Table 1. Line widths and spot recording rates.

	0.1-M	sec scan	1.0-Msec scan			
Fig.	Line width (µ)	Spots/ sec	Line width (µ)	Spots/ sec		
	1.8	1.3×10 <sup>6</sup>	2.0	1.2×10 <sup>4</sup>		
1b			2.0	$1.2 \times 10^{10}$		
1c	2.5	9.6×10 <sup>5</sup>	4.5	5.3×10		

strates. Evaporated films were generally in the 500- to 1000-Å range, and the organic coatings 4  $\mu$  or less. Of the large number of media investigated, the discussion here will be limited to the following: a 500-Å evaporated coating of lead; a 500-Å evaporated coating of tantalum; a 1.0- $\mu$  coating of a triphenylmethane dye in a plastic binder.

In-focus line patterns were recorded on the three media with beam power, horizontal velocity, and vertical velocity being the independent variables. The recorded patterns are 240 by 240  $\mu$ . A beam power of 38 mw at the recording medium was used in each case. The left half of each pattern was recorded at 0.1 msec per vertical scan line, and the right half at 1.0 msec per vertical scan line. In the case of tantalum (Fig. 1b), beam power was insufficient to record the left half of the pattern. Measurements of the width of the clear portion of the scan lines for Fig. 1, a, b, and c, were made (Table 1). Knowledge of this line scan time permits calculation of the effective spot recording rate. The minimum line scan time was limited by the apparatus to 0.1 msec.

While the measurements on the dyeplastic sample (Fig. 1c) were made with respect to clear lines, this coating also exhibits a darkening effect on the edges of the cleared tracks. At higher scan rates, or lower beam powers, or both, this can lead to an overall image which is darker than the background, and need not be accompanied by a clear track at the line center. A similar effect, but resulting from different mechanisms, occurs with a number of evaporated films.

We recorded a page of the Bible by direct document input (by means of a facsimile-type optical scanner), and an ultrasonic diffraction-grating light shutter for beam modulation. The recording objective in this case had a numerical aperture of 0.2 with a useful flat-field diameter of 3 mm. The 3-mm field contained 1600 scan lines of which 1200 were actually used in recording the document. It should be noted that the resolution of the recording was limited by the optical resolution of the document scanner rather than by the laser recorder.

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## Sedimentary Environments in a Marine Marsh

Abstract. Several foraminiferal assemblages are recognized in Spartina-Salicornia marshes along the Pacific and Gulf of Mexico coasts. Continuous recordings in one Pacific marsh show considerable diurnal and seasonal variation in pH, oxygen, water temperature, and salinity. This is related to tidal flushing, air temperature variations, sunlight duration, and marsh plant metabolism.

Modern marine sediments have been studied extensively to discover relationships between types of sediment and the marine environments in which they accumulate (1, 2). Organic sedimentary particles generally are better environmental indices than detrital mineral grains because they are produced where they are found (3, 4). Patterns of sediments in the modern oceans, including the organic particles, have been used to decipher probable environments in older oceans represented by the record in ancient marine sediments (5, 6).

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Considerable information is available on distributions of sedimentary materials in the modern ocean. Information about the marine sedimentary environments, however, generally is inadequate and is confined to a few temperature and salinity measurements, depth of water, and topographic location. Such data are of limited value in defining a marine environment and have little reality from the point of view of the living organisms which contribute skeletal material to the sediments. Extremes, durations, and means of all important environmental parameters are essential for a realistic analysis.

Marine marshes, which are widespread, are an important part of marginal marine sediments, and are extensively preserved in ancient marine rocks. Marsh sediments have been little studied, with some exceptions (7). We have examined some aspects of the field distributions of marsh sediments, and have attempted to partially define the environments in which they are accumulating in one marsh. The sedimentary particles studied are the foraminifera; they are abundant, they are important contributors of sedimentary particles, and they are produced where they are found.

Distributions of foraminifera are summarized for numerous marshes along the Texas coast in the northwestern Gulf of Mexico and for the Pacific coast of North America (Fig. 1). The vegetation of these marshes is generally composed of an assemblage dominated by Spartina at the lower elevations, just above the unvegetated tide flats, and an assemblage dominated by Salicornia at a higher elevation (8). Actual elevations of these plant communities are related to the tide range. Inorganic components of the sediment range from silty sand to silty clay, depending on the marsh and the location within the marsh.

At least three marsh zones can be identified by foraminiferal assemblages (Fig. 1). This zonation occurs in hypersaline marshes and in those having salinities less than normal sea water, and frequently is developed over a very short distance. We have attempted to define a marsh environment by measurements of as many environmental factors as possible in one marsh. Continuous and simultaneous recordings have been made of values of salinity, water temperature, air temperature, sodium ion, chloride ion, oxygen, pH, Eh, sulfide ion, light intensity, wind velocity, and tide level. These measurements have been made for approximately 1 year to obtain estimates of extremes, means, and durations of different values of the various parameters. The instruments used are mostly readily available, but many have required modification and special assembling for use under field conditions (9).

Recordings were made in a small *Spartina-Salicornia* marsh at Mission Bay, California, sufficiently near the laboratory so that the equipment could be serviced frequently. The sensors were

placed in a tidal stream within this marsh at about 1 cm above the watersediment interface. All measurements, therefore (except wind velocity, air temperature, and light intensity), are of the tidal water flowing in and out of this channel during rise and fall of the tide.

	NORTHWEST GULF OF MEXICO			PACIFIC COAST				
	ADJACENT BAY	TIDE FLAT	Spartina ZONE	Salicornia ZONE	TIDE FLAT	MARSH CHANNEL	Spartina zone	Salicornia ZONE
Ammoastuta inepta								
Ammonia becarii								
Ammotium salsum								
Arenoparrella mexicana								
Discorinopsis aguayoi								<del>Conce</del> nse
Elphidium spp.								
Jadammina polystoma								
Miliammina fusca					-			
Palmerinella palmerae								
Pseudoeponides andersoni								
Textularia earlandi	1					-		
Tiphotrocha comprimata								
Trochammina inflata								
T. macrescens						<u> </u>	-	

Fig. 1. Generalized distributions of marsh foraminifera in the northwest Gulf of Mexico and the Pacific coast of North America.



Fig. 2. Recordings for 24 hours in marine marsh, Mission Bay, California.

Our principal result is that many of the measurements have a greater variation than anticipated. This variation is both diurnal and seasonal and appears to be controlled by air temperature, amount and duration of sunlight, plant production and metabolism, and tidal flooding and ebbing. Of the parameters measured, those of salinity, water temperature, pH, and oxygen are of greatest interest. During one 24-hour period there was a higher high tide in the morning, preceded and followed by low water, and a lower high tide in the evening (Fig. 2).

Salinity variations are striking and are related to tidal flushing of the marsh. During high tide the salinity is about 34 parts per mil, which is the salinity of the adjacent bay water. By the end of the ebb tide, however, the salinity had gradually increased to about 42 parts per mil; this is high-salinity water draining from the marsh. The high salinity of the water is in part due to evaporation from the marsh. But high salinity appears on the ebbtidal flushing even at night, when evaporation is relatively insignificant, in view of the low temperatures of the air and the high humidity. It is believed that much or most of the marked increase of salinity in the marsh is due to the metabolism of the halophytic marsh plants that excrete excess salt. Water temperature is closely related to air temperature and it varies from about 12° to 20°C during the 24 hours (Fig. 2).

The diurnal regimes of pH and oxygen are closely related, being highest in the daytime when marsh plants are producing oxygen. They are also higher on the flood tide when high pH and high-oxygen water is being introduced from the adjacent bay. They are lowest on the ebb tide when low pH and low-oxygen water is being drained from the marsh. During the 24 hours of this record, pH ranged from 6.9 to 8.3, and oxygen ranged from 30 percent to 130 percent air saturation.

The distributions of values for these four environmental parameters over a long period of time are shown (Fig. 3). The extreme range of water temperature in 1964 was from 5° to 33°C. Temperatures were within the reproductive range for at least one species of foraminifera (*Ammonia beccarii*) for which there is experimental data, 19° to 32°C, about 40 percent of the time (10).

Oxygen ranged from 0 to 275 percent air saturation, and was less than



Fig. 3. Time durations, extremes, and means of values of water temperature, oxygen, pH, and salinity in marine marsh, Mission Bay, California.

100 percent saturation about 75 percent of the time during a 9-month period. The significance of this is not known, because there is little experimental evidence on oxygen consumption by foraminiferans under different conditions.

The pH values ranged from 6.7 to 8.5, with most values greater than 7.0 but markedly less than the pH of sea water in the adjacent bay. These pHvalues, which are lower than sea water, represent a marsh chemistry which probably is an important restricting factor on organisms. Laboratory experiments have been designed to test the physological effect of pH.

Salinity, with accurate continuous recordings for only 2 months, ranged from less than 30 parts per mil to more than 50 parts per mil. Salinities were higher than those of the bay about 75 percent of the time and were higher than 40 parts per mil about 37 percent of the time.

These preliminary results do not apply to every marine marsh, but similar values may be expected in many other marshes. The most striking result is the great range in values of some of the important environmental parameters 23 DECEMBER 1966

measured, and this is probably a general characteristic of marshes. It is believed that the general approach we have used is a reasonable method for defining sedimentary and biological marine environments.

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## **References** and Notes

- 1. F. P. Shepard and D. G. Moore, Bull. Amer.
- Assoc. Petrol. Geol. 39, 1463 (1955). 2. P. C. Scruton, *ibid.* 40, 2864 (1956).
- F. B. Phleger, Ecology and Distribution of Recent Foraminifera (Johns Hopkins, Bal-3.
- timore, 1960). R. H. Parker, Mem. Amer. Assoc. Petrol. 4. R. H. 331 (1964) Geol.
- Geol. 331 (1964). W. R. Walton, in Approaches to Paleoecology, J. Imbrie and N. D. Newell, Eds. (Wiley, New York, 1964) p. 151. E. L. Winterer and D. L. Durham, U.S. 5.
- 6. Surv. Profess. Papers 334-H, 275 Geol.
- (1962). R. E. Stevenson and K. O. Emery, Allan Hancock Found. Occas. Papers 20, 1 (1958). 7. R. E. B. Phleger, Limnol. Oceanog. 10, R169 8. F. B. (1965)
- J. S. Bradshaw, Tech. Rep. Mar. Foraminif-era Lab., Scripps Institution of Oceanography
- (1965). J. S. Bradshaw, Contrib. Cushman Found. 10.
- Foraminiferal Res. 12, 87 (1961). Supported by the American Chemical Society, 11.
- National Science Foundation, and Office of Naval Research.
- 20 September 1966

## **Electrode for Sensing Fluoride** Ion Activity in Solution

Abstract. Electrodes constructed from single-crystal sections of rare earth fluorides respond to fluoride ion activity over more than five orders of magnitude and show a high selectivity for fluoride over other common anions. These electrodes can be used for either direct measurement of fluoride ion activity or detection of the end point in titration.

There has been no way of determining fluoride single-ion activities in aqueous solution, although such measurements are of obvious interest in studying fluoride complexes in solution, in following uptake and metabolism in both plants and animals, and in similar applications. Furthermore, the analysis of drinking water and body fluids for low concentrations of fluoride has been a tedious procedure, usually requiring a distillation step to eliminate interferences (1).

We report the development of an electrode-type of sensor, which will give a Nernstian response over a wide range of fluoride ion activity and which is highly selective for fluoride in the presence of many ions commonly found in public water supplies and biological systems.

Construction of the electrode is similar in principle to that of a conventional glass pH electrode, except that the membrane material is a disk-shaped section of single-crystal rare earth fluoride, such as LaF<sub>3</sub>, NdF<sub>3</sub>, or PrF<sub>3</sub>. The section, typically 1 cm in diameter and 1 to 2 mm in thickness, is sealed to the end of a rigid polyvinyl chloride tube with epoxy cement. The only critical step is assembling the electrode so that the seal is watertight. The tube is filled with a solution containing both fluoride and chloride ions (typically 0.1M NaF and 0.1M KCl), and electrical contact is made with a silversilver chloride wire. The electrode is calibrated on known sodium or potassium fluoride solutions and used with an external reference electrode, such as the saturated KCl-calomel type that we used. Electrode potentials were attained rapidly and were stable. Measurements were reproducible to within less than 1 mv.

Pure rare earth fluorides are unique among known crystalline materials in having a high electrical conductance that results from mobile fluoride ions

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