that this is functionally the case, direct proof of a photoaffinity label requires demonstration that the ligand becomes covalently attached to the receptor. Noncovalent interactions would not be expected to survive the denaturing sodium dodecyl sulfate (SDS) gel conditions; thus, localization of radioactivity in a specific region of the gel (shown in Fig. 1) is indicative of a covalent label.

Pfister and Arntzen (*1*) and Pfister *et al.* (*3*) compared chloroplast membrane polypeptides from triazine-resistant and triazine-susceptible biotypes of the same weed species. Triazine resistance was shown to be due to a change in the binding affinity for atrazine. However, since functionality was lost during the analysis, it was not possible to prove which specific peptides were directly related to the phenomenon of herbicide resistance. The photoaffinity approach labels the molecule in a functional situation. Since the label is covalently attached to the receptor, it remains stable under conditions that destroy functional activity. Pfister *et al.* (*7*) showed that only in chloroplast membranes from susceptible plants was there specific covalent attachment of [^{14}C]azidoatrazine to a polypeptide of 32,000 daltons.

Mild trypsin treatment of photosystem II particles resulted in loss of sensitivity to the herbicide diuron and concomitant loss of two protein bands of molecular weight 32,000 and 27,000 (*8*). Since diuron and atrazine bind to the same site (*2*, *3*), it is likely that the azidoatrazine receptor identified here is identical to the trypsin-sensitive 32,000-dalton peptide. It is interesting to speculate that this peptide may also be the rapidly turned over 32,000-dalton membrane protein that accumulates during light-dependent chloroplast development (*9*) or the 32,000-dalton peptide implicated in proton translocation in the chloroplast membrane adenosinetriphosphatase, CF_0 (*10*).

Little is known about the biochemistry of protein-bound quinones. Azidoatrazine may be useful in the study of the detailed protein chemistry of photosystem II.

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Pelagic Sedimentation of Aragonite: Its Geochemical Significance

Abstract. *The relative importance of the pelagic flux of aragonite, as compared to calcite, to the deep-sea floor has been evaluated by means of a quantitative x-ray diffraction study of samples collected from sediment traps and from an unusually shallow portion of the open Atlantic Ocean (the Rio Grande Rise). The results suggest that the aragonite flux constitutes at least 12 percent of the total flux of calcium carbonate on a worldwide basis. The presence of high-magnesium calcite in several samples suggests that some of the calcareous material falling to the deep-sea floor may be derived from the long-distance transport of debris from shallow-water benthic organisms as well as from the settling of planktonic remains. This observation supports the contention that 12 percent represents a minimum value. Aragonite and high-magnesium calcite transported laterally from shallow-water regions, upon dissolution during settling into deeper water, may contribute to the neutralization of excess anthropogenic carbon dioxide added to the oceans.*

Large amounts of calcium carbonate ($CaCO_3$) are precipitated from seawater by marine organisms, which use the $CaCO_3$ to form shell-like exoskeletons. Upon death, lateral transport, and sedimentation, some of the carbonate undergoes dissolution in the deep sea, and this dissolution, along with the original precipitation, ultimately exerts a major influence on how much CO_2, including excess CO_2 produced by human activities, can be taken up by the sea (*1*). It is normally assumed that $CaCO_3$ falling to the deep-sea floor is present as calcite in the form of coccoliths and foram tests; however, a large proportion may instead consist of aragonite. This aragonite, which is present in the form of pteropod shells and laterally transported debris from shallow-water benthic organisms, does not accumulate in most places because it is more soluble than calcite and is highly undersaturated in the deep sea and consequently dissolves away before it can be buried. Because of the relative lack of aragonite in deep-sea sediments due to dissolution, it has been assumed that aragonite sedimentation in the pelagic realm is unimportant relative to calcite sedimentation. However, the finding of abundant aragonite in plankton and in rare pelagic sediments which are sufficiently shallow that aragonite dissolution on the bottom has not occurred (*2*) indicates that aragonite sedimentation is probably far more important than previously recognized.

In the earlier work (*2*), the quantitative

Table 1. Aragonite (A) and calcite (C) from sediment traps at the PARFLUX sites.

Depth (m)	Flux (mg m^{-2} day^{-1})								A % of total $CaCO_3$ flux
	< 63 μm		63 μm to 1 mm		< 1 mm		> 1 mm		
	A	C	A	C	A	C	A	C	
Panama Basin (station PB) (5°21'N, 81°53'W)									
667	(< 1)	20.4*	3.0	12.0			2.4	4.8	12.7
1268	(< 2)	24.4	1.0	11.6			1.7	0.8	6.9
2869	(< 1)	34.3	1.7	14.9			1.3	1.1	5.7
3769	(< 2)	28.8	0.4	12.9			1.3	0.5	3.9
3791	(< 2)	30.8	0.8	15.4			1.6	1.0	4.9
Equatorial Atlantic (station E) (13°30.2'N, 54°00.1'W)									
389					2.5	22.0*	14.3	4.0*	38.9
988					2.3	23.1*	1.1	0.6	12.5
3755					1.8	23.7*	(Total $CaCO_3$ = 0.6)		7 to 9
5068					2.0	20.5*	(Total $CaCO_3$ = 0.9)		9 to 12

*Samples containing high-magnesium calcite.

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importance of pelagic aragonite sedimentation could not be precisely evaluated because of difficulty in converting counts and estimates of shell abundance reported by other workers to the percentage of aragonite (by weight). In addition, as far as we know, no direct data on the flux rate of either calcite or aragonite to the bottom have been available. Here we attempt to rectify the situation by presenting new data, based on the use of sediment traps and x-ray diffractometry, on the rate of aragonite sediment flux to the sea floor. To complement our results, a quantitative analysis of bottom sediments from a shallow pteropod-rich locality (the Rio Grande Rise) for aragonite content was also carried out.

Samples of sedimenting solids were collected as part of the PARFLUX program (*3*). Details of the sampling are given in (*3*). Briefly, the method consists of the use of a series of sediment traps suspended for several months at fixed water depths by a taut wire moored to the bottom. Sediment samples were chosen for the present study from the trapped material collected at two localities, the equatorial Atlantic (station E) and the Panama Basin in the Pacific (station PB). Exact locations are given in Table 1. Upon return to the laboratory, the trapped sediment from each depth was split, fractionated by grain size, and dried. Subsamples were then analyzed for total $CaCO_3$ by standard gasometric and weight loss methods (*3*) and for aragonite content (relative to total $CaCO_3$) by x-ray diffractometry. The heights of the principal peaks of aragonite (111) and calcite ($10\bar{1}4$) in x-ray diffractograms were used. A standard curve relating peak height fraction to the percentage of aragonite (by weight) was constructed through the use of end-member samples consisting of weighed amounts of pure pteropods (aragonite) and planktonic forams (calcite) obtained from the traps by handpicking. We conducted the x-ray analysis by using CuKα radiation with a scan speed of $^1/_4°$ 2θ per minute (θ is the glancing angle). In several samples the calcite diffraction peak was seen to include a high-angle "shoulder" due to the presence of magnesian calcite. We determined the position of the diffraction maximum of this shoulder by subtracting the background contributed by pure calcite from the actual diffraction trace. We calculated the magnesium content of the magnesian calcite from the resulting value, using the unit cell and diffraction data of Graf (*4*).

In addition to the sediment trap material, we also studied a few samples of surficial sediment collected by gravity coring, from the Rio Grande Rise of the South Atlantic Ocean, for their relative aragonite and calcite contents by the same x-ray diffraction technique. The Rio Grande Rise was chosen as an area of study because of its unusual shallowness and great distance from land. Samples were selected from the Woods Hole core storage facility and chosen from locations that showed minimum evidence of winnowing. In two cases, earlier complete sampling made it impossible to obtain core tops.

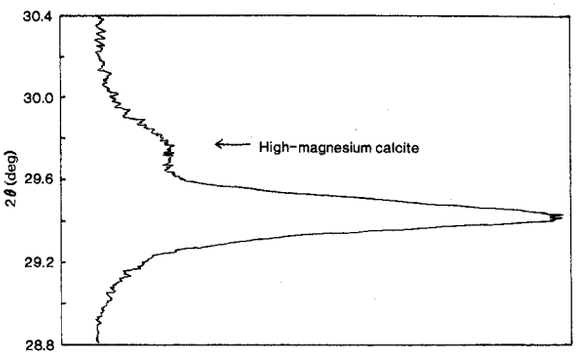

Fig. 1. Direct tracing of the x-ray diffraction pattern for a sediment trap sample from a depth of 389 m, < 1-mm fraction, station E; CuKα radiation, 1/8° 2θ per minute; time constant, 2 seconds. The large peak is the ($10\bar{1}4$) principal peak of low-magnesium calcite.

Results, reported as fluxes for aragonite and calcite at the two PARFLUX sites, are shown in Table 1. Maximum values of the aragonite flux occur in the uppermost traps. The decrease in aragonite, both absolutely and relative to calcite, with depth can be attributed to the partial dissolution of aragonite, possibly during sedimentation, but more likely while the aragonite was "sitting" on each trap. Seawater below a few hundred meters in the Pacific Ocean and below about 1000 to 2000 m in the Atlantic Ocean is undersaturated with respect to aragonite (*2*, *5*, *6*). Thus, the uppermost traps represent the least amount of dissolution and the closest approximation to the original flux prior to dissolution. (An exception is the coarse material at 389 m at station E. Here it is apparent from the presence of fresh soft tissue within shells that the sediment receptacle at the bottom of the trap was invaded by living pteropods during the trapping period. The pteropods then died upon exposure to poison retained within the receptacle intended to inhibit the microbiological decomposition of organic matter. The dead pteropods contributed their shells to the normally accumulating solids and thereby produced an anomalously high flux.)

Table 2. Aragonite, expressed as a percentage of the total $CaCO_3$ in surficial sediments of the Rio Grande Rise.

Location	Water depth (m)	Sediment depth (cm)	Aragonite (%)
30°03′S, 35°31.5′W	2343	0 to 2	21
29°38′S, 34°40′W	1840	0 to 4	10
31°58′S, 36°34′W	2739	0 to 2	~ 4
30°00′S, 35°34′W	1840	2 to 4	0
29°59.8′S, 35°34′W	2158	2 to 4	0

The percentages of aragonite determined on samples from the Rio Grande Rise are shown in Table 2. High aragonite content is present only in samples taken as close as possible to the sediment-water interface. During burial, aragonite is presumably removed by dissolution so that none is found at depth in the sediment, even at depths of 2 to 4 cm. The sample from 0 to 4 cm represents a minimum value since it is likely that it contains a mixture of high-aragonite surface sediment and low-aragonite buried sediment that has undergone dissolution. The sample at 2739 m also represents a minimum value because of probable partial dissolution of aragonite at this depth, which is well below the saturation depth for aragonite.

The results in Tables 1 and 2 indicate that, at the locations studied, aragonite constitutes at least 12 percent of the total $CaCO_3$ sedimenting to the bottom. This number is considerably less than the earlier estimate of 50 percent (*2*). However, because preferential dissolution of aragonite relative to calcite may have occurred while aragonite was "sitting" on the traps or on the bottom, and because the trap locations and the Rio Grande Rise are so far from land that little shallow water-derived aragonite is present, the actual values may be considerably higher than 12 percent (for example, the sample at 2343 m in Table 2). In support of this conclusion are our earlier measurements on Bermuda Pedestal slope sediments (*6*), where much higher aragonite/calcite peak height ratios were found, due both to less pteropod dissolution at the shallower depths sampled and to an input of detrital aragonite from

the disaggregation of benthic organisms living in the nearby shallow waters of the Bermuda Platform.

The importance of a possible input of detrital carbonate, originally secreted in shallow water, to the deep sea is supported by our sediment trap results. In the < 63-μm fraction at 667 m of station PB and at all depths at station E, the calcite x-ray diffraction peak exhibited a small high-angle "shoulder" due to the presence of high-magnesium calcite (Fig. 1). This high-magnesium calcite, with 13 mode mole percent $MgCO_3$ [determined from the unit cell and diffraction data of Graf (*4*)] could be derived only from shallow-water benthic organisms since no planktonic organism is known that secretes calcite with such a high magnesium content (*7*, *8*). High-magnesium calcite, along with aragonite, are the characteristic phases secreted by shallow-water calcareous organisms. Even though the trap locations are far from the nearest land (more than 200 km in both cases), there is still evidence of a shallow-water component of the $CaCO_3$ found in the traps. Traps located closer to continental shelves or oceanic islands would most likely show a higher aragonite content. The production rate of aragonite in shallow waters is extremely high (*7*, *9*), and just a small "leak" of shallow-water carbonate to nearby portions of the deep sea by resuspension, horizontal transport, and settling would considerably augment the pelagic flux of biogenic aragonite. There is thus additional evidence for the contention that 12 percent is an absolute minimum value for aragonite sedimentation relative to calcite sedimentation on a worldwide basis.

If aragonite and associated high-magnesium calcite fluxes to the deep sea from oceanic islands and continental shelves are quantitatively significant, then dissolution of this material at depth may constitute an important mechanism for the neutralization of excess anthropogenic CO_2 added to the oceans. This is so because aragonite and high-magnesium calcite are distinctly more soluble than low-magnesium calcite (as found in planktonic foraminifera and coccoliths), and consequently they can dissolve at much shallower depths. If the eroded aragonite and high-magnesium calcite particles are sufficiently small that they settle very slowly, then dissolution during sedimentation may occur at relatively shallow depths, and as a result some anthropogenic CO_2 that has penetrated to these depths may be neutralized. [Evidence for extensive in situ $CaCO_3$ dissolution in the Pacific Ocean has recently been given by Fiadeiro (*10*).] Sediment trap studies conducted near carbonate-rich oceanic islands are needed to test this hypothesis.

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Retinal Chromophore of Rhodopsin Photoisomerizes Within Picoseconds

Abstract. *A new picosecond resonance Raman technique shows that resonance Raman lines characteristic of a distorted all-*trans *retinal appear within 30 picoseconds after photolysis of rhodopsin or isorhodopsin. This finding suggests that isomerization is nearly complete within picoseconds of the absorption of a photon.*

The light-absorbing molecule in all known visual systems is 11-*cis* retinal, a chromophore derived from all-*trans* retinol (vitamin A) (*1*). Rhodopsin, the photoreceptor pigment in vertebrate retinal rod cells, consists of 11-*cis* retinal bound to opsin, a 38-kilodalton protein. Photoisomerization of this bound retinal chromophore from the 11-*cis* to the all-*trans* form triggers the amplification cascade that leads to a nerve impulse (*2*).

Rhodopsin has a strong absorption peak centered at 500 nm due to its 11-*cis* retinal chromophore (*1*). Absorption of a photon leads to the formation of bathorhodopsin, a photolytic intermediate with a broad absorption band centered at 540 nm (*3*). Picosecond absorption studies have shown that this 540-nm absorption band appears, and the 500-nm rhodopsin absorption band is depleted in less than 6 picoseconds after irradiation (*4*-*6*). The precise structure of this rapidly formed photolytic intermediate has been the subject of controversy. One interpretation is that the chromophore in this intermediate, presumed to be bathorhodopsin, is essentially in the all-*trans* form (*3*, *7*, *8*). However, there has been doubt as to whether the sizable atomic motion required for the photoisomerization of retinal could take place on a picosecond time scale. An alternative hypothesis attributing the formation of bathorhodopsin to a very rapid proton transfer instead of an isomerization has been advanced (*5*).

Resonance Raman spectroscopy can provide valuable information concerning the nature of the primary event in vision. Resonance Raman spectra display vibrations that are coupled to electronic tran-

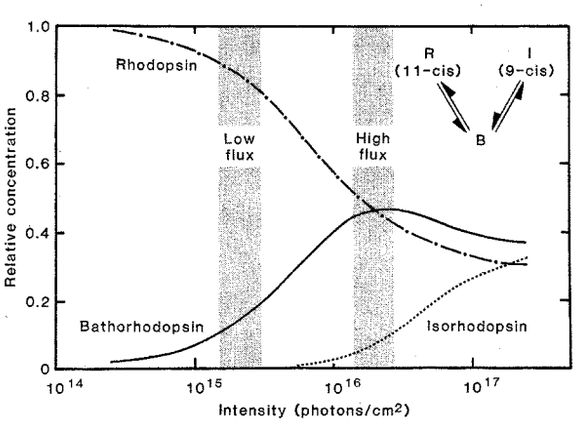

Fig. 1. Relative concentrations of rhodopsin (*R*), bathorhodopsin (*B*), and isorhodopsin (*I*) in the illuminated volume as a function of the intensity of a picosecond light pulse. The proportions of these species were calculated from known absorption cross sections and photoconversion quantum yields (*17*).

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