planet. The subsequent enrichment is then the ratio of 2×10^{-2} to the present equivalent H_2 mixing ratio. The enrichment given by the present HD/H_2 ratio of $(3.2 \pm 0.2) \times 10^{-2}$ is 100 ± 12 referred to an initial ratio of 3.2×10^{-4}. It implies that the mixing ratio of H_2O is now 200 ± 25 ppm. This is in good agreement with the 100 to 200 ppm measured by the Venera spectrophotometer (*1*, *2*).

The possibility that there is a large abundance of deuterium in the upper atmosphere of Venus was suggested by the Mariner 5 Lyman α observation (*12*). It was recently asserted again by McElroy *et al.* (*13*), who argue that a mass 2 ion detected by the ion mass spectrometer on the Pioneer Venus orbiter is D^+. The D/H ratio of about 1×10^{-2} for the bulk atmosphere implied by this interpretation is one that could have resulted from nonthermal loss of hydrogen resulting from collision of fast oxygen atoms produced in dissociative recombination of O_2^+ with hydrogen atoms. The ratio of $(1.6 \pm 0.2) \times 10^{-2}$ obtained by the LNMS agrees with the value required by McElroy *et al.* The lifetime of 9×10^8 years for hydrogen deduced from their mechanism would allow the water vapor mixing ratio to grow from 200 ppm to 2 percent in about 4.2×10^9 years. There is time enough left for hydrodynamic escape to have exhausted the equivalent of a terrestrial ocean. Although the measurement reported here cannot reveal how much additional water may have been outgassed from the planet before the critical mixing ratio of 2×10^{-2} was reached, it would be astonishing if the quantity were not considerably larger than this lower limit (0.3 percent of a terrestrial ocean).

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7. Correction was made for contributions from $^{18}O^+$, $^{36}Ar^{2+}$, $^{18}OH^+$, and $^{38}Ar^{2+}$. Interferences from other species such as HCl, F, and H_3O were found to be negligible.
8. The HDO/H_2O and HD/H_2 ratios are twice the D/H ratios. The D/H ratio for seawater is 1.56×10^{-4} [R. Hagemann, G. Nief, E. Roth, *Tellus* **22**, 712 (1970)].
9. The data for frames 75 and 77 have been corrected to allow for deliberate reduction of the ionization voltage from 70 V to 30 and 22 V, respectively, in these frames, as in frames 44, 46 and 108, 111.
10. If a 3σ error is allowed for in evaluating E_{18} and E_{19}, a ratio of 2.2×10^{-2} permits nonnegative values for frames 63 through 77. However, such a value of R calls for negative E_{18} and E_{19} for central values of S_{18} and S_{19} at all frames and for all 1σ extremes except at frames 73 and 77.
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13. M. B. McElroy, M. J. Prather, and J. M. Rodriguez [*Science* **215**, 1614 (1982)] show that the present escape modes on Venus would imply a lower limit of 800 g cm^{-2} of H_2O on Venus 4.5 billion years ago. Escape of deuterium is negligible, and it is taken to be so in this report as well.
14. We thank G. Carignan and K. C. Lohmann for useful comments. Supported by NASA grants NAS2-9126 and NAGW-64.

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Uptake of Dissolved Sulfide by *Spartina alterniflora*: Evidence from Natural Sulfur Isotope Abundance Ratios

Abstract. *The difference in the stable sulfur isotope ratios of sulfate and sulfide in marsh pore water was used to verify the uptake of hydrogen sulfide by the salt marsh cordgrass* Spartina alterniflora *in a North Carolina salt marsh. Most of the plant sulfur derived from pore-water sulfide was recovered as sulfate, an indication that the sulfide had been oxidized within the plant. The analysis of the sulfur isotope ratios of other coastal halophytes may be a useful technique for determining whether sulfide is taken up by plants in saline wetlands.*

Spartina alterniflora, the salt marsh cordgrass, is the dominant vascular macrophyte of the regularly flooded salt marshes along the east coast of the United States (*1*). The rapid rates of sulfate reduction measured in salt marsh sediments (*2*) suggest the presence of adaptive mechanisms that enable *Spartina* to persist in sediments where dissolved sulfide concentrations frequently exceed those that are toxic to rice (*3*). The diffusion of oxygen through aerenchyma (air spaces) from aerial portions of the plant to the roots combined with the leakage of oxygen from the roots to the surrounding sediments, which oxidize the pore-water sulfide, has been postulated as the mechanism that prevents sulfide toxicity in *Spartina* (*4*). The oxidation-reduction potentials in sediments of a New England salt marsh are higher in areas where *Spartina* is present than in unvegetated sediments, an indication that roots or rhizosphere bacteria possess limited oxidizing ability (*5*). However, in marshes where organic matter accumulates rapidly, the sulfate reduction rates greatly exceed the capacity of *Spartina* plants to supply oxygen to the sediments and substantial concentrations of dissolved sulfide accumulate in marsh pore waters (*6*).

Short-term hydroponic experiments have demonstrated that *Spartina* can take up ^{35}S-labeled dissolved sulfide without short-term toxicity effects (*6*). A technique was needed, however, to determine whether sulfide uptake also occurs in *Spartina* in the natural marsh environment. The isotopic fractionation effect associated with dissimilatory reduction of sulfide by bacteria seemed to present a way to determine the source of sulfur taken up and incorporated by *Spartina*. Reduction of ^{32}S-sulfate by bacteria in anaerobic marine sediments typically proceeds at a rate 1.02 to 1.03 times faster than reduction of ^{34}S-sulfate; as a result, the $^{34}S:^{32}S$ ratio in the product sulfide is 1.02 to 1.03 times lower than that of the initial sulfate (*7*). The difference between the isotopic composition of the sulfate and sulfide present in marine sediments is relatively easily resolved by mass spectrometry, and we felt that determination of the isotopic composition of plant sulfur would indicate the form of sulfur taken up by the plants from the sediments.

To determine whether sulfide was taken up and incorporated by *Spartina* in a natural marsh, the isotopic composition of plant sulfur [expressed as $\delta^{34}S$ (*8*)] was compared with the isotopic composition of sulfate and sulfide in marsh pore waters. *Spartina* plants were also grown

Table 1. Standing stock and isotopic composition of sulfur species within *Spartina alterniflora* and the external medium.

Growth environment	External medium (mmole/liter)		Plant tissue (milligrams of sulfur per gram)		
	Sulfate	Sulfide	Total sulfur	Free sulfate	Residual
		Standing stock			
Hydroponic	32.7	None	6.2	3.6	2.6†
Natural marsh	18.6*	1.4*	12.7	10.1	2.6†
		Isotopic composition (δ^{34}S)			
Hydroponic	5.3	None	4.5	5.9	2.6†
Natural marsh	30.4*	−5.4*	0.0	−0.7	2.7†

*Values determined as the mean of data points in the root zone (1 to 4 cm) shown in Fig. 1. †Calculated on the basis of mass and isotopic balance.

in aerated hydroponic culture with sulfate as the sole sulfur source to determine the extent of isotope fractionation associated with the uptake and incorporation of sulfate (*9*).

Sulfate concentrations in the natural marsh pore water declined sharply with depth as a result of sulfate reduction (Fig. 1). The δ^{34}S values of pore-water sulfate increased from +20.0 in the overlying water to +65.1 at 17 cm in a curvilinear manner. A break in the logarithmic increase of sulfate δ^{34}S values occurred between 6 and 12 cm, possibly as the result of the reoxidation of sulfide to sulfate by oxygen diffusing from the plant roots. The instantaneous isotope fractionation coefficient (α) calculated from a Rayleigh plot of the data (*10*) was 1.0254, comparable to estimates for other marine sediments (*10*). The δ^{34}S values of the sulfide, which we estimated by using the value of α (1.0254) determined from the Rayleigh plot, increased from −5.4 at the sediment surface to +41.5 at 19 cm.

The δ^{34}S of the total sulfur of the hydroponically grown plants (Table 1) showed a slight decrease from that of the sulfate in the hydroponic medium, but the δ^{34}S of the free sulfate in the plant tissue was not significantly different from that of sulfate in the external medium. The residual plant sulfur fraction, comprised primarily of organic sulfur with a possible minor contribution of elemental sulfur, had a calculated δ^{34}S value of +2.6; this value was 2.7 per mil lower than the δ^{34}S of the sulfate in the external medium and indicated that the isotopic fractionation effect associated with assimilatory reduction of sulfate by *Spartina* was low and within the range reported for other plant species (*11*).

The low δ^{34}S values of the total sulfur (0.0) and inorganic sulfate (−0.7) within *Spartina* tissue from the natural marsh indicate that sulfide was taken up by the plants. If the sulfide had been oxidized to sulfate outside the plant roots (for example, in the rhizosphere) and if sulfate were the only form of sulfur taken up by the plant, the isotopic composition of the plant sulfur would have more closely resembled pore-water sulfate values than those of sulfide, because the pore-water sulfate pool in the root zone of the marsh is considerably larger and has much higher δ^{34}S values than the dissolved sulfide pool. For example, in the root zone of the marsh that we studied, the sulfate and sulfide concentrations were 18.6 and 1.4 m*M*, respectively. Using the δ^{34}S value of +30.4 for sulfate and −5.4 for sulfide (Table 1), we would expect the rhizosphere and plant sulfur to have a δ^{34}S value of +27.9.

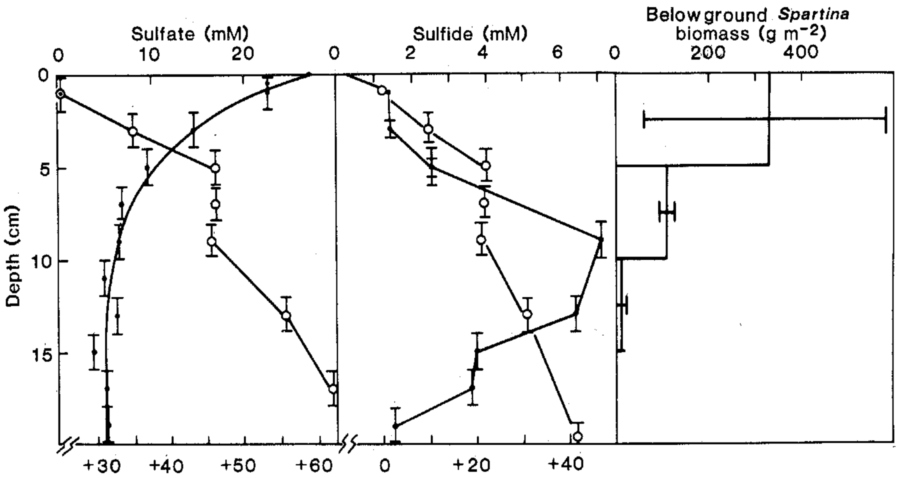

Fig. 1. *Spartina alterniflora* belowground biomass and the concentrations (closed circles) and isotopic composition (open circles) of sulfate and sulfide in marsh pore water.

The uptake of sulfide per se is not remarkable. Sulfide uptake is known to be responsible for nodal damage and yield reductions in rice (*12*). Furthermore, at the *p*H values of marsh pore water (6.0 to 6.5), most of the sulfide present is gaseous hydrogen sulfide which can readily diffuse into the roots. As far as we know, *Spartina alterniflora* is unique among vascular plants studied in that no acute toxicity effects result from sulfide uptake over a long growing season; this result suggests that internal oxidation or detoxification mechanisms exist within the plant.

The accumulation of sulfate derived from pore-water sulfide within *Spartina* plants suggests that oxidation may be enzymatic. If sulfide were oxidized by molecular oxygen during transit of the vascular tissue, thiosulfate, tetrathionate, sulfite, and elemental sulfur would be more likely products than sulfate (*13*). Although *p*H effects and microbial catalysis might also be responsible for the production of sulfate (*14*), enzymatic oxidation might be important in root tips that have high respiration rates but poorly developed aerenchyma.

Precise calculation of the sulfide contribution was not possible without more data because all the sulfide taken up by *Spartina* is probably not derived from sulfate with a constant δ^{34}S value. It seems likely that there is seasonal variation in the value of α associated with sulfate reduction in marsh sediments due to temperature variations and fluctuations in the amount and composition of carbon inputs to the sediments. In particular, the release of ethanol to the sediments by *Spartina* roots during periods when the roots experience oxygen stress may result in higher values of α and more negative values of sulfide δ^{34}S (*15*). Support for that hypothesis comes from estimates for α of 1.03 to 1.06 obtained in the same marsh during October 1977 when *Spartina* was senescing (*6*).

The ratios of stable sulfur isotopes have been used to determine the incorporation of anthropogenic sulfur dioxide by plants (*16*) and have been suggested as indicators of photosynthetically reduced sulfur in the atmosphere (*17*). Our data indicate that the stable isotope composition of sulfur pools in *Spartina alterniflora* demonstrates the uptake and internal oxidation of sulfide by the plant and may be useful in determining sulfide uptake by other plant species growing in anaerobic sediments.

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8. $$\delta^{34}S = \frac{^{34}S/^{32}S_{sample} - {}^{34}S/^{32}S_{standard}}{^{34}S/^{32}S_{standard}} \times 100$$
   where $^{34}S/^{32}S_{standard}$ refers to Canyon Diablo meteoritic hydrotroilite and $\delta^{34}S$ has the units per mil (*7*).
9. Our experimental methods may be summarized as follows. The plants (all representing the medium-height form of *Spartina*) were washed free of sediment and transferred to aerated hydroponic culture from marsh sediments in March 1979. We gradually salinized the hydroponic medium by replacing transpired water with Instant Ocean water until a salinity of 35 per mil was attained. The medium was aerated constantly and replaced weekly until 5 September 1979, when the plants were harvested. During the 6-month period, the culms increased in wet weight from between 0.8 and 1.0 g to between 7 and 10 g. Aboveground tissue was separated from roots and rhizomes, washed in distilled water, dried to constant weight at 60°C, and ground in a Wiley mill. On 23 August 1979, aboveground tissue of *Spartina* was collected from plants in the same marsh from which the hydroponically grown plants had been collected. Cores were also taken from the marsh sediment for the determination of concentrations and isotopic composition of sulfate and sulfide in pore water.

   Our analytical procedure consisted of the following. Pore water was separated from 2-cm-thick segments of cores by centrifugation. Sulfide (5-ml aliquots) was precipitated with zinc acetate and subsequently acidified and swept by a nitrogen stream into aqueous silver chloride and precipitated as silver sulfide. Pore-water sulfate and sulfate within the plants were determined gravimetrically after precipitation as barium sulfate. Total plant sulfur was also determined gravimetrically as sulfate after combustion in a Parr oxygen bomb. For isotopic analyses, barium sulfate precipitates and total sulfur analyses were reduced with a mixture of hydriodic, phosphorous, and hydrochloric acids to form hydrogen sulfide, which was swept in a nitrogen stream and collected as silver sulfide. The isotopic composition of the sulfide was determined by combustion of the silver sulfide in a stream of oxygen and mass spectrometry of the resultant sulfur dioxide by the procedure of J. Forrest and L. Newman [*Atmos. Environ.* **7**, 561 (1973)].
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Curiosities in Periodic Precipitation Patterns

Abstract. *Observations have been made of several types of Liesegang patterns that are more complex than the usual concentric rings or parallel bands of precipitate. The structures observed show radial gaps, segmentation, irregular patterns within concentric rings, and the formation of spiral precipitation bands instead of sets of parallel Liesegang bands.*

In a series of investigations of periodic precipitation processes, in part reported in (*1*, *2*), we found some interesting curiosities to be described briefly here. In a standard Liesegang experiment a soluble electrolyte diffuses into a solution, containing another electrolyte, to which a gel-forming material has been added. On interdiffusion a chemical reaction occurs in which a weakly soluble salt is formed and precipitated in discontinuous bands parallel to the front of the diffusing electrolytes (*3*). In an effectively "one-dimensional" Liesegang experiment the two electrolyte solutions are placed in a cylindrical container, such as a test tube, and a set of parallel bands of precipitate appears perpendicular to the axis of the test tube. A typical "two-dimensional" Liesegang system is prepared in a flat container, such as a petri dish, so that initially a thin circular section of one of the two solutions is surrounded by a layer of the second electrolyte medium. Interdiffusion takes place in the radial direction and the resulting pattern consists of concentric rings of precipitate. Depending on the initial salt concentrations, the rings form either in the inner or in the outer section of the container. In this report we present observations of radial gaps, pocket-like structures, segmentation, and irregular patterns within concentric Liesegang rings and of spiral precipitation bands in one-dimensional Liesegang experiments (*4*).

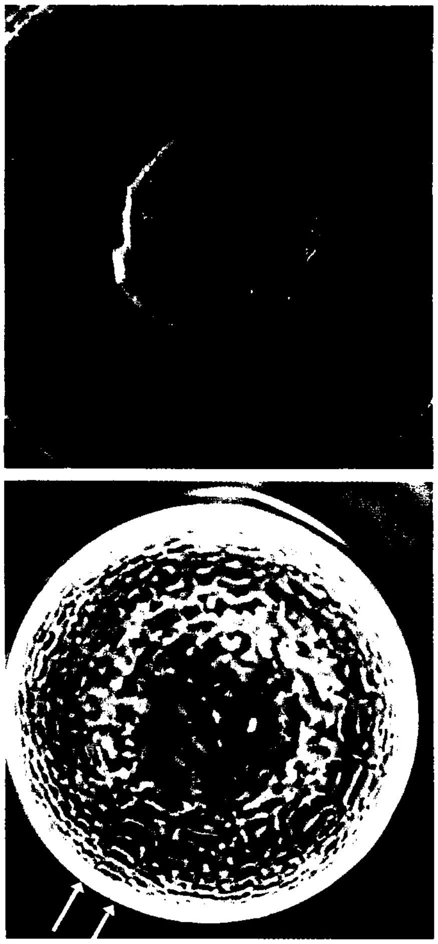

Fig. 1. Radially aligned gaps in concentric rings of PbI_2 precipitate in Liesegang systems with ring formations away from (top) and toward the center of (bottom) a petri dish, after 5 days. The arrows point to one of the regions in which a radial set of pocket-like structures appears. Initial electrolyte concentrations in the inner and outer sections of the containers: (top) 0.12*M* KI and 0.012*M* $Pb(NO_3)_2$; (bottom) 0.006*M* $Pb(NO_3)_2$ and 0.12*M* KI with 0.3*M* $Ba(NO_3)_2$ added (*16*). All solutions contained 1 percent agar-agar gel. Nearly to scale.

We obtained two-dimensional Liesegang structures with lead iodide as the precipitate by covering the bottom of a petri dish (diameter, 90 mm) with a layer 1 to 4 mm thick of 0.005 to 0.015*M* $Pb(NO_3)_2$ in 0.5 to 1.0 percent agar gel. After the gel had solidified we removed a circular portion of the layer (diameter, 30 to 60 mm) from the center of the dish and subsequently filled this empty section to the same height with 0.06 to 0.12*M* KI also containing 0.5 to 1 percent agar (*5*). Within a period of typically 2 days a set of concentric rings of PbI_2 precipitate appeared in the lead solution [outer region of the dish (Fig. 1, top)]. Ring formation occurred in the inner circular section when the $Pb(NO_3)_2$ solution was placed in the center of the dish and the