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Fossil Humic Acids in Southern Brazil

(humic acid|radiocarbon|Alexandro submergence)

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INTRODUCTION

We have found extensive deposits of fossil humic acids, possibly related to sea levels, on the southern coast of Brazil, namely in the coastal part of the Ribeira valley, in the state of São Paulo. They extend from the town of Peruibe, at 24°S, 20°W, to the town of Cananéia, at 25°S, 48°W, both on the Atlantic Ocean. No effort was made do assess the total extent of the deposits but they have been observed not only close to the shore but also as far as 20 km inland.

MATERIALS AND METHODS

a) Instruments and Chemicals

Beckman Liquid Scintillation LS-330 was used for counting with 20 ml low potassium glass vials. The scintillator cocktail was prepared with 4g of 2,5-di-phenyl oxazole (PPO), 0,1g of 2,2'-phenilene bis (5-phenyloxazole) (POPOP) in 1000 ml of toluene. All the chemicals were of scintillation grade (Koch-Light Laboratories Ltd, England).

b) Benzene synthesis for radiocarbon dating

The benzene production is carried out by the following reactions:

$$3C_2H_2 \longrightarrow C_6H_6$$
 (d)

A benzene synthesis vacuum line and the operating precautions are described by Tamers,

Four milliliters of benzene were dissolved in 15 ml of the toluene scintillator cocktail and the mixture was poured into 20ml low potassium glass vials. The activity of this material has been checked against the ¹⁴C standards issued by the National Bureau of Standards, Washington, D.C.

RESULTS AND DISCUSSION

The desposits on the vicinity of Cananéia were studied in more detail. We have found them on the mainland and on two islands, Cananéia and ilha Comprida. The latter is a long and narrow island stretching from close to Cananéia in the South, at 24°S 44°W, to the town of Iguape, in the North. On this island the deposits had a different aspect from the ones found on the mainland and on the island of Cananéia; they were lighter in color and were made up of a smaller proportion of organic material in the sand-humic acid mixture, typically 1.8% instead of about 10%.

The individual sand grains were covered with a layer of organic material. This organic material was not soluble in neutral water but could be readily extracted by slightly alcaline solutions. To do this we have used either 0.5% ammonia or sodium hydroxide solution. With a few successive extractions a perfect removal is achieved. The remaining sand looks like sand

found on nearby beaches open to the ocean. Its distribution revealed by a granulometric classification is given in Table I. There was however an additional fraction in the mineral component besides sand. During the extraction a small fraction (0.35%) formed a suspension which, after being recovered from the filter, looked like clay. No further analyses were made. The alcaline extract could be precipitated by dilute hydrochloric acid. This characteristic, according to Duchafour, 1965, classifies the organic material as being humic acids.

TABLE 1

Granulometric Classification of 200 g of Sand from Ilha
Comprida, Free of Organic Matter

Sieve	Opening (mm)	mesh	mass (g)
8	0.707	24	0.81
9	0.500	32	3.21
10	0.351	42	11.90
11	0.246	60	32.55
12	0.175	80	58.36
13	0.124	115	79.59
14	0.088	117	13.20
bottom	-	-	0.38

On Ilha Comprida these deposits of lighter colored material occurred in a layer usually about three meter thick, it starts about 0.5 m above sea level so that the portion that reaches the beach is actually washed over at high tide.

On the island of Cananéia the deposits occur in much thinner layers, about 0.7 m thick, but they are much richer in organic material. Concentrations ranging from 8.6 to 13.1% of extractables were found over a stretch 1000 m long. Over the same stretch nitrogen content was measured in sites 2 and 5. On site 2, at the top of the 0.7 m thick layer, the extracted humic acids contained 0.12% nitrogen; for the bottom of the layer a value of 0.142 was found. On site 5 a value of 0.088 was found at the bottom. Site 2 is about 200 m inland from the SW shore of the island of Cananéia, while site 5 is about 1200 m. The humic acid bearing layer is 4.9 m above sea level. The signs suggest that this humic acid bearing sand was deposited under water. On site 5, which is in a sandpit, an exten-

sive stretch of neatly and recently cut sand embankment is exposed. It can be seen in some stretches that the humic acid layer is perfectly horizontal and that it rests on horizontally stratified sand, the strata being obvious because of slight variation in texture.

The lighter colored deposits existing on Ilha Comprida, on the other hand, do not show such marks and could actually be the result of reworking of some more concentrated deposits. Evidence of possible reworking was found in two places. On Isha Comprida itself one can see creeks discharging dark colored water into the ocean at the same time as the wind sweeps, on the open beach, precipitated humic acids as foam from sea to shore. We suggest that the humic acids dissolved in the creek water are being salted out by the sea salt in the ocean and that instead of sinking to the bottom they concentrate in the foam generated by the surf. In fact, close to the mouth of the creeks the foaming is very obvious and on the more windy days the beach becomes covered with foam. As the water dries and the bubbles collapse a grayish colored organic material is left behind.

The other place where signs of reworking were found was at a distance of about 8 km West from the open beach. There, close to site 5, a thickening of the humic acid bearing layer is observed and the underlying horizontal strata run out into a meanderlike up and down pattern.

The proposition that humic acids can be salted out by sea salt was confirmed in the laboratory.

The aforementioned site on Ilha Comprida (site 0) and five sites on the island Cananéia (sites 2 to 6) were radiocarbon dated. The results are shown in Table II. If the top layer date of site 2 is discarded on grounds of possible contamination by recent carbon, and if the reamining dates for the bottom layer of sites 2 to 6 are averaged, an average age of 5312 years results. This would place the age of formation in the Alexandro Submergence, as given by Fairbridge, 1976.

TABLE II

Radiocarbon Age of Humic Acids from South American Atlantic Coast, at Latitude of about 25°S

Site	Location within layer	Apparent ¹⁴ C age (years BP)
0	bottom	4576 ± 540
2	top	1675 ± 65
2	bottom	3558 ± 98
4	bottom	7466 ± 361
5	bottom	3460 ± 191
5	bottom	6284 ± 531
5	bottom	5925 ± 771
6	bottom	5179 ± 270

CONCLUSIONS

The humic acid deposits in the coastal part of the Ribeira valley in Southern Brazil are probably related to sea levels and can be used as a complement for sea level chronology studies.

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SUMMARY

Deposits of fossil humic acids, possibly related to sea levels, have been found in southern Brazil. Partial chemical and physical characterization of the deposits, as well as their ages, are given. Their use for sea level chronology studies is proposed.

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achieved. The remaining sand looks like sand