ing to a minimum of 9.92 Å at 300°C. Since hydrogen was the only cation introduced into the system in addition to the lithium saturating the clay initially, the failure of the mineral to collapse to a spacing of 9.24 Å indicates that an ion much larger than lithium and similar in size to potassium is preventing the silicate layers from making the closest possible approach. The keying effect and maintenance of the mica spacing of 9.92 Å is interpreted as an indication that hydronium ions are occupying the interlayer cation positions normally occupied by potassium ions. Thus, the absorption bands at 3472 cm^{-1} are probably due to the hydronium ions, which have been isolated in the environment by the heat treatment producing collapse of the expanded mineral to a minimum spacing of 9.92 Å. Furthermore, the fact that the 3470 cm^{-1} band persists even above 600°C for the hydrogen-saturated mica strongly suggests that the species involved is the hydronium ion and not an uncharged water molecule.

On the basis of the apparent relationship between the wavelength of the O-H stretching frequency of a H-bonded solid and the O-O bond distance suggested by Nakamoto, Margoshes, and Rundle (*7*), the O-O distance for the hydronium ion and the oxygens of the silicate surface is 2.88 Å. This corresponds to the nearest-neighbor distance of 2.88 Å (*8*) for water at room temperature. The K-O distance for the six inner oxygens surrounding the potassium ion in muscovite is 2.81 Å (*9*).

Since the hydronium ions are virtually all associated with exchange sites on the mica mineral, their environment differs from that in a system such as acid hydrates and aqueous mineral acids.

In samples that had been exposed to a high relative humidity or had not been completely air-dried, a band at 1723 cm^{-1} was observed. This disappeared when the sample was thoroughly air-dried or heated. This band probably corresponds to the bands at 1700 to 1750 cm^{-1} observed in aqueous solutions of mineral acids. When the water content of the clay is reduced by drying, the nature of the water remaining is such that hydrogen bonding between the hydronium ion and the surrounding water molecules is not possible to the same extent as in the initial system.

Thus, it should be possible to detect hydronium ions in hydromicas and illites by infrared spectroscopy. Examination of Fithian illite under similar experimental conditions did not reveal any significant band at 3470 cm^{-1}.

Addendum. After this report had been accepted for publication we found a reference (*10*) to a paper in which the authors claim to have proved the presence of H_3O^+ ions in vermiculite. We believe that the claim is invalid because there is an insignificant amount, if any, of H_3O^+ in vermiculite (*11*); the authors generate a fictitious H_3O^+ in the chemical formula from a basic error in calculation of the formula. Although the chemical analysis shows that the vermiculite contains 24 percent MgO, they give the following formula:

$$[K_{0.04}(H_3O)_{0.96}\ Mg_{0.08}]$$
$$Mg_{2.73}Fe^{+3}_{0.26}Fe^{+2}_{0.01}$$
$$[Al_{1.22}Ti_{0.02}Fe^{+3}_{0.12}Si_{2.64}O_{10}]$$
$$(OH)_2 \cdot 3.17\ H_2O$$

Their formula is calculated on the basis that only seven cations are coordinated with each 12 oxygen atoms as is the case for talc—but the actual count would be about seven and one-half. The one-half divalent ion which they omitted affords the one H_3O^+ which they generated. On the basis of the formula which they calculated, they then state that the ratio H_2O:H_3O^+ is about 3:1. The scheme which they show would generate 2 milliequivalents of H^+ when 1 g of vermiculite is in NaCl solution; the actual operation does not even cause methyl red to change color, but it does yield Mg^{++} in the salt solution.

A second reason to believe that their claim is invalid is that of the five infrared assignments they attempt to make for the H_3O^+ ion in vermiculite, two are completely by inference since they coincide with the stretching vibrations of water and the Si-O bands of the vermiculite so that detection of the H_3O^+ vibrations is virtually impossible. The other three assignments are made on the basis of the infrared assignments of Ferriso and Hornig (*5*) for oxonium in halogen acids; these specific assignments have been questioned by Falk and Giguere (*6; 12*).

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Size Distributions of Sedimentary Populations

Abstract. *Separate sedimentary populations are not all characterized by lognormal size distributions. Populations of different sizes of material are produced by different mechanisms of abrasion: pebbles and gravel by single-stage crushing; sand by repeated abrasion; and silt and clay by chipping from larger grains. Each mechanism imposes a different size distribution on the product.*

The polymodal nature of many sediments has been emphasized in a number of recent publications (*1, 2*). In particular, Spencer (*2*) has proposed that sediments can be considered to consist of mixtures of one or more of three separate populations, which he terms "gravel," "sand," and "clay." Such separate populations of sedimentary materials may be regarded as having originated from different methods of production of source material (*2*) or from different effects of transportational processes (*1, 3*).

Though it is commonly assumed that the size distributions of each of these separate populations are lognormal, the object of this report is to show that the populations are characterized by different distributions. Specifically, it is proposed that three distinct populations

Table 1. Size distributions produced by ideal fracturing and abrasional processes. The size and frequency parameters that must be measured to obtain the theoretical distributions are listed, and references are given to the experimental evidence (exptl.) and natural materials that support the theory.

Process	Theoretical distribution	Size scale	Frequency scale	References	
				Exptl.	Natural
Single-stage crushing	Rosin's law (truncated?) (*4*)	Volume	Weight	(*4*)	(*5*)
Repeated abrasion	Lognormal (*10*)	Volume or diameter	Weight or number	(*11*)	(*12*)
Chipping from large grains	Arithmetical normal?	Diameter	Weight	(*7*)	(*8*)

(gravel, sand, and silt-clay) are produced by different mechanisms of fracturing and abrasion and that each mechanism imposes a different size distribution on the product.

Three ideal mechanisms of size reduction may be envisioned: (i) single-stage random crushing; (ii) sequentially repeated crushing; and (iii) removal of chips from material of effectively infinite size. In the first two methods, the entire material involved in the process is included in the final measured size distribution; in the last method, only the chips are measured. Table 1 lists these various processes, the size distributions produced by them, and the references which demonstrate the validity of the distributions with regard to theory, experimental investigations, and natural materials.

Rosin's law has been applied primarily to the crushing of coal (*4*), but it has also been found applicable to weathered materials (*5*). Coarse sedimentary debris which has not undergone extensive transport apparently shows this type of distribution (*6*). A Rosin's law distribution (possibly truncated by transportational removal of fine material) may, therefore, be considered characteristic of pebble- or gravel-sized sedimentary populations. Sedimentary processes occurring in areas of high-gradient streams, however, may yield coarse material which has passed through several abrasional cycles, and a Rosin's law distribution will probably not characterize such material. The "size" measured in establishing a Rosin's law distribution is the volume of the grains, though it is more common to use a parameter that is essentially a geometric mean diameter; the frequency scale is the weight of grains of the given "size."

A unique feature of the lognormal distribution is that the form of distribution is independent of whether a volume or linear dimension is used for "size" and whether the weight or number percentage of grains is used for frequency. Most unimodal sands have size distributions that are either approximately lognormal or may be described in terms of their departure from lognormality, and this distribution must certainly be considered characteristic of the ideal sand-sized material.

Only a limited amount of evidence is available concerning the size distributions of very fine-grained sediments. A simple random removal of fragments from a source of infinite size should produce an arithmetically normal distribution, but whether it is normal with respect to volumes, diameters, or other measures of the grains is uncertain. The problem is further complicated by the fact that frequencies measured by number and by weight, though not equivalent, are sufficiently similar in form through much of the size range that they are difficult to distinguish. On the basis of the evidence available (*7, 8*), silt- and clay-sized sediments produced in this abrasional manner are presumed to have arithmetically normal distributions of linear dimensions with frequencies measured by weight of grains.

Only a partially satisfactory proof can be given to the effect that materials in the different size ranges discussed above are not produced by abrasional mechanisms other than the ones proposed. The general ineffectiveness of normal stream abrasion on particles smaller than 1 to 2 mm (*9*) precludes the formation of silt and clay by continued size reduction of coarse materials. Furthermore, lognormal distributions are not formed by single-stage crushing processes. Thus, the general correspondence between fracturing processes, size distributions produced, and size range affected is fairly strong.

The separation of sediment into populations of differently sized material is probably valid. The apparent fact that each population has a different type of size distribution lends support to the hypothesis that the populations are produced by different abrasional and fracturing mechanisms. Transportational processes either move whole populations or truncate populations by moving their finer portions, but transportation does not control the nature of the characteristic size distributions of the populations. Regardless of the accuracy of the conclusions drawn here, it is not necessarily correct to assume that the different populations of sedimentary material each have a lognormal distribution.

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Infrared Radiation from the Atmosphere over the Arctic Ocean

Abstract. *The emission spectrum of the atmosphere over the Arctic Ocean was observed during a period when atmosphere and snow surface temperatures were about −40°C. The main contributions to the emission in the 5- to 21-micron range came from ozone and carbon dioxide, with water vapor playing a minor part.*

A major portion of the heat received by the surface of the Arctic Ocean ice pack in winter must be that due to long wave ($\lambda > 5\mu$) radiation from the atmosphere. Since both nitrogen and oxygen are almost completely transparent to radiation in this