mon source for β radioactivity and particles. In 1972, however, the seasonal peak of microparticle concentration was weak (Fig. 3), whereas that of β radioactivity was no less developed than in other years (Fig. 4). It is recalled that 1972 was an unusual year when the El Niño current extended along the coast of Peru; it was characterized by an anomalously high sea temperature, abundant rainfall, and low atmospheric pressure.

The extreme atmospheric and hydrospheric regimes of El Niño and their antithesis are tropical phenomena that can be identified from instrumental records for most of the 20th century (*13*, *17*, *18*) and from historical sources for the more distant past. It may be possible to ascertain from a deep ice core whether the variation in the seasonal microparticle peak at Quelccaya is characteristic of these large-scale circulation and climate anomalies.

From the data presented in Figs. 3 and 4 and the measured snow densities the annual net balance can be reconstructed back to 1969 (Fig. 5). When an ice core to bedrock is obtained it may be possible to extend this record back to A.D. 1500. In Fig. 5 the annual values of net balance are compared with an index of annual precipitation compiled from eight rainfall stations in the vicinity of Quelccaya. A positive correlation is apparent although the series are short. A further correlation is indicated with the annual changes in water level of Lake Titicaca and with precipitation at the Observatorio San Calixto in La Paz, Bolivia. Quelccaya net balance data from a deep ice core could be compared with Lake Titicaca water levels back to 1912, and this would allow us to relate the hydrometeorological changes on the Quelccaya Ice Cap to the regional climate.

Thus an attempt is being made to reconstruct a tropical climatic record on the basis of microparticle and isotope analyses of ice cores. Studies of the present climate and its relation to the microparticle and oxygen isotope variations in the current snowfall will allow a paleoclimatic interpretation of deep core records. The results to date indicate the need for a revision of isotope "thermometry" for application in the tropics. However, isotope thermometry will probably not be as important at low latitudes as it is in the polar regions, where annual and climatic temperature ranges are pronounced. At low latitudes the most useful paleoclimatic parameter is likely to be the variation in precipitation. The pronounced seasonality of β radioactivity, microparticle contents, and isotope ratios offers the prospect of a net balance chronology. The 8-year record of net balance obtained so far for the summit site parallels the hydrometeorological conditions in neighboring regions of the Andes. Both the Quelccaya net balance and the various hydrometeorological indices reflect control by the large-scale circulation rather than by local conditions. Retrieval in 1979 of a 100-m ice core and later of an ice core to bedrock may thus provide a key for the reconstruction of climate and circulation history in tropical South America in the recent past.

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L Amino Acids and D-Glucose Bind Stereospecifically to a Colloidal Clay

Abstract. *L-Leucine, L-aspartate, and D-glucose bind in a stereospecific manner to a colloidal clay, bentonite. This binding has high-affinity, saturable characteristics. The biologically uncommon enantiomers, D-leucine, D-asparatate, and L-glucose, do not exhibit any selective absorption on bentonite. It is suggested that this difference between stereoisomers could account for the evolution of life forms possessing a great preponderance of L amino acids and D-glucose.*

The reason for the occurrence of L rather than D amino acids as protein constituents is unclear. It may be that a random event early in biogenesis led to a preferential selection of L amino acids and this condition persisted throughout biological evolution. It was suggested (*1*) that an unknown process may have presented a slight advantage to L over D amino acids during early evolution. The concept that amino acid stereoisomers have a different susceptibility to decomposition by ionizing radiation has been investigated and disproved (*2*). The designation L amino acid implies that such compounds are stereochemically related to L-glyceraldehyde, rather than that they are levorotatory (*3*). While L and D amino acids are chemically identical, they may have different properties when covalently bound to or complexed with other molecules that are themselves chiral. In an analogous manner, D-glucose is found in a wide variety of organisms while L sugars occur much more rarely in nature. The evolution of this distinction has also been attributed to the stabilization of an event that was originally a random selection. Before the onset of life forms, the earth's primitive oceans may have contained low concentrations of organic molecules including amino acids, nucleotides, and sugars. These molecules have been experimentally formed from methane, ammonia, and water by using high temperature, ionizing radiation, light, and electric discharges to simulate prebiotic conditions (*4*). The stereoisomers of compounds formed in this way are present in similar amounts. If

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there were a difference in the ability of such enantiomers to be absorbed onto solid surfaces (and thus concentrated), this could increase the possibility of a single isomer participating in the complex chemical interactions that must have preceded the appearance of viable organisms.

We have studied the binding characteristics of the D and L isomers of leucine, aspartic acid, and glucose. It is known that organic ions can occupy ion exchange sites on clay crystals and that polar organic molecules can be absorbed on clay mineral surfaces (*5*). However, the stereospecificity of such events has not been investigated.

Two milligrams of bentonite (colloidal hydrated aluminum silicate) were incubated for 15 minutes at 30°C in 1 ml of 50 m*M* tris-hydrochloride (*p*H 7.1) together with a radioactive compound, L-[4,5-^{3}H]leucine (58 Ci/mmole), D-[4,5-^{3}H]leucine (1 Ci/mmole), L-[2,3-^{3}H]aspartic acid (15 Ci/mmole), D-[2,3-^{3}H]aspartic acid (16 to 18 Ci/mmole), D-[1-^{3}H]glucose (18 Ci/mmole), or L-[1-^{3}H]glucose (17.5 Ci/mmole). Final concentrations of labeled compounds were $1.2 \times 10^{-8}M$ (L-leucine), $1.3 \times 10^{-8}M$ (D-leucine), $3.0 \times 10^{-8}M$ (L-aspartate), $2.9 \times 10^{-8}M$ (D-aspartate), $2.7 \times 10^{-8}M$ (D-glucose), and $2.8 \times 10^{-8}M$ (L-glucose). The radiochemical and optical rotatory purity of all isotopically labeled compounds was greater than 98 percent. In a parallel series of experiments, the same compounds were incubated in the presence of the corresponding nonradioactive D and L compounds, present at $10^{-4}M$. Bound radioactivity was assayed by centrifugation of samples (50,000*g* for 10 minutes at 0°C) to precipitate the bentonite. These pellets were then taken up in 4 ml of 50 m*M* tris-hydrochloride (*p*H 7.1) and the suspension recentrifuged. The final residues were then suspended in 0.5 ml of water, and radioactivity was assayed in a compatible scintillation fluid with a Beckman scintillation counter at an efficiency of 20 to 22 percent.

The biologically common molecules (L-leucine, L-aspartate, and D-glucose) bound to bentonite in a stereospecific and reversible manner to a much greater extent than did the homologous compounds that are rarely found in nature (D-leucine, D-aspartate, and L-glucose) (Table 1). The binding of these latter three species was not stereospecific. Tritiated L-valine but not D-glucose was previously shown to bind to clay minerals such as kaolinite from $10^{-8}M$ solution (*6*). A series of kinetic and concentration studies was carried out on the strongly binding species. The dissociation constants and density of binding sites for these interactions with bentonite were determined by Scatchard analysis of binding (*7*) over a range of concentrations (Table 2).

It was necessary to ensure that these results were not due to bacterial contamination of the bentonite. Any protein present was removed by heating samples of bentonite in 0.5*N* NaOH at 90°C for 1 1/2 hours. The clay was then washed with distilled water and the dried sediment was pulverized in a mortar. The binding characteristics of this treated bentonite toward labeled enantiomers of aspartic acid were indistinguishable from those obtained with untreated bentonite.

The ability of some molecules of ubiquitous biological distribution to bind selectively in a nonenergy-requiring way and with high affinity to a colloidal clay suggests a means by which such species could tend to be absorbed onto solid surfaces from dilute solutions. The less biologically common stereoisomers do not possess this property. If L amino acids were continuously absorbed by particulate matter and thus removed from a primitive ocean, racemization of the remaining D amino acids would continuously replenish the L form. The time for such a process is of the order of 10^5 years (*1*). The concentration of molecules by absorption on solid surfaces may have facilitated critical covalent or other interactions.

The extreme fineness of clay results in a large surface-to-weight ratio, and Bernal (*8*) has pointed out the possible importance of clays for "prereproductive metabolic processes." Condensation products between D sugars and L amino acids (humic acids and melanoidins) have been recognized for many years (*9*). Such condensation products can be formed on and absorbed to clay surfaces. Thermally induced polymerization of amino acids absorbed onto a clay (montmorillonite) has been reported (*10*). In this manner, increasingly complex molecules could have been assembled, ultimately leading to the formation of systems capable of replication. The binding differences reported here may account for the development of organic life forms preponderantly based on L amino acids and D-glucose.

Table 1. The binding of leucine, aspartate, and glucose to bentonite. Two milligrams of bentonite were incubated for 15 minutes at 30°C in 1 ml of 50 m*M* tris-HCl (*p*H 7.1) together with a labeled compound at concentrations between 1.2×10^{-8} and $3.0 \times 10^{-8}M$. In some experiments, nonradioactive D and L compounds were present at $10^{-3}M$ concentration. Bound radioactivity was assayed by centrifugation of particulate material (50,000g for 10 minutes). Pellets were washed in 4 ml of 50 m*M* tris-HCl and radioactivity in the final residue was measured. Binding is expressed as picomoles of labeled compounds per 10 mg of bentonite. Standard errors of the mean of 6 to 18 determinations are presented.

^{3}H-labeled compound	Additions	Binding
L-Leucine		26.8 ± 3.3
L-Leucine	L-Leucine	2.7 ± 0.4
L-Leucine	D-Leucine	25.3 ± 2.1
D-Leucine		4.1 ± 0.6
D-Leucine	L-Leucine	3.2 ± 0.6
D-Leucine	D-Leucine	3.6 ± 0.7
L-Aspartate		2.2 ± 0.3
L-Aspartate	L-Aspartate	0.2 ± 0.1
L-Aspartate	D-Aspartate	1.7 ± 0.3
D-Aspartate		0.3 ± 0.1
D-Aspartate	L-Aspartate	0.4 ± 0.1
D-Aspartate	D-Aspartate	0.3 ± 0.1
D-Glucose		2.6 ± 0.3
D-Glucose	D-Glucose	0.5 ± 0.2
D-Glucose	L-Glucose	2.6 ± 0.2
L-Glucose		0.23 ± 0.05
L-Glucose	D-Glucose	0.11 ± 0.03
L-Glucose	L-Glucose	0.20 ± 0.02

Table 2. Kinetics of the stereospecific component of compounds binding to bentonite.

Compound	Dissociation constant, K_d	Binding sites (pmole/mg bentonite)
L-Leucine	$4.6 \times 10^{-6}M$	4.6
L-Aspartate	$1.7 \times 10^{-6}M$	1.9
D-Glucose	$0.73 \times 10^{-6}M$	5.8

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