

Biology and Physics of Peloids.

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PELOIDS CONSIST OF humus and minerals formed over a very long period by physical, chemical, biologic, and geologic processes. They are used in treatment either in their natural state or after fermentation. They are applied as poultices or in the forms of baths. They are sometimes used internally. Of the many classification proposed, we shall discuss only the more important ones: humolites and muds. In humolites, organic matter, especially humus components, predominates.

The most important humolites are the high-moor and low-moor peats. In muds, minerals predominate. Although high-moor and low-moor peats may be quickly differentiated by their characteristics, they occasionally have properties that are so similar that an accurate differentiation becomes difficult. Often, we need to know the geographic origin of a specimen to classify it.

- High-moor peat bogs usually contain mosses (*Sphagnum*, *Hypnum*, *Drepanocladus*, *Camptothecium*, and *Cratoneuron*) and phanerogamae (*Spermatophyte*, *Eriophorum*, *Trichophorum*, *Vacciniaceae*, and *Scheuchzeria*).
- Low-moor peats contain *Phragmites*, *Carex*, *Equisetum palustre*, *Equisetum limosum*, and *Iris*. They may also contain the mosses of *Hypnum*, *Drepanocladus*, *Camptothecium*, and *Cratoneuron*.

The properties of peloids depend also on the humified material and the regional rock. Sometimes the horizontal layers of high- and low-moor peat alternate, indicating that there were great climatic variations during their formation. Where peloids occur naturally, the water and ground are usually rich in microvegetation as well as in macrovegetation. Even though most people consider the gross appearance of microbial colonies and algae as ugly dirt, not realizing their diverse and microscopic beauty, they represent the chief factor in the development of the therapeutic qualities of the sediments. Peloids could not form without the activity of certain microorganisms.

Humus Formation (Humification)

The term decomposition of organic substances in humus formation may be applied correctly only to the physical structure of plant material. Older books stressed the importance of anaerobic surroundings in the development of humus, but we have known for some time that oxidation ("a partial supply of oxygen") is necessary to the humification process. Once the humus has formed, its preservation and accumulation depend upon anaerobiosis. The amount of humus in the soil will depend upon the equilibrium between its formation and its mineralization (oxidation).

Chemical Properties

Peloid extracts have great reducing properties. The oxidoreduction potential of humic substances corresponds approximately to that of ascorbic acid. In addition to free water, there is also water bound in firm chemical combination, as well as colloid hydration. The capillary water is more freely mobile, and water in spaces of diameters larger than 1 mm. is entirely free. Sulfur can be present in elementary form. The quantity and quality of inorganic components (ash) are important in peloid classification. Minerals enter peloids underground as well as from the surface. They are leached out of the surrounding earth into the peloid bed. Atmospheric dusts may also be washed down into the peloid bed. The trace elements that are found in peloids include boron, cobalt, copper, iodine, and manganese.

Diffusibility

In order to evaluate the biologic properties of peloids, we must know the form and penetration of chemicals into them. It is necessary to consider the function of the peloid as an ion exchanger (ionex). A layer of Piestany mineral water with 50 to 100 micro curies of P32 was stratified over a column of Piestany mud in a thin-walled test tube with minimal disturbance (turbulence) at the mud surface. Measurements indicated that phosphates penetrate the mud only a little; that is, through a layer of 50 mm. Only about 0.05% of the dissolved phosphate penetrated in 28 days. In the surface layer the activity was 40 times greater than that of water, and at a depth of 2 to 4 mm. It was 7 times as great (34). This is in agreement with experiments on the penetration of phosphates into lacustrine sediments and their precipitation by ferric iron. In the same manner we (33) tested the penetration of phosphate and iron in high-moor peat and found much greater mobility.

Humus

The most important organic components of peloids are humus substances, humic acids, and fulvoacids. These have been studied extensively by Waksman (43), Kononova (24), and Flaig (15). To study the effect of humus fractions on organisms, we began a normal humification of radioactive beet sugar (Beta saccharifera) leaves and extracted the radioactive substances with the usual alkali extraction process. When drops of a solution or of brushings with a lanolin paste with radioactive fractions of humic substances are applied to the leaf, the alcohol and ether-soluble portions penetrate into the vascular bundles of the leaves. The active component of humic acid does not spread; the same fulvoacids in some plants does not penetrate the tissue, whereas in other plants they spread as much as several centimeters. We were not able to repeat this experiment on animal skin.

Ergons

An ergon is a substance that is biologically active in very low concentrations. Some of the substances present in peloids may not influence the body cells when applied to the skin. These substances may become more significant if taken internally in low-moor peat water or as peat drugs. The major components of the more important peloids are regarded by some authors as stimulants or excitants, although there has been no scientific proof of this until now. Hormones have been found in some peats. Except for estrogenic substances, little attention has been given to them. Little is known about the vitamin content of peloids. In peloid extracts, with dichlorophenol-indophenol titrable ascorbic acid is destroyed more rapidly than in a control water solution of ascorbic acid in a ratio of about four to one. The large-scale occurrence of the Flagellate *Euglena* (*E. mutabilis* Schmitz, *E. thionophila* Skuja) found in the low-moor peat water of Frantiskovy Lazne points to the presence of vitamin B 12. Although it has been known for some time that soil decomposes hydrogen peroxide, it was not until the appearance of Hofmann's (21) reports that Boil enzyme research became intensive; there is still little reported on peloid enzyme research. Vegetable debris of roots and green parts in varying degrees of humification is less important in the production of enzymes than those connected with microbiology.

There are two catalytic properties of peloids. (1) Some substrates can be decomposed by inorganic components of peloids, or by the active surfaces, and (2) active enzymes act in different ways on various substrates. Pokorna (32) studied eleven kinds of enzymatic splitting in peloids, but as yet only the results concerning catalase are published. The catalytic activity of peloids results not only from the enzymatic action of catalase but also from the catalytic splitting by iron and manganese compounds, or substances with an active surface. The catalase activity diminished with profile depth in high-moor peats (*spagnosum*) as well as in low-moor peats (*uliginosum*). The catalase activity of live *Spagnum* drops to one half after it dies off, in peat it decreases to as little as a tenth. Muds decompose hydrogen peroxide faster than humolites, but it is a non-enzymatic splitting. The effect of iron can be eliminated by means of complexone to permit the investigation of those peloids with a high iron salt content. Oxibase reactions were negative, positive in muds; the per oxidative reactions were positive in humolites as well as in muds. The dehydrogenase test (triphenyltetrazolinum) was negative, except in Piestany mud, where it was positive. It can be used to control the ripening of mud. Tributyrin was decomposed by various kinds of peloids in different ways. Since the activity was decreased in dried samples and was completely blocked in heating to 95° C., the presence of lipase in peloids can be presumed. Asparaginase and urease were not found. Proteolytic activity was very low. Even if an active pepsin preparation was added to the peat, its activity was checked. This may be related to the peloid therapy of peptic ulcers.

All peloids have amylolytic properties; they are lower in muds than in humolites. From their inactivation they are probably an enzymatic activity. Humolites possess a great capacity for inverting saccharose; in muds, it is much lower. The thermolability indicates an enzyme; acid peloids, however, hydrolyse saccharose by their acid reactions. Cellulytic power is present in most soils; however, in humolites there were negative findings during aerobiosis even after a month. Anaerovic decomposition indicated clear differences between high-moor peat, which remained inactive, and low-moor peat and mud, which decomposed after four to fourteen days. The Co 2 production varied, but in muds it represented only about a fourth of the amount produced in humolites. Samples kept in dark bottles for more than a year showed only small changes in catalytic action. Since catalytic actions are very sensitive, they can act as sensitive indicators of changes and characteristics of peloids. Sometimes even amino acids are considered as stimulators (effective substances). We know very little of the structure of nitrogen in peloids, but since we know much about the nitrogen of soil we may be able to extrapolate these findings. Many plants that grow in peat bogs are rich in tanning minerals and glycosides (Vacciniaceae, Ericaceae). Manskaja and Drozdovava (29) described glycoside compounds in moss (Sphagnum) membranes. These might be very effective biologically, but their determination and separation from humus complexes of polyphenolic character present a difficult chemical task. We know very little of the alkaloid content of peloids.

Regeneration of Used Peloids

The regeneration of peloids has interested investigators for some time (19, 23). There is as yet little scientific knowledge on the subject, probably because we do not know all the conditions of natural peloid formation and so cannot reproduce them. It is not simply a matter of long periods, as we can see from the quickly proliferating peat bogs and the continuous layer formation of humus in the woods. An example of recent humolite formations can be seen in the muds of Libisany near the Bohdanec Spa. After mining the low-moor peat, new layers were formed in the pools within ten to twelve years. A comparative analysis of the two types of peat may be seen in Table I.

TABLE I.

	Water	Dry Weight Ash %	Precipitated Humic Acids
Newly Formed Layers	9-12	16-35	12-45
Original low-moor peat (not exhausted)	5-8	17-23	26-31

TABLE 2

	Surface Layer %	Less Decomposed Ground Layers %
HCl extract (fulvoacids)	5	1.5
Alcoholic extract (humatomelanic acids)	3	2.0
NaOH extract (humic acids)	20	15.0

An experiment was conducted with high-moor peat moss *Sphagnum cuspidatum* samples from a layer under live plants of dead but not morphologically decomposed individuals and pressed into a bottle. After two to three weeks a 5 to 10 mm. Dark band formed on the surface. After a total of four months it was analyzed. The results may be seen in Table 2. This shows show rapidly humification can proceed in the morphologic (tissue decomposition) as well as in the chemical sense (formation of humus substances). The moss *Drepanocladus* humified in the same manner as did *Sphagnum*. Thus, the possibilities of forming new active humus substances exist if we can meet the requirements for development. If there is a yearly increase of about 1 to 2 cm. In high-moor peat, as is stated in the literature, it is obvious that this addition of active substances can change the properties of the gradually regenerating peloids. One of the most important considerations for peat development is the question of the growth of living plants and of its gradual humification after their decay in layers near the surface. These layers must always be covered by living plants. By the pressure of their weight they sink slowly into deeper layers of water and are surrounded by the anaerobic conditions that preserve the humus formed in the surface layers. Peloids are heated before application: they are often superheated by a stream of hot water. This affects the microflora in a manner that has not yet been determined.

Mineral Low-Moor Peats

The mineral low-moor peats are humolites that have been saturated by underground springs rich with soluble salts, freed by weathering, usually a pyrites oxidation and for that reason usually ferric or sulfurous-ferric. The ripening of ferro-sulfides is a physiochemical process, but even here biologic processes proceed simultaneously.

Muds

Muds, also called fangi, are predominantly mineral with only about 2 to 4 per cent organic substances, which nevertheless play an important role in their therapeutic use. Mineral muds may be ripened in warm (Piestany) or cold (Smraky) mineral water through complicated biologic processes associated with oxidation and reduction in the relatively short period of 6 to 12 months, but only in the presence of organic substances (26). The most important of these are the blue-green algae (Cyanophyceae), but other algae and plants are included. At Piestany they include the green algae *Chara pistienensis* and the blue-green algae Oscillatoriaceae. We (13) have shown how the addition of such organic material can accelerate the ripening of mud. The progress of mud ripening is characterized by changes in electrical potential. A fresh sediment of Piestany mud or the brown unripened mud of a branch of the river Vah has an average value of +50 mV. During the ripening the potential changes to 150 to 200 mV., and the brown mud becomes black through the action of a therloophilic strain of desulfurating bacteria, which reduce sulfates to sulfides. In Baar's nutrient solution black ferrous sulfide appears after 48 hours of cultivation (14). These processes are accompanied by changes of the redox potential from +350 mV. To a minimum of about -250 mV. And to a state of equilibrium between -200 and -50 mV. When organic substances such as the dry debris of Cyanophyceae (*Mastigocladus*) or green algae such as *Chara* are added to the culture medium, the reduction process will accelerate in proportion to the quantity of organic material added. If the control series potential changes from positive to negative (0 mV.) within a period of about 25 hours, the minimum potential in 40 to 50 hours is reached in series with organic substances added, these values are reached in 5 to 15 hours and 15 to 20 hours respectively (12). Native Piestany mud is continuously being mixed by mineral spring water in natural ponds, while organic matter is constantly added from the natural vegetation on the surface layer. Thus, the ripening process of the mud is opposite to the ripening process of sulfurous-ferric low-moor peats.

PHYSICS

When the particle size of peloids is greater than 0.05 mm. (grains of sand, quartz, silicate, and heavy minerals of different sizes and shapes with a solitary granular structure), they are held together in so-called false cohesion. In wet sands the particles are bound to one another by a water film produced by the surface tension of the water; thus, when they dry the cohesion ceases. In this case, the volume of the pores is less than that of the solid particles. When the particles are smaller than 0.05 mm. But larger than 2 μ (fine sand, coarse clay, microscopic plant fragments), there is a honeycomb structure and true cohesion. The molecular forces of the particles are stronger than their gravitation; once attracted, they stick to one another and to their position, thus forming lineal to three-dimensional chains. In this case the volume of the pores is greater than the volume of the solid particles.

Particles of less than 2 μ (physical clays, such as kaolins, montmorillonites, clay mica, chlorite, allophane, and humus particles, such as lignin, lignocellulose, celluloses, and other organic matter) form a spongy colloidal structure, which appears when all particles have a small electric charge of the same sign and the liquid is charged oppositely. This condition (cataphoresis) occurs in nature in high-moor peats, which have an insignificant mineral content. This humus and other organic particles contain the fewest neutralized active centers: they repel one another. In peloids in the liquid phase, the negative charge of humus clay, and other particles is neutralized by cations. When the neutralized (electro neutral) particles collide they stick to one another and form flakes, which coagulate into a honeycomb structure of the second order (spongy). The volume of the pores is greater than the volume of the solid components. Particles smaller than these can be considered as dissolved in the peloid water.

Water bound in the solid phase may be divided into (1) water in an ionic state (OH), hydroxyl or constitutional water, and (2) water in the molecular state (H₂O), which is chemically influenced or physically influenced (sorption water, capillary water, osmotic water, or gravitational water [moisture]). The ionic water occurs in the lattice of the mineral particles-crystals-and eventually in the organic particles in the form of OH groups on geometrically distinct centers. The ionic water is bound more firmly than the molecular water under the influence of electric charges. The chemically influenced molecular water may behave like solid matter in clay minerals (2); the cations may be bound by chemisorptions. The sorption water (adsorbed = hygroscopic + cohesive) is bound by molecular force in a molecular layer of several thicknesses on the surface of colloids and crystals. The sorption water may also behave like a solid, as does that part of the capillary water, which is bound by absorption to the capillary walls. The capillary water behaves as a liquid inside the pores; it enters the capillaries mainly by capillary vapor condensation.

TABLE 3

Type of Particle	Loss of Water at t° C. and Atmospheric Pressure				
	110	170	300	500	500
Organic Particles	1,2,3,4 5		5		
Clays	1,2,3,4,=part	4	5-part		5

1 = gravitational; 2 = osmotic, 3 = capillary; 4 = sorption-chemically influenced H₂O; 5 = ionic-OH

Osmotic water behaves as a liquid inside the pores; it reacts on the changes in pressure, temperature, and moisture. The gravitational water acts as a liquid and is fully separable by squeezing or other pressures. There are no sharp boundaries between molecular water types, that is, in the line of sorption, capillary, osmotic, or gravitational water, which is understandable with regard to the polydispersity of the solid constituents of peloids. Water can reach pores of large size by either capillarity or osmosis. The capillarity of finely granulated peloids is influenced by friction and gravitation.

Peloids with water content equal to their water capacity never have only gravitational water. Even in nature the gravitational water flows from the peloid on hydraulic and hydro mechanical principles. As peloids experience dehydration and dehydroxylation, the solids change, as shown in Table 3. After a loss of molecular water, it is most difficult to rehydrate clays; in halloysite it is not possible (40). Their dehydroxylation is irreversible and leads to a structural change. Rehydration of humus particles is difficult; they are incomplete after a partial loss of capillary and osmotic water, and there is a diminution of sediment volume and swelling capacity (X) and water capacity in low-moor peat (Y), as seen in Figure 39. Humus particles gain volume in dehydration, which can be specified as an inverted process of volume contraction—a well-known phenomenon on mixing two liquids.

The specific volume of dried high-moor peat is about 0.760; the volume contraction is 0.08 or 10.5 percent. The more it has been dehydrated, the harder it becomes to rehydrate peat, for the porosity is lowered and the pores are filled with air and eventually by water through capillary condensation in the pores. Peats are difficult to wet with water and thus are more suitable for application with gases. The formation of peloid solids and their union with liquids and gases will depend upon where the solids originated and what their relations were to ambient air and water. In a liquid environment the pores are filled by osmotic, capillary, and gravitational water; the larger the pores, the more important the gravity effect. The capillary phenomena cease in homogenous sediments with grains greater than 2.5 mm., and peloids do not belong to this type of mass.

Physical Constants of Peloids

The term "solid components" of peloids refers to what is left after the peloid has been exposed to a temperature of 105° C. until complete drying occurs. To determine ash content, the peloid is exposed to a temperature of 850° C. (5,6,7,10,14,19,40). Water retentivity is the greatest amount of water that 1 gram of solid peloid in its native state will hold (Water capacity, H). The values of H for different peloids are shown in Figure 40. It will be seen that the value of H falls as the ash content rises. H fluctuates widely, especially for peats (combustible peloids); it is related to previous drying (the greater the drying, the lower the H; H falls with humification). Peloids with a water content equal to their water capacity are said to have a normal consistency. If water is added to a peloid in excess of its water capacity, the liquid separates. If the additional water is stirred into the peloid vigorously, the solid structure collapses and the particles sediment according to Stokes' law; subsequently they reunite into larger units. The pores of the newly formed sediment usually contain more water than the pores in the original state. The space occupied by 1 gram of solid substance in the peloid in its native state is the sediment volume. In high-moor peats this value may be as high as 45 cm³. Or as low as 15 cm³. The values of inorganic muds usually range from 2 cm³ to 4 cm³. In general, sediment volume is inversely proportional to ash content. The swelling capacity is usually given as the ratio of sediment volume to dry solid volume in the natural state. In the preparation of compresses, packs, tampons, and other commercial preparations, tests of plasticity are used.

The upper limit of fluidization indicates the passage from a "porridge" to a muddy state. The lower limit of fluidization indicates the passage from a "pasty" to a "porridge" state. The difference between these two values is called the plasticity number. Tests of plasticity indicate roughly the rheologic properties of peloids. Thixotrophy, the lowering of viscosity caused by mechanical agitation and its rise when the agitation ceases, is also recorded. The rise of viscosity under the influence of heat and its reversal are also rheologic properties. Ostwald (30) found by viscometry that the gels of humic acids are peptized by freezing and boiling. Brozek (12) obtained similar results when he measured the structure viscosity of humic acid gel suspensions at temperature from 20° to 80° C. and of ferric sulfate low-moor peat by repeated exposure to steam. Hintzelmann and Lapke (20) observed the phenomenon in inorganic muds on measuring their plasticity from 18 to 50° C. Souci (40) described a relative viscosity of Kissingen low-moor peat with 80 percent water content at 20° C., a fluidity of 0.00025 cm/sec, 2.21×10 centipoise. The value of viscosity η falls on every addition of water; the η of peats with normal consistency is about 100 times that of water. Figure 41 shows the specific weights of solid components of peloids. The value ρ_0 rises as the ash content increases. The wide fluctuation among peats depends upon the degree of hydration of the solid phase (the greater the hydration, the less the ρ_0) and the grade of humification (the higher the humification, the higher the ρ_0). The weight of watery peloids (p) depends upon water content and can be calculated from the formula on page 269. The values of some peloids are shown in Figure 42; the hydrostatic presconductivity of peloids with a water content equal to their average water capacity is shown in Figure 45. Heat retentivity $R = cX p^2$ was introduced into balneology by Lewis (28) and is an expression of the speed with which the temperature of a cc. Of peloid will lose 1° C. when the decrease of heat per second equals the number of calories given by the thermal conductivity value. It is also the reciprocal of the coefficient of heat conduction ($2/cZp$), the significance of which is that the asymmetrical distribution of heat in a medium is proportional to its conductivity and inversely proportional to its thermal capacity. Figure 45 shows this relationship for several liquid peloids. The R of peloids increases with the water content and the water value without convection. It falls in peloids in which the solid component has less than 40 percent ash and rises in peloids with more than 40 percent ash. The maximum and minimum values of R are given by the water capacity of peloids; its variation is negligible in practice. From the foregoing we can see that the combustible peloids such as peats and a sapropelites have low thermal conductivity and high heat retentivity. The transfer of heat into a human body is a thermal transmission between two media. The amount of heat transmitted is proportional to the difference of the temperatures, the size of the contact surface (P) and the time (t) as follows:

$$Q = \alpha(T_1 - T_2)Pt$$

The coefficient α is the amount of heat passing through a surface of 1 square centimeter per second at a difference of 1° C. It is complicated by the shape of the surface, the absolute temperature maximum, and the difference between the two temperatures. It can be determined experimentally by measuring the temperature of each medium.

With simple geometric forms, such as a cube or a ball, thermal transfer can be calculated from the simple formula of Gröber (18). The transfer of heat from a compress into the body depends upon the heat gradient between the two surfaces, the thickness of the layer, and the retentivity of the compress (10), as shown in Figure 46.

The total dosage is proportional to the heat gradient, and its time course is the same. It is possible in proactive to regulate the heat so that skin tolerance is not exceeded, especially with the poorly conducted peats, of which the high moor is best. The transfer of heat depends upon the thickness of the compress of inorganic mud (with a water content of almost .50 percent). A compress with a 1 cm. Layer transmitted all the heat in 5 minutes; the thicker the layer, the more symmetrical and greater the thermal transmission. Again, the high-moor peats are more suitable, with respect to the hydrostatic effect. The total amount of heat delivered by various peloids does not vary greatly; peats deliver heat more symmetrically than muds because of superior heat retentivity. The transfer of heat from a peloid bath into the human body is difficult to predict. Ipser (22) showed that the thermal resistance of the body falls during a bath in peat at about 37° C. due to increased skin circulation. He also showed that the thermal input was several times greater than the heat loss through respiration and the skin and much higher than the heat produced by metabolic activity. By autocalorimetry (22) he measured the circulatory requirements of thermoregulation in the bath, for both peat and water baths. From these findings we may conclude that there are no great differences in the thermo therapeutic values of different peloids.

Physical Constant Determination

For practical purposes, the important peloid constants may be determined with sufficient recision from graphs if the ash content and water retentivity are known. For example, strata of a peloid may be said to consist of layers B and C; B contains 20 percent ash in dry soils and has a water capacity of 10; C contains 34 percent ash in dry solids and has a water capacity of 7. The average ash content in the strata of peloids is 27 percent in dry solids; the average water capacity lies above the curve of average values.

$$10 + 7 H = + 8.5, \text{ and } 2$$

Since $H = 8.5$, the peloid of normal consistency contains $100 H/(+H)$, which equals 89.4 percent water (w); dry solids = $s = 100-w = 10.6$ percent. The specific heat (c_0) of its solid component also lies above the curve of average values = 0.266. The specific heat of its normal consistency (s) equals the sum of the specific heat (c_0) of water and solid component, or dry solids, contained in 1 g. of peloid of normal consistency, that is:

$$c = 0.894 + (1 - 0.894) \cdot 0.266 = 0.922.$$

The weight of dry solids (p0) of an average sample lies somewhat higher as a result of volume contraction; thus, approximately, p0 = 1.75. The measuring weight of its normal consistency p can be calculated by the formula: $100 p = \frac{w}{w + sV}$

Where:

$$1 V = \frac{1}{p_0}$$

In this case

$$1 V = \frac{1}{1.75}$$

$$\text{Thus } 100 p = \frac{1.048 \times 89.4}{1.048 \times 89.4 + 10.6 \times 0.571}$$

The heat capacity can be derived from the formula:

$$K = cp = 0.921 \times 1.048 = 0.965.$$

The heat conductivity of its normal consistency 1 can be subtracted according to the ash content (Figure 4.5) with the content of water and ash = 0.00121. The heat retentivity R can be calculated according to the formula $R = c \times p/2 = 0.797$

It is always necessary to determine the portion of water that must be added to a natural peloid to regain its normal consistency, as follows:

$$W_1 = \frac{(S_o(1 + H) - 1)}{100} * N$$

With respect to weight, and

$$W_1 = \frac{(S_o * (1 + H) - 1)}{100} * Mp_1$$

with respect to volume, where W_1 equals the amount of water added; S_o equals the percentage of dry solids in natural sample; N equals the weight of the natural peloid; M equals the volume of the natural peloid; $p_1 = [100/(w_0 + s_0V)]$ = weight of natural sample; $w_0 = 100 - s_0$ = percentage of water in natural sample; and $V = 1/p_0$.

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