

Specific Surface Determination of Expansible Layer Silicates

Abstract. The vacuum-oven technique for quantitative sorption of a glycerol duo-interlayer by montmorillonite at 35°C is adapted to 130°C to obtain a mono-interlayer of glycerol, glycerol vapor relative pressure being controlled by temperature differential. Values obtained for montmorillonite agree closely with theoretical values based on liquid glycerol density, while vermiculite retains a mono-interlayer of somewhat less than liquid glycerol density.

The determination of specific surface area of expansible layer silicate clays has been under study for several years, as reviewed (1) in presentation of a method whereby montmorillonite and vermiculite could be differentiated by means of specific surface determinations. Montmorillonite sorbed glycerol as a duo-interlayer (one layer on *each* surface) in a vacuum oven at 35°C. X-ray evidence for sorption of a duo-interlayer by montmorillonite had been presented earlier (2). Maintenance of the proper relative vapor pressure deficit, $1-(P/P_0)$, at the sample surface is of primary importance in a glycerol sorption method for specific surface. In the analogous ethylene glycol specific surface method, a relative pressure of less than unity was obtained by use of a CaCl_2 absorbant (3) and later by use of an ethylene glycol-bentonite mixture (4). The assumptions required and problems which remain unsolved in the ethylene glycol method were discussed (4).

Problems have been encountered in consistently maintaining proper equilibrium conditions for a mono-interlayer of glycerol in montmorillonite and vermiculite in an air oven at 110°C (5) even as modified (6). The new procedure presented herein employs the vacuum oven (1), but at an increased temperature and with a systematic control of less-than-unity relative vapor pressure (P/P_0) of glycerol at the sample surface (Fig. 1) by differential temperature between the free glycerol surface (100°C) having vapor pressure P and the sample (130°C) where free glycerol would have vapor pressure P_0 . From published (7) glycerol vapor pressure values P/P_0 is calculated (0.27 mm/1.24 mm) to be approximately 0.2 at the sample temperature.

In approaching equilibrium, the excess free glycerol vaporizes from the sample surface (Fig. 1) in the "warmer" region which has an unsaturated atmosphere because the glycerol vapor

Table 1. Glycerol retention by montmorillonite and vermiculite in a vacuum oven at 110°C.

Sample	Size fraction (μ)	Glycerol retained		Planar surface (m ² /g)	Expansible layer silicates (%)
		Total (%)	Ext* (%)		
<i>Montmorillonite (Wyoming bentonite) with no NaOH treatment</i>					
a	2 to 0.2	20.0	0.2	759	94
b	2 to 0.2	20.5	0.2	778	97
c	2 to 0.2	20.0	0.2	759	94
d	2 to 0.2	20.2	0.2	767	95
e	2 to 0.2	19.8	0.2	752	93
f	2 to 0.2	19.8	0.2	752	93
g	2 to 0.2	19.9	0.2	756	94
<i>Montmorillonite (Wyoming bentonite) with NaOH treatment (8)</i>					
a	0.2 to 0.08	22.4	1.5	823	102
b	0.2 to 0.08	21.8	1.5	799	99
c	—0.08	23.4	4.4	796	98
d	—0.08	23.2	4.4	788	97
<i>Vermiculite (source unknown) with no NaOH treatment</i>					
a	2 to 0.2	14.3	0.2	542	71
b	2 to 0.2	14.5	0.2	553	73
c	2 to 0.2	14.6	0.2	557	74
d	2 to 0.2	14.2	0.2	541	71
Average					72
Percentage of expected† expansible					84

* External edge sorption calculated (9); deducted from total to get net planar basis. † Sample contains 1.6 percent K_2O , equivalent to 16 percent mica (6), giving 84 percent expected expansible. Any (small amounts of) chlorite present would correspondingly lower this "percentage of expected" figure.

moves away by simple diffusion and subsequently condenses at the free glycerol surface at the "cooler" oven door (Fig. 1). At equilibrium, the only free glycerol surface is located in the "cooler" (door) region. Here the atmosphere is saturated with glycerol vapor at glycerol vapor pressure (P), which prevails throughout the oven atmosphere. The glycerol adsorbed on the clay sample at 130°C, has had its vapor pressure (P_0) lowered by adsorption so that $P_e = P$.

The development of the desired relative vapor pressure is dependent on differential temperatures which are obtained by balance of oven insulation and heat conduction by the metal parts, but which also could be achieved by heating elements and thermostatic controls in different areas of the vacuum oven.

Use of a vacuum oven (<1 mm-Hg) for the mono-interlayer equilibration is advantageous (i) because the relative vapor pressure conditions required for

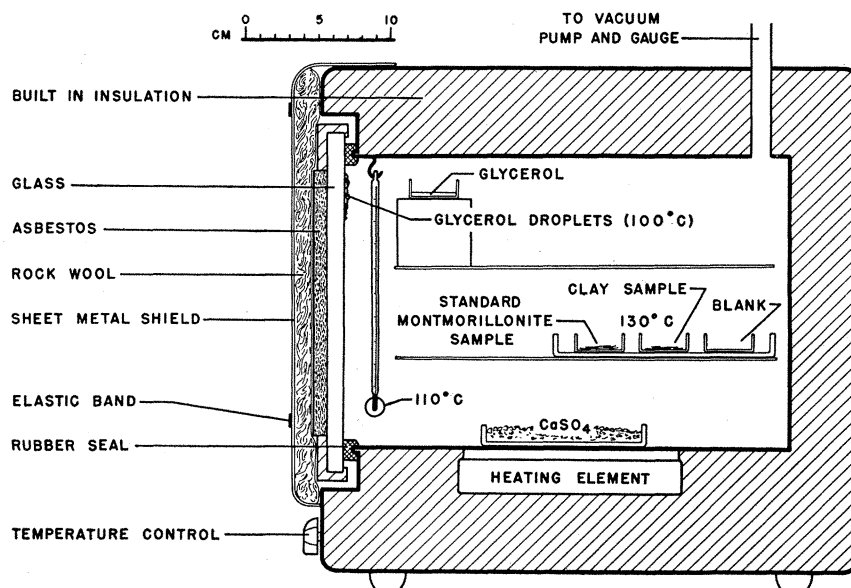


Fig. 1. Cross section of the vacuum oven for obtaining relative glycerol vapor pressure (P/P_0) at less than unity in the atmosphere around the samples through a temperature differential. The temperatures in the different portions of the oven were determined by differential thermocouple measurements.

the desired equilibrium state are more easily controlled in the closed system and (ii) because faster vapor diffusion and uncovered dishes allow the equilibrium state to be reached more rapidly than in the air oven (5, 6).

The medium- and fine-clay fractions are given a NaOH treatment (8) for the removal of amorphous and poorly crystalline materials (1). The sample is then boiled in a NaOAc buffer at pH 5 and magnesium-saturated by MgCl_2 and $\text{Mg}(\text{OAc})_2$ washings (9, pp. 183-4). Magnesium saturation was adopted because hydrogen saturation (1, 6, 9) liberates aluminum from the clay and apparently causes polymerization of the glycerol molecules in the montmorillonite interlayer positions when the clay is subjected to a high temperature in an evacuated atmosphere. Also, magnesium-saturated samples are commonly used for identification of layer silicates by x-ray diffraction (9).

The aluminum dishes, of heavy duty foil shaped over a square bottle (1.25 inches on a side), are passivated by half filling with distilled water and evaporating it prior to addition of the sample. An empty aluminum dish (weighing blank) and a standard montmorillonite sample are run with each group of 8 to 14 clay samples, all of which are placed in a large aluminum tray. Periodically, a dish of glycerol is placed in the oven to maintain the droplets on the glass in the door (Fig. 1); however, the dish is not left in the oven longer than necessary (usually 3 or 4 hours). A dish of CaSO_4 desiccant is kept on the oven floor to provide an absorbant for any water vapor in the oven. Samples reach equilibrium in 24 to 48 hours and are weighed at 8- to 12-hour intervals after 24 hours until constant weight is reached. Weighings are made promptly after the dishes are removed from the oven, and, where possible, in an atmosphere of less than 40-percent relative humidity. Calculations, including those for external edge surface, are made according to the published procedure (1; 9, pp. 331-341).

Under the conditions of the proposed method, montmorillonite sorbed a mono-interlayer of glycerol having liquid glycerol density, thus providing quantitative specific surface analysis (Table 1). The 2- to $0.2\text{-}\mu$ fraction contained 5 percent illite based on the K_2O content (6) and a trace of quartz as determined by x-ray diffraction analysis. Vermiculite apparently adsorbed

a mono-interlayer of somewhat less than liquid glycerol density. The only impurity detected in the vermiculite was illite (16 percent); therefore, the surface results appear low (10).

M. H. MILFORD
M. L. JACKSON

Department of Soils,
University of Wisconsin, Madison

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Devonian Plants from the Type Section of the Ghost River Formation of Western Alberta

Abstract. Plant fossils, including branched axes, foliar structures, fructifications, and dispersed spores have recently been discovered from the type section of the Ghost River formation. The megafossils, although commonly fragmentary, suggest a late Middle or early Upper Devonian age for the beds. This discovery suggests that equivalent strata in other regions may also contain plant remains, the discovery of which would add significantly to our knowledge of Devonian floras in western North America.

Compressions of vascular plants, including isolated sporangia, sporangiferous branches similar to *Svalbardia* (Protopteridiales), laminae superficially resembling *Platyphyllum* (affinities unknown), and branched and unbranched axes containing scalariform tracheids, have recently been discovered in the type section of the Ghost River formation. Triradiate spores with an observed size range of 30 to $98\text{ }\mu$ have also been found in specimens of shaly dolomite, and include species of *Leio-triletes*, *Punctatisporites*, *Ambitisporites*, and *Retusotriletes*. This discovery is the first record of plants from the

Ghost River formation, and is also the only record of Devonian plant megafossils from western Canada south of the Yukon Territory.

The type section of the Ghost River formation is located in the Front Range of the Rocky Mountains, on the west side of the north branch of the Ghost River, a few miles north of Lake Minnewanka. The locality was designated by Walcott (1) as follows: "The type locality is about 51 miles west 20°N of Calgary, Alberta, Canada, in the first small canyon south of Ghost River canyon and opening on the Ghost River as the river bends south."

Walcott (1, 2) originally assigned 285 feet of red and green shales, and buff-weathering dolomites, to the Ghost River formation, believing that these rocks constituted a completely new formation representing an interval from Middle Cambrian to Devonian. However, this series is very similar to the underlying Arctomys formation of Cambrian age, and field geologists have long been confused as to the age of the Ghost River formation and its stratigraphic relationships to surrounding Cambrian and Devonian strata (3).

Field investigations of 1959 and 1960 revealed that the Ghost River formation, as defined by Walcott, is split by an unconformity rather than bounded above and below by unconformities. This intraformational unconformity has been recognized in two different sections that were measured in the cirque draining into Walcott's "first small canyon south of the Ghost River canyon." The fossil plants were found in beds 25 to 30 feet above the unconformity, and suggest a late Middle or early Upper Devonian age for the upper series of rocks.

As a result of the discovery of the sub-Devonian unconformity and Devonian fossil plants, it is herein proposed that the Ghost River formation at its type locality be restricted to a thickness of 145 feet, consisting of an interbedded and variable sequence of red and green dolomitic shales, together with buff weathering, pale brown, and green-grey dolomites. The Ghost River formation rests unconformably on the Cambrian Arctomys formation, and interbeds above with the basal few feet of the overlying Fairholme group of Upper Devonian age. The overall thickness and approximate contacts are shown in Fig. 1a.