jedoch keine bedeutenden Unterschiede in der Mikrostruktur einzelner Aggregate beobachtet, wo der größere Anteil der Gasadsorption tatsächlich abläuft.

Резюме — ИК-спектрами поглощения и рентгенографическим исследованием изучалась адсорбция двуокиси углерода при низкой температуре (−70°C) на тонких пленках гомоионных смектитов. При адсорбции двуокиси углерода наблюдалось увеличение расстояния d_{001} этих глинистых пленок. Кроме того, сравнивая ИК-спектр при двух различных ориентациях, т. е. при нормальном положении пленки и при наклоне на 35° по отношению к ИК-лучу ясно замечается дихроизм смектитовых пленок. Для инфракрасного исследования использовалось колебательное растяжение двуокиси углерода при 2350 $см^{-1}$. Эти наблюдения окончательно доказывают, что двуокись углерода включается в структуру смектита, а не адсорбируется на порах или на такдойдах глины, — ограниченный процесс, предполагаемый другими исследователями.

Повторно рассматриваются данные об изотерме адсорбции путем применения уравнения Дубинина, и снова демонстрируется включаемость двуокиси углерода.

Сканирование электронных микрографов Li- и Cs-смектитов представляют добавочные показания, что разница соединения частей не отвечает за замеченную чрезвычайную разницу в площадях поверхности BET, полученных для этих смектитов с двуокисью водорода в качестве адсорбированного вещества. При небольшом увеличении, видимы разницы в макросоединении частей, но при большом увеличении, заметной разницы в макроструктуре индивидуальных агрегатов, там где действительно происходит главная адсорбция газа, не наблюдается.

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