Research Report 218

PHASE COMPOSITION OF FROZEN MONTMORILLONITE-WATER MIXTURES FROM HEAT CAPACITY MEASUREMENTS

by

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PREFACE

This report was prepared by Dr. Duwayne Anderson, Head, Earth Sciences Group, Research Division (Mr. James A. Bender, Chief), U. S. Army Cold Regions Research and Engineering Laboratory.

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SUMMARY

Equations are written that form the basis of a method for determining the unfrozen water content of frozen clay-water mixtures from heat capacity measurements. The heat capacity of frozen sodium-montmorillonite water mixtures was determined at -4.7 and -9.6C with a Calvet Microcalorimeter. The data were then used in conjunction with the method described to obtain the unfrozen water content of these clay water mixtures. The data obtained indicate that the method is applicable at temperatures below about -5C. The amount of unfrozen water found in the frozen clay-water mixtures at -5 to -10C is equivalent to an interfacial surface layer of water of from one to two molecular diameters in thickness. Most of this water can be accommodated and is thought to be located in interlamellar regions.

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INTRODUCTION

It is well established that frozen clay-water mixtures contain a significant quantity of water that does not undergo an abrupt change in phase when the mixture is frozen or thawed; this water is commonly referred to as "unfrozen water." The amount and properties of the unfrozen water in frozen soil materials have been the topics of many investigations. It has been established that many factors are involved, but for a given soil material the amount of unfrozen water present is known to depend principally upon temperature and to a lesser extent upon pressure; except for very low water contents, it is virtually independent of the total water content. At a given temperature and pressure, the principal factors governing the unfrozen water content are the specific surface area of the soil, its chemical and mineralogical character, the number and kind of the exchangeable ions, and the species and concentrations of soluble substances present (Nersesova and Tsytovich, 1963). The liquid-like behavior of the unfrozen water has been inferred from the fact that transfer of water in frozen, water-saturated soil can be readily accomplished by the imposition of electrical or thermal gradients (Khakhimov, 1957; Nersesova and Tsytovich, 1963); the occurrence of electroosmosis in frozen soil recently was verified by Hoekstra and Chamberlain (1964).

Determinations of the amount of unfrozen water in frozen soil have been accomplished by: the dilatometer method (Buehrer and Aldrich, 1946); the calorimetric method (Nersesova and Tsytovich, 1963; Kolaian and Low, 1963); and an X-ray diffraction method (Anderson and Hoekstra, 1965). Although all three methods unquestionably establish the existence of substantial amounts of unfrozen water, they do not indicate the same quantity of unfrozen water in similar samples at a given temperature and pressure. Because the clay-adsorbed water has a density less than that of pure water in bulk (Anderson and Low, 1958), the dilatometer method yields values for the quantity of unfrozen water that probably are too high. Likewise, because the computations require the assumption that the specific heat and the latent heat of freezing the clay-adsorbed water are the same as for pure water in bulk, the calorimetric method as usually employed yields values that probably are too high (Martynov, 1956; Anderson, 1963). The X-ray diffraction method is applicable only to mixtures with water of 2:1 expanding lattice clay minerals. Because the method cannot account for the possible existence of unfrozen water located outside the interlamellar space, it may underestimate the unfrozen water content. In general, it is found that unfrozen water contents for similar samples obtained by the three methods show deviations in accord with expectation; the higher values result from the dilatometer and calorimeter methods and lower values result from the X-ray diffraction method.

This paper contains the results of heat capacity measurements made on frozen Wyoming bentonite-water mixtures previously studied by the X-ray diffraction method. It will be shown that the unfrozen water content of frozen mixtures of water and soil materials can be estimated from a determination of the heat capacity of the frozen mixtures as a function of total water content. For sodium-montmorillonite, the results derived from heat capacity measurements are consistent with the unfrozen water contents obtained by the X-ray method.

THEORY

A frozen clay-water mixture may be regarded as a two component system consisting of three phases viz., ice, unfrozen water and the clay particle matrix. Although the distinction is not actually necessary, the exchangeable ions will be regarded as belonging to the clay. The heat capacity of the system can be expressed as a sum of the heat capacities of the three phases plus an additional term accounting for the latent heat effect corresponding to the specified temperature change. Thus, immediately one can write

$$Q = [(C_c M_c) + (C_i M_i) + (C_u M_u)] \Delta T + \int_{T_1}^{T_2} L \left(\frac{\partial M_u}{\partial T} \right) dT. \quad (1)$$

In eq 1, Q is the heat capacity per g of mixture over the temperature interval ΔT ; C_c , C_i , and C_u are the partial specific heat capacities of the clay, ice and unfrozen water, respectively; M_c , M_i , and M_u are the weight fractions of the three phases, clay, ice and unfrozen water, respectively; and L represents the latent heat of phase change of the unfrozen water. The last term accounts for the heat involved in the possible changes in relative amounts of ice and unfrozen water that accompany the temperature change, ΔT . Since the total weight of water present may be written

$$M_w = M_i + M_u \quad (2)$$

eq 1 may be combined with eq 2 yielding

$$Q = \left\{ C_i M_w + [C_c M_c + M_u (C_u - C_i)] \right\} \Delta T + \int_{T_1}^{T_2} L \left(\frac{\partial M_u}{\partial T} \right) dT. \quad (3)$$

Dividing through by ΔT and M_c yields

$$q = C_i W_w + [C_c + W_u (C_u - C_i)] + \frac{1}{\Delta T} \int_{T_1}^{T_2} L \left(\frac{\partial W_u}{\partial T} \right) dT \quad (4)$$

in which q is the heat capacity of the mixture per degree per unit weight of clay, W_w is the total water content and W_u is the unfrozen water content of the frozen mixture. Equation 4 is arranged to facilitate a discussion of the conditions under which the specific heat capacity of a frozen clay-water mixture may be linearly dependent on its total water content; obviously, it will be linear provided that the terms in brackets together with the last term do not vary with water content.

The first term in the brackets, the partial specific heat of the clay, can to a good approximation be regarded as independent of water content and, therefore, constant. Nersesova and Tsytovich (1963) maintain that the unfrozen water content, W_u , is practically independent of the total water content; according to them, it depends principally on temperature. Then for a given temperature, W_u can be regarded as constant. Hence, the second term in brackets can be taken as constant if the difference between the partial specific heats of the ice and the unfrozen water does not change significantly with a change in water content. If the unfrozen water content itself does not vary with W_w it is unlikely that a change in W_w at constant temperature will cause a significant change in these two partial specific heats; therefore, the second term in brackets also may be taken as constant.

The last term in eq 4 represents the heat of phase change accompanying any change in the ratio of unfrozen water to ice due to the temperature fluctuation necessitated by the measurement itself. If the conditions of the measurement are kept invariant from sample to sample, the limits of integration, T_1 and T_2 , will be the same and ΔT must be constant. Finally, if it can be accepted that the amount of unfrozen water present is independent of the total water content and depends principally upon temperature then it may be accepted that the functional relationship between $(\frac{\partial W_u}{\partial T})$ and T and between L and T will, to a good approximation, be the same for each sample. Hence, it may be argued that the value of the last term in eq 4, to a good approximation, is independent of water content and may be regarded as constant. Thus it is established that as long as the foregoing assumptions are valid, a plot of the heat capacity (per unit weight of clay) of a frozen clay water mixture versus its total water content will yield a line having a slope equal to the partial specific heat capacity of the ice in the mixture and an intercept equal to the sum of the last two terms of eq 4. Moreover, it becomes apparent that the plot must depart from linearity when the water content decreases below the point at which the ice phase disappears, for at this point the amount of unfrozen water, W_u , no longer can be independent of water content.

Equation 4 then, offers a means of determining unfrozen water contents in frozen clay-water mixtures by determining the water content at which the ice phase disappears. This can be accomplished by determining the point at which plots of the heat capacity per g clay of frozen clay-water mixtures versus total water content depart from linearity. A check on the determination may be made by setting the extrapolated intercept equal to the sum of the last two terms in eq 4 and solving for W_u . The validity of this check, however, depends upon the validity of the values used in the computation; good estimates are possible but at present these values are not accurately known.

APPARATUS AND EXPERIMENTAL METHODS

One pair of a four cell, Calvet Microcalorimeter was utilized to obtain the ratio of the heat capacity of frozen Na-bentonite-water mixtures to that of mercury. Details of the construction and operation of the Calvet Calorimeter have been given by Calvet and Pratt (1963). A schematic diagram of the apparatus is shown in Figure 1. The instrument was operated in the differential mode to accomplish automatic compensation for minute variations in the internal jacket temperature of the calorimeter. About 2/3 of the active thermopile was utilized in the measurements; the other 1/3 was used to lower the sample temperature by means of the Peltier effect.

Sodium-saturated Wyoming bentonite was prepared by first suspending the raw clay in distilled water and allowing it to settle until particles larger than 1 micron (equivalent Stokes' law diameter) had settled out. The remaining suspension was then passed through a column of Amberlite IR-120 cation exchange resin that had previously been saturated with sodium ions. Care was taken to exclude small particles of resin in the effluent and the amount of clay passed through the column before regeneration was limited to 10% of the total exchange capacity of the column; the suspension was passed through the column drop by drop and subsequent analysis verified that exchange was nearly complete. The water content of the resulting homo-ionic bentonite suspensions was successively reduced in a pressure membrane apparatus. In this way, slurries and pastes of different water contents were prepared; these were then stored until needed in glass containers capped with Mylar film vapor barriers.

The heat capacity determinations proceeded as follows: A weighed sample of Na-bentonite having a known water content (checked by a gravimetric determination at the conclusion of the calorimetric measurement) was placed in a specially fitted stainless steel container and pressed into the sample receptacle of the calorimeter via the access tube. The temperature of the internal calorimeter jacket was

Figure 1. Schematic diagram of the Calvet Microcalorimeter showing the sample holder receptacle, A, and one of the thermopiles, B, that make up a microcalorimetric element. Two microcalorimetric elements are shown embedded in a massive aluminum block, C, capped by massive aluminum cones, D, shaped to optimize the equipartition of ambient thermal perturbations. The sensitivity of the apparatus is regulated by the switch, E, which taps all or a portion of each thermopile. The sample in a suitable container is placed in the sample holder receptacle through an access tube, F. The output of the thermopile is taken to a junction box, G. The interior of the calorimeter is thermostated and protected by several heat shields.

then fixed at a desired value. A DC current of exactly 2.50 ma was passed through 1/3 of the active thermopile in the proper direction to cool the sample cell by the Peltier effect. Cooling was continued until a steady emf was read at the output of the remaining portion of the active thermopile. This output was always found to be 190 ± 0.5 V, corresponding to a difference in temperature between the sample and the massive surrounding aluminum heat sink of about 0.01°C .

Here it may be helpful to explain that when the steady Peltier current was turned on, the cell containing the sample began to cool; cooling continued until a steady state of heat transfer prevailed. At the steady state it can be seen that: (a) the temperature must be everywhere uniform within the sample; (b) for a given, constant Peltier current (i.e., a given rate of heat transfer), the difference, θ , between the sample temperature and that of the massive aluminum heat sink must be the same regardless of the nature or amount of the cell contents; (c) on interruption of the Peltier current, a quantity of heat, Q , will be transferred from the heat sink back into the cell as the value of θ decreases monotonically to zero; (d) the quantity of heat transferred will depend upon the nature and amount of the sample and upon the properties of the sample container and the calorimeter cell. For the Calvet microcalorimeter employed, the dependence of Q on these factors was verified to be given by

$$Q_i = (a + m_i c_j) \theta \quad (5)$$

in which a is the calorimetric constant; m_i is the sample weight, and c_j is the specific heat capacity of the sample or a reference substance. Q_i is proportional to the area under the curve resulting from a plot of θ versus time. By repeating the experiment under identical conditions, but with a different weight of the same sample and finally with a sample of a reference substance for which the specific heat capacity is known, a set of equations of the form of equation 5 result from which a and θ may be eliminated, giving the specific heat capacity of the unknown in terms of that of the reference substance.

At the moment the Peltier current to the sample cell was interrupted, 2/3 of the thermopile was utilized in conjunction with a sensitive potentiometer to measure

θ as a function of time. When θ had decayed to zero ± 0.5 V the Peltier current was reinstated and the above procedure was repeated twice. In this way, three sets of θ versus time data for the same sample under identical conditions were obtained. Subsequently, the above procedure was followed using three different weights of reagent grade mercury. Thus the required set of equations was obtained with two degrees of redundancy. Values of Q were obtained from the numerical integration of the six sets of θ versus time data by means of a digital computer. These values were then used in conjunction with equation 5 to compute the specific heat capacity of the sample relative to that of mercury. The entire procedure was repeated at various temperatures and with samples of different water contents. As a check, the relative specific heat of aniline, crystalline and powdered ice was determined in the same way.

RESULTS AND DISCUSSION

Average values of the specific heat capacities of the frozen bentonite-water mixtures, with their respective standard deviations, and the heat capacity of mixtures containing one gram of clay calculated from these values are shown in Table I for sample temperatures of -4.7°C and -9.6°C (rounded to -5 and -10°C in the following discussion). * Table II is a comparison between handbook and observed values of the specific heat of aniline and ice at 0.3°C . It also contains the results of four separate determinations of the specific heat of the oven-dry clay. Figure 2 shows the data of Table I plotted according to eq 4.

Figure 2. Heat capacity of frozen bentonite water mixtures in calories per degree of a sample containing one gram of clay.

* Data taken at temperatures near the freezing point were not reproducible. This could have been due to evaporation-condensation phenomena occurring within the sample container, since at temperatures near 0° it was noticed at the end of the calorimetric measurements that small droplets of water were often found clinging to the walls at the top of the sample container. Another possibility arises from the fact that the last term in equation 4 becomes important at these temperatures. It could be that this contribution is not reproducible because of irreversibility over the small temperature increments employed. These data, therefore, are not reported. Meanwhile, further investigation is in progress and it is hoped that this question can be resolved.

PHASE COMPOSITION OF FROZEN CLAY-WATER MIXTURES

Table I. Heat capacity of frozen bentonite-water mixtures at -4.7 and -9.6C.

Temperature (°C)	Water content (gH ₂ O/g clay)	Specific heat of the mixture (cal/g-sample/deg)	Standard deviation	Heat capacity of the mixture containing one gram of clay (cal/g-clay/deg)
-4.7	0.500	0.523	0.018	0.785
	2.011	0.550	0.017	1.66
	2.922	0.545	0.017	2.14
	0.000	0.158	0.009	0.158
	0.443	0.409	0.010	0.592
-9.6	1.662	0.483	0.012	1.29
	1.888	0.519	0.016	1.50
	2.648	0.520	0.013	1.90

Table II. Specific heat of reference substances.

Substance	Temperature (°C)	Specific heat		Standard deviation
		Handbook values	Observed values	
Ice	-4.7	0.50	0.507 (solid)	0.016
	-4.7	0.50	0.482 (powder)	0.015
			0.49 Average	
Aniline	0.3	0.48	0.465	0.018
	0.3		0.490	0.019
	0.3		0.504	0.020
			0.48 Average	
Dry Bentonite	-9.6		0.158	0.009
	-2.3		0.170	0.013
	-2.2		0.169	0.013
	-2.2		0.160	0.014
			0.164 Average	

For water contents above about 0.5 g water per g clay the relationship between the heat capacity of the mixture per g of clay and the total water content was found to be linear. This indicates that the unfrozen water content is practically independent of the total water content, verifying the opinion of Nersesova and Tsytovich cited above. The slopes of the linear portions of the curves in Figure 2 were found to be about 0.58 cal per g water and the extrapolated intercepts of the linear portions were found to be about 0.30 and 0.46 cal/g clay/deg at -10 and -5C, respectively.

It has been shown that if a plot of the data is linear above a certain water content, an estimate of the unfrozen water content can be obtained by identifying the water content at which the curve departs from linearity. In Figure 2, the scarcity

of data in the region of low water content contributes to the difficulty of precisely locating the point at which the curves become non-linear. More data would be desirable, but as is evident from the description of the apparatus and methods, the determinations were exceedingly time-consuming; for this reason it became impractical to obtain more experimental points at the two temperatures shown. However, Figure 2 shows sufficient data to see that for either line the point is less than 0.5 g water per g clay. Reasonable values are 0.3 and 0.4 g water per g clay for -10 and -5°C, respectively. If the last term of eq 4 is neglected, the intercepts of Figure 2 should correspond to the term in brackets. Taking the difference in the partial specific heats of ice and of the unfrozen water as 0.5 cal/deg-g, and taking the specific heat of the clay as 0.164 cal/deg-g, the unfrozen water contents calculated from the intercepts are 0.59 and 0.27 g water per g clay at -5 and -10°C, respectively. Although these values may be slightly in error since they depend on the accuracy of the specific heats used in the calculation and upon the validity of neglecting the last term in eq 4, the error is not likely to be large. It has been shown recently that the ice in frozen bentonite is present in the form of normal hexagonal crystals (Anderson and Hoekstra, 1965); hence, as a first approximation the value of the specific heat of bulk ice can be used for the partial specific heat of ice in eq 4. Likewise, in view of the mobility of the unfrozen interfacial water in response to thermal and electrical gradients (Nersesova and Tsytovich, 1963; Hoekstra and Chamberlain, 1964), it is only reasonable in the temperature range of interest here to ascribe to it the properties of the liquid. Oster and Low (1964) determined the partial specific heat capacity of the surface-held, interfacial water in sodium-bentonite-water mixtures and showed that it ranged from about 1.0 cal/g-deg in the very wet state to 1.1 cal/g-deg in the nearly dry state. They explained the variation by reasoning that the increase in the partial specific heat capacity in the thinner surface water layers was due to the partial melting of structures in the liquid next to the clay surface. Now the unfrozen water in a frozen clay may be identified as the surface-held water that does not freeze and since the specific heat capacity of water is relatively insensitive to moderate changes in temperature and pressure, it is a safe assumption to take the partial specific heat capacity of the unfrozen water as approximately 1.0 cal/g-deg. Finally, it should be emphasized that the unfrozen water contents calculated from the intercepts in Figure 2 using this value are consistent with unfrozen water contents found from the point at which the heat capacity-water content relationship departs from linearity.

In a preceding report (Anderson and Hoekstra, 1965) it was noted that conflicting data on the quantity of unfrozen water in frozen sodium-bentonite-water mixtures appear in the literature. Determinations at -5 and -10°C by dilatometric and calorimetric methods have yielded values as high as 0.99 and 0.86 g water unfrozen per g clay, respectively (Kolaian and Low, 1963; Buehrer and Aldrich, 1946). If 0.99 g unfrozen water per g clay were present at -5°C one would expect in Figure 2 a line giving an extrapolated intercept of about 0.7 and the line would be expected to depart from linearity at a water content of 0.99; the data shown strongly argue against this. A similar calculation for an unfrozen water content of 0.86 at -10°C leads one to expect a line yielding an extrapolated intercept of 0.6 and showing curvature at a water content of 0.86; the data of Figure 2 clearly rule out this possibility.

The most complete unfrozen water content data presently available for a comparable sodium-bentonite are those of Nersesova and Tsytovich (1963) shown in Figure 3. The data were obtained by a calorimetric method, the details of which have not yet become available. Consequently, it is not possible to assess their method. Also shown in Figure 3 are the unfrozen, interlamellar water contents of frozen sodium-bentonite determined by the X-ray diffraction method (1965). Recalling that the X-ray diffraction method may under-estimate the total unfrozen water content and accepting the data of Nersesova and Tsytovich, one would conclude from Figure 3 that salt-free, frozen sodium-bentonite-water mixtures at temperatures ranging from -5 to -10°C contain from 0.4 to 0.3 g unfrozen water per g clay.

Figure 3. Total unfrozen water and unfrozen interlamellar water in sodium-bentonite.

values of the intercepts of Figure 2; and unfrozen water contents calculated from the intercepts by neglecting the possibility of a heat effect due to change of phase yield values consistent with those obtained by other methods. One notes, however, that the intercept obtained at -5°C is larger than that obtained at -10°C and the unfrozen water content calculated from the intercept at -5°C therefore is higher. This is partly explained by the fact that, as the interlamellar spacings and calorimetric data show, there really is more unfrozen water at -5°C than at -10°C . But according to the data of Figure 3, the value calculated from the intercept at -5°C (0.59 g unfrozen water per g clay) is somewhat high. Hence it is possible that at -5°C the last term in eq 4 is becoming significant and could amount to as much as 0.1 calorie.

The slopes of the lines drawn through the data of Figure 3 give $\frac{\partial W}{\partial T}$ and it is clear in any case that at temperatures above about -2°C the last term in eq 4 becomes dominant. The data of Williams (1964) illustrate this effect.

The slopes of the linear portions of the curves in Figure 2 are calculated to be about 0.58 cal/g. According to eq 4 the slope should correspond to the partial specific heat of the ice in the mixture. Table II shows that the discrepancy between handbook and observed values and the value obtained from the slopes of the curves in Figure 2 is about 0.09 cal/g. Although it is difficult to know exactly the error involved in evaluating slopes of the lines in Figure 2 it is possible that it may be as large as ± 0.1 cal/g. An error of this magnitude is not large enough to change the foregoing estimates of the unfrozen water contents substantially but would account for the discrepancy. A more plausible explanation, however, is that the ice formed in the sample contains impurities; it is known that the effect of impurities in ice is to increase its apparent specific heat and that this effect is sufficient to account for the discrepancy (Dorsey, 1940).

CONCLUSION

In conclusion, a method that permits the determination of unfrozen water contents of salt-free, frozen, soil- and clay-water mixtures from their heat capacity has been derived and the assumptions and restrictive conditions required in the

Thus the values determined from heat capacity data agree with those obtained by the X-ray diffraction method and are in rough agreement with the calorimetric values of Nersesova and Tsytoovich. The values derived from heat capacity data are also in accord with those found by Wu (1964) from the proton resonance line width of comparable frozen sodium-bentonite-water pastes.

Let us now return again to the question of the last term in eq 4. Arguments presented earlier have established that if the conditions of measurement are kept constant from sample to sample the last term becomes a constant. From eq 4 it can be seen that if this term is large enough to be significant its effect must be to augment the apparent heat capacity and hence to increase the extrapolated intercepts of Figure 2. Apparently, it did not constitute a large contribution to the apparent heat capacity judging from the

method have been discussed. The method was used successfully to estimate the unfrozen water contents of frozen sodium-bentonite pastes for comparison with values obtained by other methods. At -5 and -10°C the unfrozen water contents determined by this method are only slightly higher than the unfrozen, interlamellar water content determined on the same clay-water mixture by X-ray diffraction. The results also agree with the unfrozen water contents reported by Nersesova and Tsytoich (1963) and by Wu (1964) for comparable sodium bentonite clay-water mixtures. The data indicate that at -5 to -10°C the amount of unfrozen water present is equivalent to a surface-held layer of water only one or two molecular diameters in thickness, assuming that the water is uniformly distributed over the entire ($8 \times 10^6 \text{ cm}^2/\text{g}$) surface area of the clay. Most of this unfrozen water can be accommodated by, and is thought to be located in the interlamellar regions.

Although this method of determining unfrozen water contents is neither rapid nor easy, it is important because it offers an independent check of results obtained by the conventional dilatometric and calorimetric methods. Moreover, in writing the equations for the heat capacity of a frozen clay-water mixture, attention has been focused on the importance of studying the partial specific heat capacities of the three phases present and the last term of eq 4. It has been pointed out in a thermodynamic argument (Anderson, 1963) that L in eq 4 must vary with W_u but as yet data giving this relationship directly are lacking. Work on these and related topics is now in progress.

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13. ABSTRACT Equations are presented which form the basis of a method for determining the unfrozen water content of frozen clay-water mixtures from heat capacity measurements. The heat capacity of frozen sodium-montmorillonite water mixtures was determined at -4.7 and -9.6°C with a Calvet Microcalorimeter. The data were then used in conjunction with the method described to obtain the unfrozen water content of these clay water mixtures. The data obtained indicate that the method is applicable at temperatures below about -5°C. The amount of unfrozen water found in the frozen clay-water mixtures at -5 to -10°C is equivalent to an interfacial surface layer of water of from one to two molecular diameters in thickness. Most of this water can be accommodated and is thought to be located in interlamellar regions.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Soil solutions--Freezing Soil solutions--Phase transition Soils--Moisture content--Temperature factors Calorimeters Frozen ground--Unfrozen water content						

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