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FREEZE-DRIED AND THAWED CLAYS

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Abstract—Heating montmorillonites to their dehydroxylation temperatures destroyed their ability to form an aerogel. The breakdown of the aerogel structure coincided with the loss of hydroxyl water from the montmorillonite. Apparently, this loss of water was accompanied by a loss of the layer charge. Particle size and aerogel-forming ability appear to be inversely related properties for at least some montmorillonites. The kaolinite investigated did not form an aerogel in any size fraction. The formation of montmorillonite aerogels from various concentrations of clay was investigated. The texture and physical appearance of these aerogels was examined and presented herein.

Thawed clay suspensions exhibited a variety of behaviors. The Volclay bentonite, which apparently formed a true sol was unaffected by freezing. In all other clays at least some of the fine clay particles agglomerated on freezing and large clumps were observed dropping out of the melting ice. After stirring the thawed suspensions less clay was dispersed than in the unfrozen suspension counterparts. Addition of a dispersing agent to these suspensions caused more clay to remain dispersed following freezing–thawing–stirring.

INTRODUCTION

FREEZE-dried clays have been prepared by several investigators, e.g. Call, 1953; Ahlrichs and White, 1962; and van Olphen, 1967. Ahlrichs and White gave X-ray diffraction data for freeze-dried clays and provided some photomicrographs. Norrish and Rausell-Colom (1962) and Anderson and Hoekstra (1965) also investigated the X-ray diffraction characteristics of frozen and thawed clays.

We have investigated the effect of pre-heating and particle size of clay minerals with respect to their aerogel-forming ability in order to determine some of the factors that may influence the formation of an aerogel from a clay–water system. During the course of this investigation some phenomena were observed concerning the presence or absence of aerogels after freeze-drying clay sols and suspensions. In addition the agglomeration of clay particles upon thawing was observed for different clay species.

The terminology in this study referring to colloidal phenomena are taken from van Olphen (1963).

MATERIALS

The clay minerals investigated were a Wyoming bentonite (Volclay) obtained from the American Colloid Company, a montmorillonite from Otay, California and hectorite from Hector, California both obtained from Ward's Natural Science Establishment and a kaolinite obtained from the Edgar Minerals Corporation.

EXPERIMENTAL PROCEDURES

All clays were separated into three size fractions, -44μ, -2μ and $-0{\cdot}2\mu$. The -44μ fraction was obtained by dry screening, the -2μ fraction was obtained by settling in distilled-demineralized water and the $-0{\cdot}2\mu$ fraction was obtained by means of a supercentrifuge. The concentration of the clay suspensions was set at 0·25 wt. % clay for all size fractions (except where noted). The Otay and Hector samples required hand grinding prior to dispersal in water. No dispersing agent or other treatment was used to obtain any size fraction. Freeze-drying was performed on a VirTis apparatus.

Portions of the -44μ fraction of three clays (Volclay, Otay, and Edgar) were fired at 250°C, 450°C, 650°C, 850°C, and 1050°C for 12 hr. The heated powders were remixed with distilled water in a Waring blender to a 0·25 wt. % concentration and the suspensions sprayed into ultra cold pentane and freeze-dried by a method outlined by Lincoln, Miller and Tettenhorst (1970). Separate portions of the three size fractions of each clay were also prepared and freeze-dried in this manner.

A method was used to determine apparent density which gave consistent relative data but did not guarantee absolute results. A given volume of sample was weighed in either a graduated cylin-

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der or a calibrated glass tube. The samples were loaded with a spatula and tapped down against a table to provide the proper volume. An average value of apparent density was determined from three measurements on each sample (Tables 1 and 2).

Table 1. Apparent densities of freeze-dried Volclay montmorillonite, Otay montmorillonite and Edgar kaolinite after firing at different temperatures. Particle size was $< 44\mu$

Temp. (°C)	Apparent density in gm/cm³ Volclay	Otay	Edgar
N.H.*	0·006	0·037	0·115
250	0·005	0·039	0·101
450	0·006	0·082	0·118
650	0·287	0·253	0·135
850	0·334	0·405	0·146
1050	0·319	0·425	0·206

*N.H. refers to non-heated portions of each clay.

Table 2. Apparent densities of freeze-dried Volclay montmorillonite. Otay montmorillonite and Edgar kaolinite for different particle sizes

(μ)	Apparent density in gm/cm² Volclay	Otay	Edgar
< 44	0·006	0·037	0·115
$< 2·0$	0·004	0·020	0·032
$< 0·2$	0·003	0·004	0·014

FREEZE-DRIED CLAYS

Volclay and Otay montmorillonites and Edgar kaolinite samples were freeze-dried under various conditions of temperature and particle size. In addition Volclay was freeze-dried in beakers at different concentrations and the resulting aerogels described.

Heating

Apparent density determinations were made on the freeze-dried clays to provide some measure of their aerogelforming ability prior to heating and after heating to successively higher temperatures. All of the Otay montmorillonite and Edgar kaolinite freeze-dried samples crumbled to a powder upon sublimation and gave relatively high apparent densities (Table 1). The increase in apparent densities of the samples heated to relatively high temperatures probably reflects their inability to be dispersed following heat treatment (Table 1). An aerogel structure formed in the non-heated Volclay montmorillonite and those Volclay samples heated to low temperatures. Loss of aerogel-forming ability appears to occur with a loss of structural water, i.e. upon dehydroxylation.

Particle size

Particle size seemed to be related to aerogel-forming ability of the montmorillonites studied and the apparent density of Otay montmorillonite and Edgar kaolinite (Table 2). The apparent density of the normally non-aerogel-forming Otay montmorillonite decreased with a decrease in particle size. The $-0·2\mu$ fraction formed a fluffy structure that resembled loosely packed snowflakes very similar to the Volclay montmorillonite. No volume loss was observed in the $-0·2\mu$ freeze-dried fraction of Otay. The -2μ Otay sample formed a granular mass whose character seemed intermediate between the high density non-aerogel powders and the low density fluffy aerogels. The -2μ Volclay and Otay samples are pictured in Fig. 1 to show their appearance and relative volumes for a given weight of clay.

The apparent density of Edgar kaolinite also decreased with a decrease in particle size but the freeze-dried $-0·2\mu$ fraction could hardly be termed an aerogel since the volume loss on freeze-drying was about 90 per cent. Volclay experienced a very small volume loss in the -44μ fraction and no volume loss in the two smaller fractions. The apparent density was little affected by the different size fractions.

In aqueous suspensions, gels form at lower concentrations with smaller particle sizes (van Olphen, 1967). This condition could likely be applied to aerogels also if the same type forces (net edge and face charges) produce the structure. It would appear then that Volclay has a greater percentage of small particles than does Otay due to the fact that Volclay forms an aerogel at all the three size fractions investigated and Otay at only the smallest. Roberson, Weir, and Woods (1968) have shown that only 10 per cent by weight of Volclay particles are greater than $1·0\mu$ equivalent spherical diameter. However, these data do not quantitatively consider the results of particle agglomeration.

Clay concentration

The effect of clay concentration on the resulting aerogel structure was investigated in a separate experiment. A one per cent suspension of Volclay montmorillonite whose particle size was -2μ was prepared and compared with a 0·25 per cent

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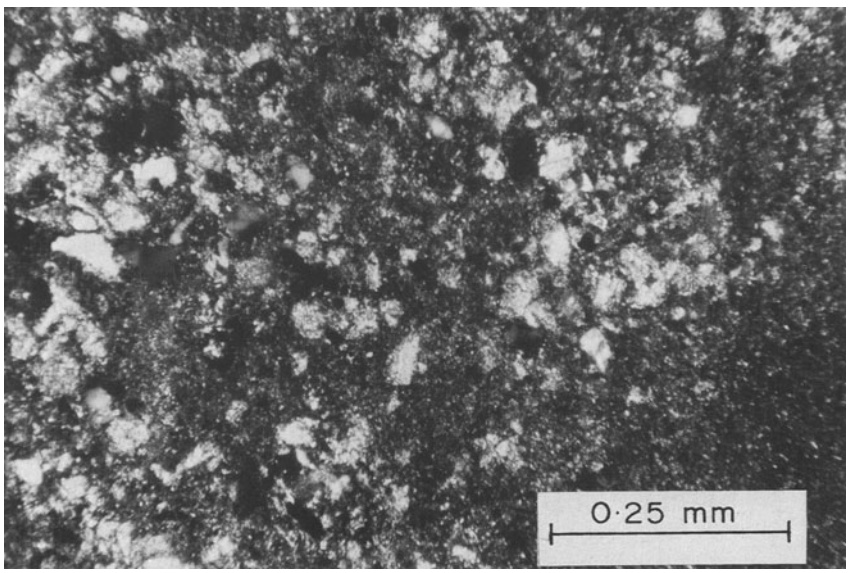


Fig. 1. Photomicrograph of thin section of shale No. 1, crossed polars. Lighest areas mainly represent highly birefringent calcite. Some quartz grains are clear, whereas others are dark at extinction positions. Approximately one-third of this rock section is calcite. Some opaque spots are partially oxidized pyrite.

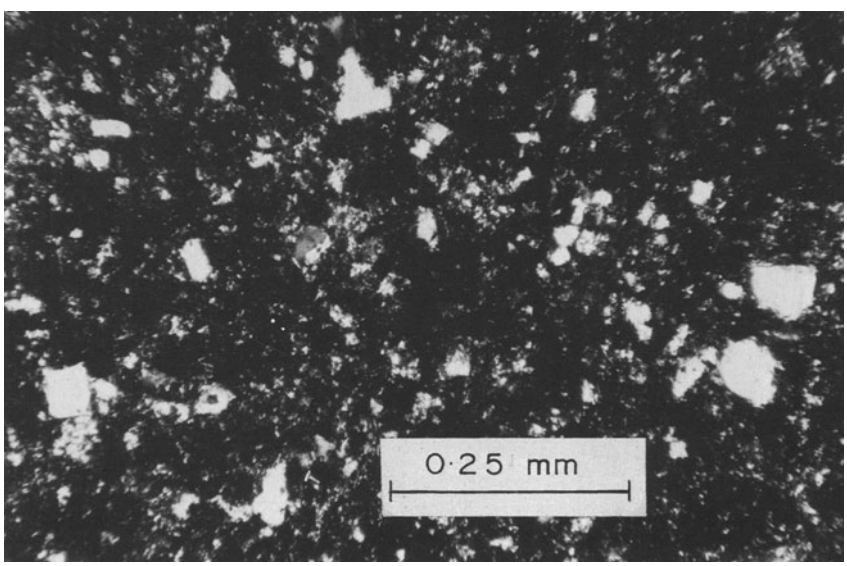


Fig. 2. Photomicrograph of thin section No. 2, crossed polars. Quartz silt shows as bright, birefringent spots. All birefringent calcite, as seen in No. 1, has been removed. The dark background represents dark iron-oxide, and low-birefringent clay mineral (kaolinite and illite). Bar length represents 0·25 mm.

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Volclay suspension having the same particle size. 200 ml of both samples were placed in a refrigerator freezer and subsequently placed in the freeze-drying unit. The one per cent clay sample formed an aerogel and maintained its original volume after freeze-drying. The 0·25 per cent clay sample formed a structure that resembled a spider's web which could not be termed an aerogel as it collapsed after freeze-drying because the framework was too delicate to support its own weight.

Van Olphen (1963) defines aerogel as a dry framework of solid material which retains some strength and maintains a constant volume after freeze-drying a hydrogel. Shrinkage and collapse of structure is prevented in an aerogel but this does not establish that the same structure existed in the hydrogel state (van Olphen, 1967). Sodium bentonite hydrogels are obtained at clay concentrations of about 2 per cent by weight or higher (van Olphen, 1967). The concentrations of clay in this study that formed aerogels were well below this figure. Thus, it seems likely from this study that aerogels can form from bentonite sols and suspensions as well as hydrogels. This would suggest that the absence of an aerogel upon freeze-drying was due to insufficient or no layer charges present on the clay.

Aerogel texture

The aerogel formed from the one per cent suspension appeared as a fibrous mass (Fig. 2); this feature had previously been noted and photographed by Ahlrichs and White (1962). An irregularly lineate structure was observed on the top of the clay–ice mass after freezing but before subliming, which indicated the fibers were formed upon freezing. The fibers were irregular and flat and resembled loose whitish chrysotile. The length of the fibers was determined by the depth of the suspension when frozen as the majority of the fibers formed perpendicular to the surface of the suspension. Fibers as large as $1\frac{1}{2}$ in. in length were observed. A quickly frozen sample seemed to form thinner and more perfect fibers than a slowly frozen sample.

Electron micrographs were taken of a fiber obtained from the 1 per cent suspension (Lincoln, 1969). The pictures were similar to those shown by Jonas and Oliver (1967) for spray-dried montmorillonite. An electron diffraction pattern of 25 square μ area taken with the electron beam perpendicular to the flat surface of the fiber showed the presence of diffraction rings all of which were indexed as *hk* reflections. These data suggested that the clay particles were oriented with their basal planes parallel to the flat fiber surface but randomly around an axis perpendicular to the flat fiber surface. In contrast to the aerogel flakes, X-ray diffraction patterns (Lincoln, Miller and Tettenhorst, 1970) indicated that spray-frozen, freeze-dried Volclay and Otay particles approached a random arrangement in all directions.

FREEZE-THAWED CLAYS

Some observations were made on the behavior of clay suspensions that were allowed to thaw at room temperatures following freezing. These experiments were performed for the most part on the -2μ fractions of suspensions that contained less than one percent by weight of clay. The clays investigated were Volclay and Otay montmorillonites, Edgar kaolinite, and hectorite. 200 ml of the clay suspensions were frozen in glass beakers in a refrigerator freezer. All clays but the Volclay montmorillonite occupied the central portion of the clay–ice mass upon freezing; clay-free clear ice was observed on the bottom and the sides of the beakers. Apparently the first water to freeze expelled all clay particles except those of Volclay, which were distributed throughout the frozen volume.

Upon thawing all of the clays except the Volclay montmorillonite came out of the thawing ice mass in clumps. The aggregation of the fine clay particles caused the clay to settle immediately upon being released from the ice. After the ice had completely melted the hectorite and Otay clays were on the beaker bottom, while some of the Edgar kaolinite remained in suspension. The aggregation of the clay particles into clumps probably occurred on freezing.

The Volclay montmorillonite apparently formed a true sol prior to freezing. This material did not come out of the ice in clumps but formed an apparent gel on thawing with the clay occupying $\frac{1}{2}$–$\frac{3}{4}$ the original suspension volume. The clay was easily returned to its original sol state by gentle swirling. Refreezing and thawing the Volclay sol several times caused no apparent change in state. Additions of sodium metaphosphate also caused no change in the behavior of the Volclay sample.

Gentle stirring of the thawed suspensions of Edgar kaolinite, Otay montmorillonite, and hectorite caused more of each of these clays to be dispersed when observed 24 hr after stirring. The stirred kaolinite suspension was nearly identical to the original unfrozen suspension; only a slight aggregation of particles had actually occurred on freezing. The stirred hectorite suspension showed no visible particles but the entire clay occupied a volume smaller than the original with clear water above, it had a fleecy appearance and acted as a gel. The stirred Otay montmorillonite suspension showed that a considerable amount of clay had

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fallen to the bottom of the beaker, which indicated that freezing had caused considerable agglomeration of clay particles. Pretreatment of the Otay, Edgar, and hectorite clay suspensions with sodium metaphosphate caused more clay to remain dispersed following the freezing, thawing and stirring cycle compared with the suspensions not treated with the dispersing agent.

Geologic implications

The settling characteristics of clays subject to thawing from a frozen ice–clay mass have some geological implications because freezing of clay–water systems is common in nature. Fresh-water bodies invariably contain clay in suspension. In appropriate climates part of the clay could experience a freezing-thawing cycle. The resulting effects of the settling of clays may exert an important influence on clay deposits such as varves and also affect the water chemistry. This condition would result in rapid deposition of clay during the spring thaw if sufficient quantities of clay were contained in the ice.

Glaciers contain clay and rock material of all sizes. The aggregation of clay particles may influence deposition of material escaping at the melting face. Soils are also affected by periodic freezing and thawing, however, the concentration of clay compared to water in soils is much higher than the dilute systems in this study. However, it is still possible for a change in particle size and/or the colloidal properties of the clay fraction of a soil after a freeze-thaw cycle.

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Résumé – Le chauffage des montmorillonites jusqu'à leur température de déshydroxylation détruit leur aptitude à former un aérogel. L'effondrement de la structure aérogel coïncide avec la perte de l'eau de constitution de la montmorillonite. Apparemment, cette perte d'eau s'accompagne de la disparition de la charge du feuillet. La taille des particules et l'aptitude à former un aérogel apparaissent comme des propriétés variant en sens inverse, au moins pour certaines montmorillonites. La kaolinite étudiée ne forme pas d'aérogel, quelle que soit la fraction granulométrique. On a étudié la formation d'aérogels de montmorillonite à partir de différentes concentrations en argile. La texture et l'aspect physique de ces aérogels ont été examinés, et sont présentés ci-dessous.

Les suspensions d'argile qui ont dégelé présentent toute une gamme de comportements différents. La bentonite Volclay, qui formait apparemment un sol vrai, n'est pas affectée par la congélation. Dans toutes les autres argiles, au moins certaines particules d'argile fine se sont agglomérées lors de la congélation et on a observé de gros flocons tombant de la glace en train de fondre. Après agitation des suspensions dégelées, moins d'argile s'est dispersée que dans les témoins constitués par la suspension non congelée. L'addition d'un agent de dispersion à ces suspensions a entraîné le maintien à l'état dispersé d'une plus grande quantité d'argile après le cycle, congélation–réchauffement–agitation.

Kurzreferat – Die Erwärmung von Montmorilloniten auf ihre Dehydroxylierungstemperatur zerstörte ihre Fähigkeit zur Formung eines Aerogels. Der Zusammenbruch des Aerogelgefüges erfolgte gleichzeitig mit dem Verlust an Hydroxylwasser aus dem Montmorillonit. Dieser Verlust an Wasser war scheinbar begleitet von einem Verlust an Schichtenladung. Es scheint, dass zum mindesten für geweisse Montmorillonite die Teilchengrösse und die Fähigkeit zur Bildung eines Aerogels umgekehrt zu einander proportional sind. Der zur Untersuchung gelangende Kaolinit bindete kein Aerogel und zwar in keiner Grössenfraktion. Die Bildung von Montmorillonit Aerogelen aus verschiedenen Tonkonzentrationen wurde untersucht. Das Gefüge und die äusserliche Beschaffenheit dieser Aerogele wurde untersucht und wird hier dargelegt.

Aufgetaute Tonsuspensionen verhielten sich auf verschiedenartige Weise. Der Volclay Bentonit, der scheinbar einen echten Sol bildete, wurde durch das Erkalten nicht beeinflusst. Bei allen anderen

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Tonen ballte sich zum mindesten ein Teil der feinen Tonteilchen beim Erstarren zusammen und es konnte das Herausfallen von grösseren Klumpen aus dem schmelzendem Eis beobachtet werden. Nach dem Umrühren der aufgetauten Suspensionen war weniger Ton darin dispergiert als in den entsprechenden nicht-gefrorenen Suspensionen. Ein Zusatz eines Dispergierungsmittels zu diesen Suspensionen verursachte mehr Ton nach dem Kühl-Auftau-Rührvorgang in Dispersion zu verbleiben.

Резюме — Монтмориллониты, нагретые до температуры дегидроксилации, теряют способность к образованию аэрогелей. Нарушение структуры аэрогеля совпадает с потерей гидроксильной воды монтмориллонитом. Очевидно, потеря воды сопровождается потерей заряда слоями. Размеры частиц и способность к образованию аэрогелей представляются свойствами, связанными обратной зависимостью, по крайней мере, для некоторых монтмориллонитов. Изученные каолиниты не образовывали аэрогелей ни при каких размерах частиц. Исследовалось также образование монтмориллонитовых аэрогелей при различных концентрациях глин, их текстура и физические свойства; результаты изложены в настоящей статье.

Оттаявшие глинистые суспензии обнаруживают разнообразные свойства. Бентониты вулканических глин, которые, очевидно, образуют нестоящий золь, нечувствительны к замораживанию. В других глинах по крайней мере некоторая часть частиц тонких фракций агломерируется при замораживании с образованием крупных сгустком, исчезающих по мере таяния льда. После размешивания оттаявшей суспензии наблюдалось меньше диспергированной глины, чем в не подвергнутой замораживанию суспензии. Добавление диспергирующих добавок повышало количество глины, остающейся в диспергированном состоянии после замораживания, оттаивания и размешивания.

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