Naval Research Reviews

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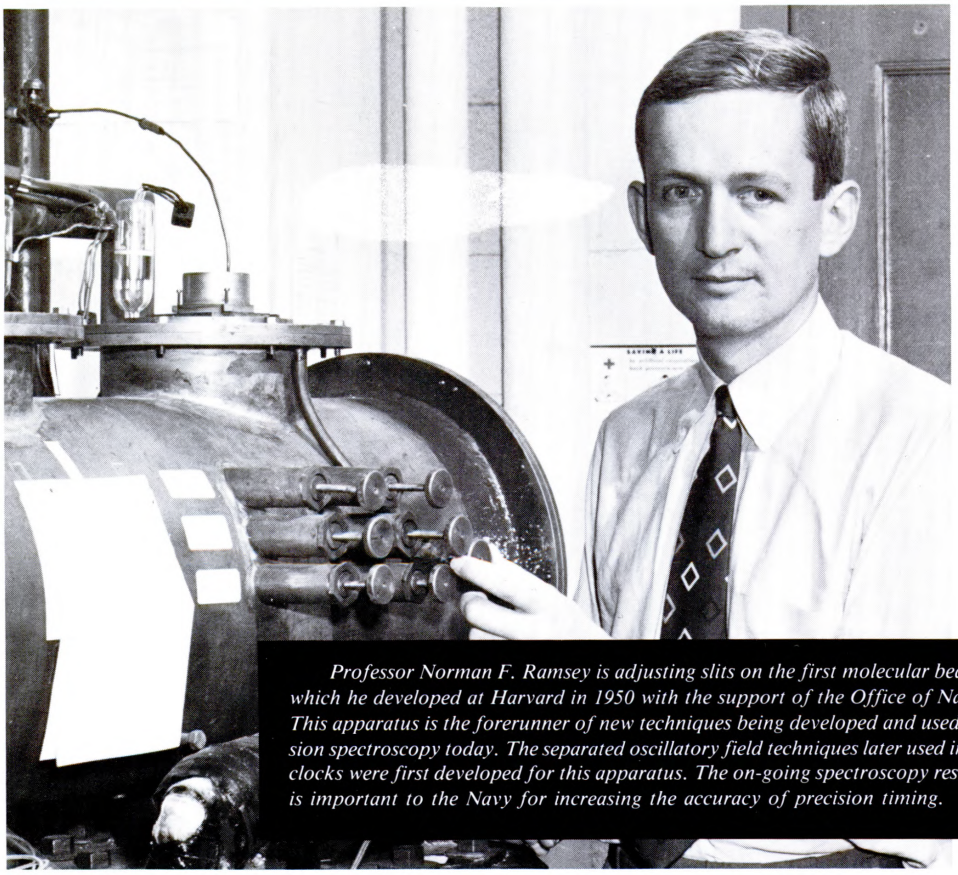
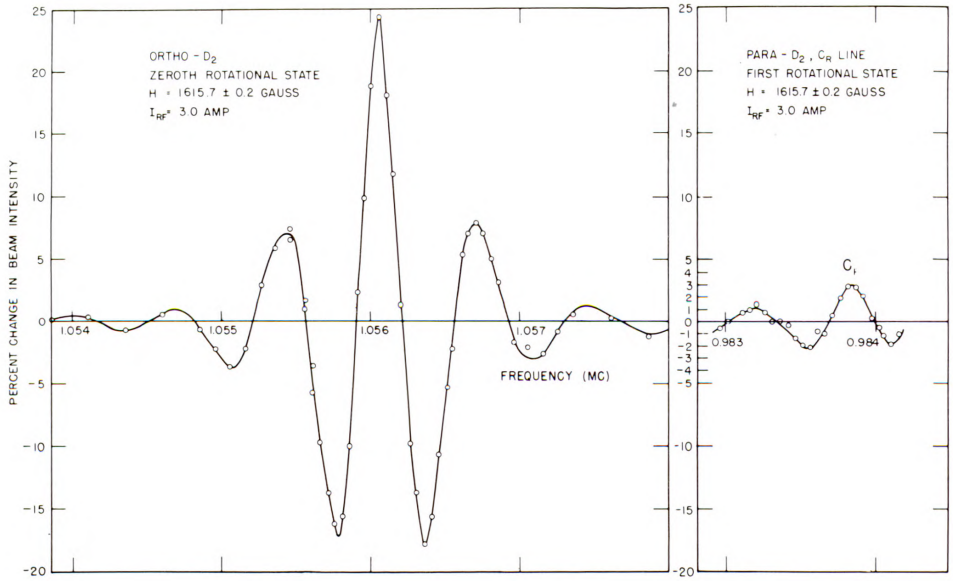
Ocean Chemistry



Professor Norman F. Ramsey is adjusting slits on the first molecular beam apparatus, which he developed at Harvard in 1950 with the support of the Office of Naval Research. This apparatus is the forerunner of new techniques being developed and used in high precision spectroscopy today. The separated oscillatory field techniques later used in cesium beam clocks were first developed for this apparatus. The on-going spectroscopy research of ONR is important to the Navy for increasing the accuracy of precision timing.



An example of high precision spectroscopy using the separated oscillatory field molecular beam resonance technique is shown by this D_2 Spectrum produced by Professor Ramsey's apparatus in 1950. These measurements provided a precision value for the quadrupole moment of deuteron.

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ARTICLES

DEPARTMENTS

About Our Cover

This busy scene shows a crab trap with a brachyuran crab entering it. To the left is a weight that has been jettisoned by Alvin (a submersible owned by the U.S. Navy) to adjust buoyancy, and at far left is a clam basket containing clams that have been collected by Alvin's pincer arm. Such marine life clusters around chimmey-like vents on the seafloor. This picture was taken by Roberta Baldwin of Scripps Institution of Oceanography while on the OASIS Expedition which was coordinated by Scripps and funded by the National Science Foundation. See article on page 15.

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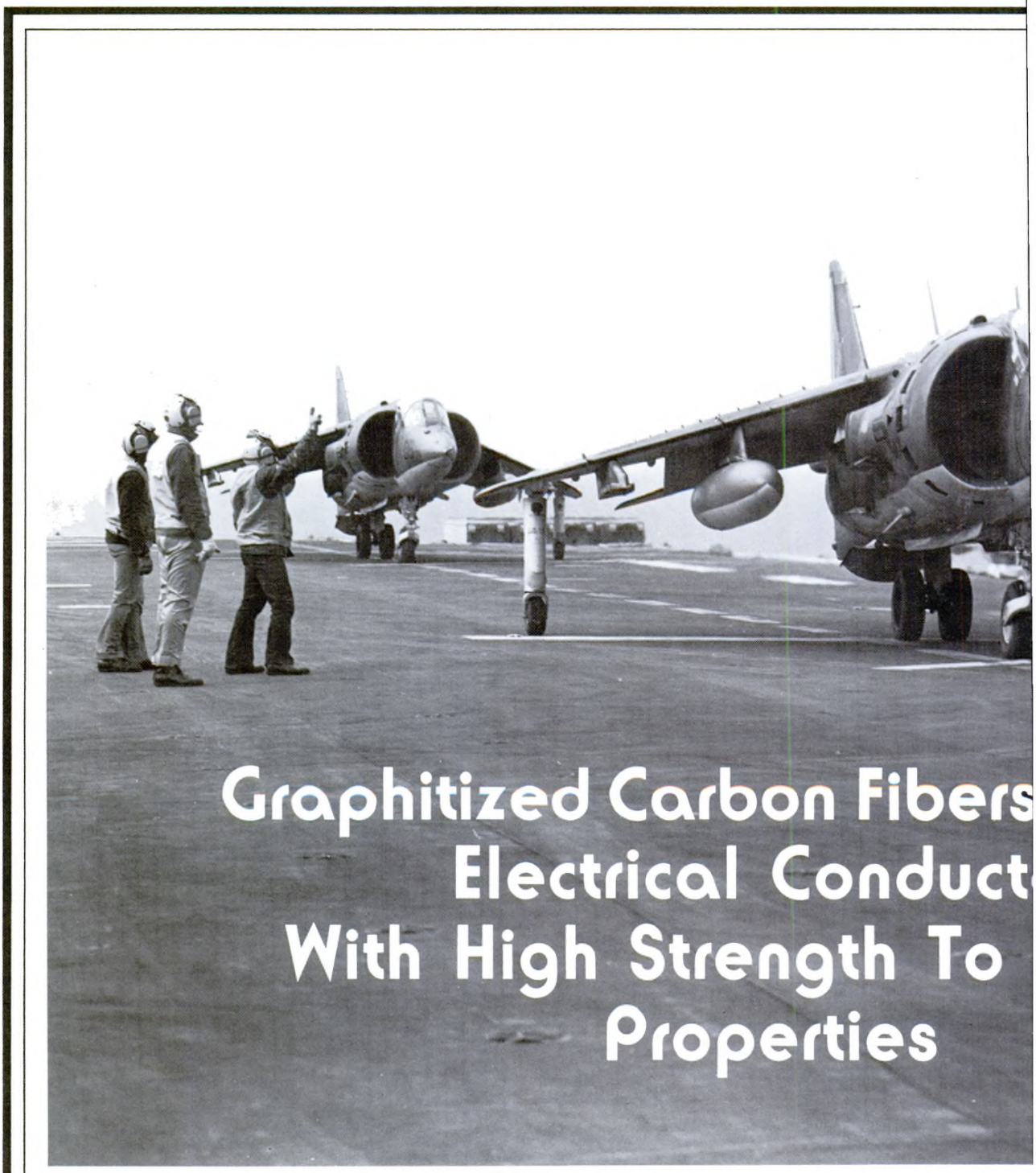

Graphitized Carbon Fibers Electrical Conduct With High Strength To Properties

by

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Introduction

The fact that carbon fibers have very good strength to weight properties is well known; advertisements tout the advantages of carbon fiber golf club shafts and tennis rackets. Carbon fiber/epoxy composites are also used as replacements for conventional structural materials in aircraft, automobiles and other areas where strength to weight ratios are of concern. The Navy is presently using fiber/epoxy composites for the skin of the high performance AV-8B and F-18 aircraft, and far broader applications can be expected in the future.

While the strength to weight ratio of carbon fibers has been the feature attracting the most interest, it is also true that the electrical conductivity of these fibers can be equal to that of metals. This fact has been useful in the military aircraft application where electromagnetic interference (EMI) shielding by the composite aircraft skin is important. The idea of a high strength electrical conductor with a specific weight one quarter that of the transition metals such as Fe, Cu, and Ni is very appealing. Antennae, guy wires and power transmission lines could be made with far less weight. In a sea environment, the buoyancy of the water would amplify the advantage, making the effective weight with carbon fibers about one-eighth that of transition metals. Cables might be lightened considerably. Furthermore, carbon does not corrode like conventional metals.

As will be shown later in this article, the mechanical and electrical properties of graphitized carbon fibers approach those of the a-axis of graphite. Table I presents a comparison of the graphite properties to those of some common metal alloys. The properties of the graphite a-axis are equivalent or better in all respects except for a deficiency of 10-20 in electrical conductivity. However, there are known ways to chemically modify the graphite by intercalation which improve the conductivity by factors of 10-20.[1] Figure 1 shows examples of that improvement for several chemical species; note that the improvement is substantial ($\sim$X10) over a wide range of intercalant concentrations.

While the a-axis properties of graphite are impressive, they must be imparted parallel to the axis of a graphitized filament for the uses envisaged above. In fact, carbon chemists have been quite successful in doing just that (Table 2), but there are issues to explore before one can best exploit the graphitized car-

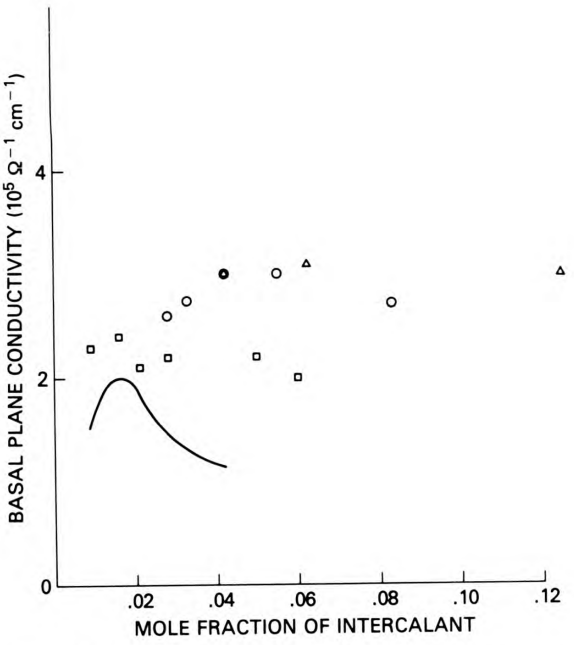

Figure 1. *Basal plane electrical conductivity of graphite intercalated with various specification: oC_{6n} HNO_3; ΔC_{8n} AsF_5; $\square C_xBr_2$;—alkali intercalated graphic. The basal plane conductivity of pristine graphite is $2.5x10^4\ \Omega^{-1}\ cm^{-1}$.*

bon fibers. How much more of the a-axis properties of graphite can be imparted to the filament configuration? Will the chemical modification schemes necessary to improve the electrical conduction in pure graphite also work in the fibers? Will the modifications be stable for years or tens of years? Will modification impair the other desirable properties? Can appropriate graphitized carbon filaments, which now cost on the order of $1000/lb., be made cheaply enough to compete with conventional materials? The purpose of this article is to discuss these questions.

In the next section we will examine the fundamental chemistry and physics which impart to graphitized carbon its unique properties. Some conclusions and prognostications are presented.

Carbon Fiber Properties

Manufacture

Most commercial graphitized carbon fibers are presently made from one of three precursor polymeric materials: rayon, polyacrylonitrile (PAN) or mesophase pitch. In general processing, the fiber is formed, satbilized, carbonized, and then

TABLE 1

*Properties of Conductive Materials Used in Power Transmission**

	C10500 Cu	1350 H19 Al	AISI-SAE 1078 Zinc Coated Steel	Single Crystal Graphite (a-axis)
Density gm/cm³	8.9	2.7	7.8	2.26
Electrical Volume Resistivity at 20°C μohm -cm	1.7	2.8	19	40
Temperature Coefficient of Resistance per °C at 20°C	.004	.004	.004	.002
Thermal Conductivity watts/cm °K	3.8	2.3	0.5	3
Coefficient of Linear Expansion per °C x 10^6	17	23	11	-1.5
Tensile Strength GPa	0.3	.2	1	20
Young's Modulus GPa	120	70	200	1000

1 gm/cm³ = 0.036 lb/in³
1 μohm cm = 6 ohm-cir mil/ft
1 GPa = 0.145 Mpsi

**Metal properties from Metals Handbook, 9th Ed. (American Society for Metals, Metals Park, OH 1978).*

graphitized.[2,3] The polymeric fibers are first stablized via an oxidation process to increase the char yield and/or retain any axial alignment imparted during fiber formation. The stabilized polymer is then pyrolyzed at temperatures in the vicinity at 1000 °C. This removes most of the foreign atoms (O, N, etc.) and begins the growth of extended hexagonal networks. To some extent, the carbon can now be viewed as sheets of two dimensional polymer made from phenyl rings. Further heat treatment at higher temperature extends the networks and leads to the formation of three dimension islands. The islands have a turbostatic graphite structure, i.e., the two dimensional planes are stacked, but are rotationally misoriented. Higher temperature treatments (2000-3000 °C), where the planes reorient to form the three demensional graphite structure, are referred to as graphitization. Both carbonization and graphitization processes are likely to be done with the fibers under tension to orient networks parallel to the fiber axis. The carbon in a graphitized fiber is believed to be a set of tangled ribbons or sheets of layered networks (see Figure 2). The size of the networks, their prefered orientation, and the extent of layering depend on the starting material and the processing parameters. Structural alignment is generally better with higher processing temperature and strain.

An alternative technique for producing high quality graphitized carbon fibers has been developed by Endo and coworkers.[4] They form the fiber by pyrolyzing a mixture of benzene and hydrogen at temperatures around 1100 °C. The fibers are subsequently graphitized at temperatures above 2800 °C. Fibers made in this way and those made from mesophase pitch by conventional spinning techniques show the greatest potential for very high electrical conductivity.

In carbon fiber manufacturing technology, the structure of the polymer precursor, the nature of the precursor treatment, and hot stretching play significant roles in final fiber properties. In general, the desired properties in all carbon fibers improve with higher heat treatment temperatures (HTT). One can study the increased ordering caused by heat treatment and strain by means of X-ray diffraction techniques.[5] The averaged planar spacing can be measured from the 001 diffraction angle. The polar width of the 001 lines provide an estimate of the coherence length L_C (i.e. number of stacked planes $n = L_C/d$); the azimuthal width of the 001 lines provides an estimate of the preferred orientation of the crystallites. One can also obtain a coherence length L_a for the in-plane hexagonal network from the widths of the 001 and hk0 diffraction lines. Given the structure shown in Figure 2, the measured coherence length is likely to be related

TABLE 2

*Representative Properties of Graphitized Carbon Fibers**

Manufacturer Precursor	Celanese PAN		Hercules PAN			Union Carbide PAN		Pitch		Benzene	Graphite a-axis
	GY-50	GY-70	AS	HTS	HMS	T-300	T-50	P-55	P-100		
Density gm/cm³	1.8	1.9	1.8	1.7	1.8	1.7	1.8	2.0	2.1		2.26
Electrical volume Resistivity at 20 °C μohm -cm	1000	650	4700	2000	2100	1800	950	750	250	80	40
Thermal Conductivity watts/cm °K			.26	.29	1.2	.85	0.7	1.0			3
Coefficient of Linear Expansion per °C x 10^6			-0.4	-0.4	-0.5	-0.5	-0.7	-0.9			-1.5
Tensile Strength GPa	2.4	1.8	3.1	2.8	2.2	3.1	2.4	2.1	2.4	4.4	20
Young's Modulus GPa	350	520	230	250	370	230	390	380	700	180	1000

1 gm/cm³ = 0.036 lb/in³
1 μohm cm = 6 ohm cir mil/ft
1 GPa = 0.145 Mpsi
1 W/cm °K = $\frac{58 \text{ Btu ft}}{\text{hr-ft}^2 \text{ °F}}$

Commercial fiber properties from company technical literature; benzene decomposition fiber properties from Reference 4.

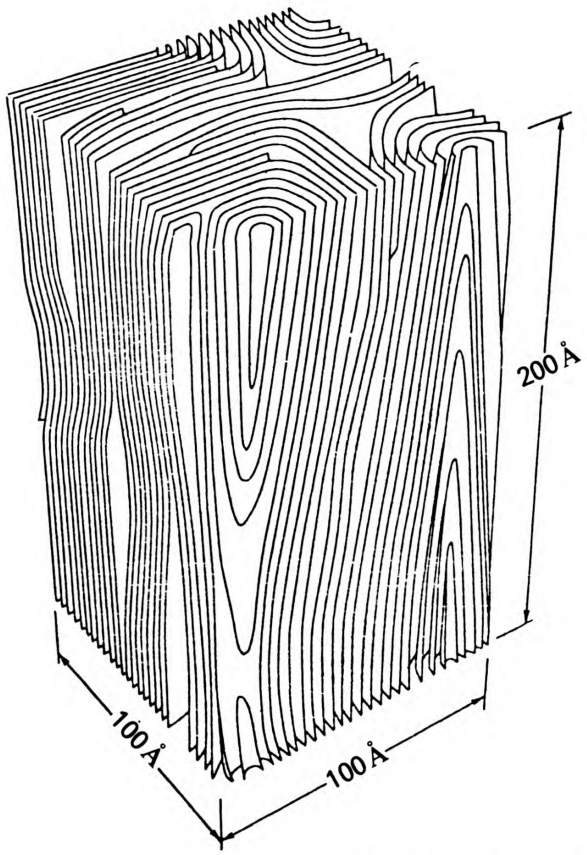

Figure 2. *Schematic representation of the interpenetrating ribbons and planes of carbon believed to constitute carbon fiber structure. Figure from B.J. Wicks,* Journal Nuclear Material; *56 (1975), 287.*

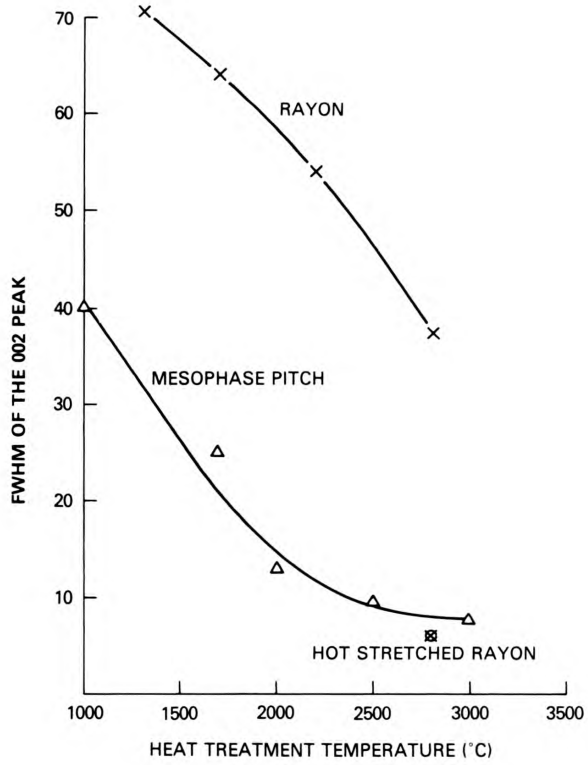

Figure 3. *Preferred orientation of carbon networks parallel to the fiber axis as measured by the full with half maximum angular spread of the 002 peak in X-ray diffration. (Rayon data from Reference 22; pitch data from A.A. Bright and L.S. Singer,* Carbon 17 *(1979), 59.*

to a radius of curvature rather than to the true extent of the hexagonal network. The evolution of oriented "crystallites" with heat treatment temperature (HTT) and strain is illustrated in Figure 3.

Microstructural observation of fibers by optical, high resolution scanning electron microscopy and scanning transmission electron microscopy have also contributed to the knowledge of fiber structure.[6] Three basic microstructural types are commonly recognized in graphitized carbon fibers: radial structures with a preshaped missing wedge, random structures, and onion skin. Scanning electron microscopy of GY-70 and TP 4104B, two highly graphitized fibers that are mentioned extensively in this article, showed concentric and radial structures, respectively.[7]

One interesting result of Naval Research Laboratory (NRL) research has been the discovery that nuclear magnetic resonance (NMR) of fluorine-bearing intercalants in fibers can be used to study the fiber microstructures. NMR has been shown to confirm the X-ray diffraction conclusion that orientation of the graphitic c-axis is perpendicular to the TP 4104B fiber axis.[8]

The general trend toward improved graphitization with HTT is consistent with changes in elastic modulus and tensile strength as presented in Figure 4 and in electrical conductivity as presented in Figure 5. The preferred orientation of the turbostratic graphite "crystallite" c-axis perpendicular to the fiber axis is precisely what is needed to maximize the fiber electrical conductivity and tensile modulus. As a general rule, soft carbons (such as from a mesophase pitch precursor, so called because they are relatively soft mechanically and graphitize more readily at lower temperatures than do hard carbons) provide better electrical and mechanical properties than do hard carbons (such as from a PAN precursor) for a given treatment temperature.

The HTT is not sufficient in itself to specify fiber properties; it is important to have some way in which to predict those properties. The ordering parameters

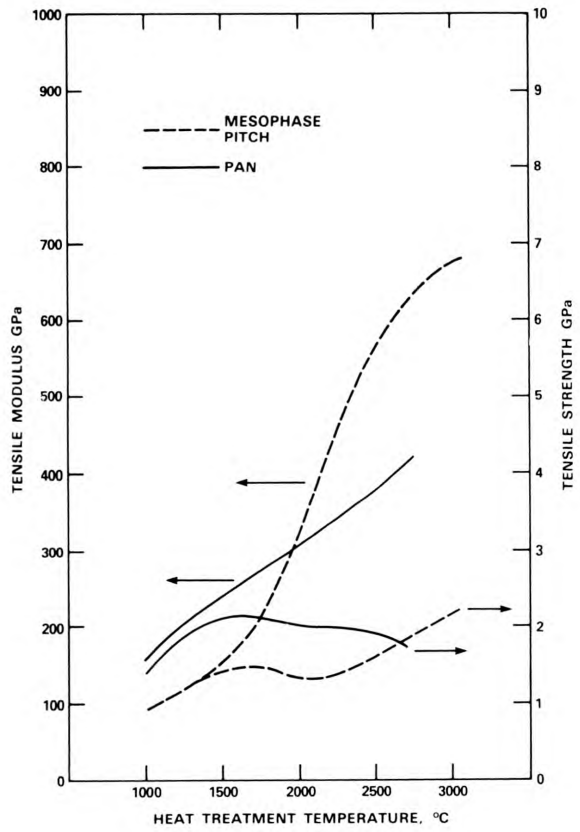

Figure 4. *Carbon fiber tensile strength (right) and Young's modulus (left) as a function of heat treatment temperature. (Pitch data from A.A. Bright and I.L. Singer* Carbon 17 *(1979), 59, PAN data from Reynold, Reference 9).*

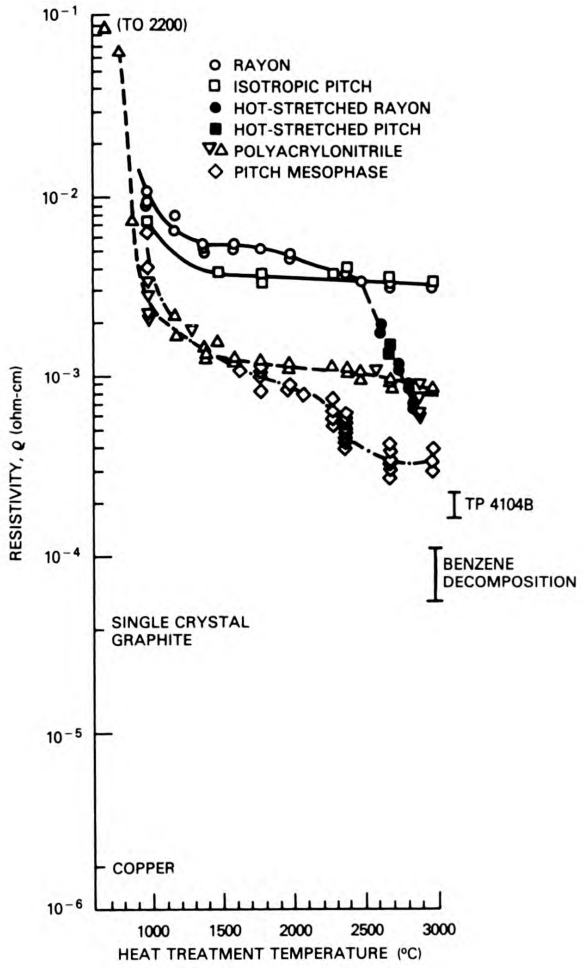

Figure 5. *Resistivity as a function of heat treatment temperature HTT for various carbon fiber types. (Data points from D.B. Fischbach and K. Komaki,* Extended Abstract, 14th Biennial Conference on Carbon, *American Carbon Society (1979), 191; Benzene data from Reference 11).*

L_a, L_c and c-axis orientation are not commonly cited in the literature. The value of the electrical conductivity itself is frequently measured and is likely to be a good indicator of fiber properties. The work of Ezekiel[9] has shown that the values of the tensile modulus and electrical conductivity are closely related.

Intercalated Fiber Electrical Conductivity: Empirical Development

The effect of chemical dopants on transport phenomena in carbons has been examined theoretically in a rigid band approximation. Extensive band calculations on intercalated graphite have been carried out to examine the modified electron density of states and the carrier effective mass, but little has been done on the less ordered sytems such as fibers. However, there has been considerable research in recent years to determine empirically the effect of chemical dopants on fiber electrical conductivity.[10 – 16] The major results are summarized in Table 3.

One can draw several conclusions from the data in Table 3. First, the conductivity of carbon fibers can be improved by the same intercalants as with graphite. That improvement can be X10-25 for *in situ* measurements on highly graphitized fibers and X5-10 for residue compounds. (A residue compound is made by doping the fiber and then removing any volatile material.) When several fibers have been intercalated under the same conditions, the more graphitic ones [as determined by σ (300 °K) and E] improve the most. This has been shown by Herinckx[12] on rayon based fibers with K as intercalant, by Goldberg and Kalnin[13]

*TABLE 3. Resistivity of Virgin and Intercalated Carbon Fibers**

Fiber			Intercalated	Resistivity $\mu\Omega$-cm		TCR ($°K^{-1}$)	
				Virgin	Intercalated	Virgin	Intercalated
1.[12]	a. Union Carbide WYD	Rayon	K	930	50	-0.6×10^{-3}	$+0.8\times10^{-3}$
	b. Union Carbide WYB	Rayon	K	2300	180	-0.4×10^{-3}	$+.05\times10^{-3}$
	c. Union Carbide VYB	Rayon	K	6900	2500	-0.9×10^{-3}	-0.3×10^{-3}
2.[4]	a. Endo	Benzene	HNO_3	80	6	-0.1×10^{-3}	
	b. Endo		HNO_3(R)		12		$+1.4\times10^{-3}$
	c. Endo		Br_2		15		
	d. Endo		Br_2(R)		20		$+0.9\times10^{-3}$
	e. Endo		AsF_5		5		
3.[16]	Union Carbide	Mesophase Pitch	$CuCl_2$	150	10		
4.	a. Union Carbide TP 4104B	Mesophase Pitch	Br_2	200	20	-2×10^{-3}	
	b. TP 4104B		Br_2(R)		70		4.4×10^{-3}
	c. TP 4104B		IC1		12		
	d. TP 4104B		IC1 (R)		40		$+0.6\times10^{-3}$
	e. TP 4104B		K		30		
	f. Union Carbide TP VSO-022	Mesophase Pitch	IC1 (R)	600	320	-0.5×10^{-3}	
	g. TP VSO-022		K		440		
	h. Celanese GY-70	PAN	IC1-Br_2	500	100	-1.5×10^{-3}	
	i. GY-70		$ICBr_2$ (R)		110		~0
	j. GY-70		IC1		70		
	k. GY-70		IC1 (R)		275		$+0.2\times10^{-3}$
	l. GY-70		K		230		

* *Cross sectional area of intercalated fiber assumed to be twice original area.*

on PAN based fibers with various flourinated acceptors, and by NRL workers on PAN and mesophase pitch based fibers with K, BR_2 and IC1 as intercalants. Second, the relative improvement in fiber conductivity by a given intercalant can be greater than that observed for the same intercalant in graphite. Third, the intercalated fiber conductivity can be as high as 10^5 $(\Omega cm)^{-1}$ which is equivalent to iron ($\sigma = 10^5$ $(\Omega cm)^{-1}$) and within a factor of 6 of copper ($\sigma = 5.8\times10^5$ $(\Omega m)^{-1}$). Fourth, the enhancement of fiber conductivity is always accompanied by the change of the temperature coefficient of resistance (TCR) toward a more positive value. All virgin fibers showed negative TCR at room and lower temperatures. The more graphitized intercalated fibers showed positive values of TCR, suggestive of metallic-like behavior. Fifth, the conductivity enhancement can be stable in an ambient of air and at elevated temperatures. The work of Oshima et al.[16] on a mesophase pitch fiber demonstrated air stablility to 100°C. The residue compounds of Br_2 and HNO_3 are also air stable; the Br_2 residue compounds showed stable conductivity up to 300°C. Deitz and Hooley[17] have reported Br_2 residue compounds in TP 4104B can be stable up to 900°C in vacuum. Sixth, the NRL work has shown that the more graphitized fibers intercalate more readily. For instance, at 23°C, TP 4104B intercalates Br_2 at $(p/p_0)_{Br_2} \sim 0.6$ whereas GY-70 does not intercalate Br_2 even at $(p/p_0)_{Br_2} = 1$. To intercalate the latter with Br_2 it was necessary to first intercalate IC1 which is known to intercalate graphite more readily than Br_2. The IC1 could then largely be pumped away and Br_2 could be inserted.

These experimental results demonstrate an exciting potential for highly conductive, stable carbon fibers. But the research to date is not adequate to answer the question of how good one can make fiber conductivity. To answer that question, one needs to know more about the basic physical/chemical processes that determine electronic transport in carbon and carbon fibers.

Electronic Transport in Two Dimensional Conjugated Carbon Bonds

The improvement of electrical conductivity of graphitized carbon fibers as the structure becomes more nearly like graphite suggests two things: 1) the mechanisms of a-axis conductivity of graphite can serve as a model for conduction in the fiber; the fiber will differ in the lack of three dimensional order, in increased number of defect sites and in the need to transfer electrons between planes; and, 2) the chemical dopants which enhance electrical conduction in graphite will also work in the fibers.

The properties associated with electronic transport in carbon fibers are not unique to that geometry.[10] Various pyrocarbons, chars and cokes have also been examined as a function of heat treatment temperature. Conductivity, Hall coefficient, thermoelectric power, and magneto resistance and their temperature dependences have all been measured. A general review of this information has recently been published by Spain.[18]

In 1971, Mrozowski proposed a heuristic model for the carbon density of states to explain carbon electrical properties as a function of heat treatment temperature.[19] The model is schematically illustrated in Figure 6. The carbon $2p_\pi$ electrons in benzene form bonding/antibonding orbitals separated by 3.6 eV. As the two dimensional hexagonal network grows, these orbitals begin to form into the valence and conduction bands, respectively. In an infinite two dimensional network, the valence band would be full, the conduction band empty, and the Fermi level at midgap. However, edge sites and other localized defects trap electrons. This extracts the electrons from the delocalized band structure and causes the Fermi level to dip into the valence band. The carbon in this state is called a "hole semimetal," i.e., some charge can flow because of the few unoccupied electron states at the top of the valence band. As the networks grow in extent and assume three dimensional ordering, the two bands migrate toward each other until they overlap slightly (40 meV). The number of defects decreases and the Fermi level moves into the overlap region.

This model has evolved somewhat in the past ten years but remains substantially intact. Bright has tested its present form and achieved good agreement with reasonable physical values of five fitting parameters.[20]

It is likely that this picture, which presumes a free electron-like behavior in the p_π bands, is not totally correct. Localized states at the band edges, due to the presence of disorder in the two dimensional network, are predicted by band theories. Localized states would lead to conduction by hopping mechanisms; there is evidence to support this mechanism in carbon and in carbon fibers.[21]

Band structure calculations on a two dimensional hexagonal network show that the valence and conduction band edges just touch at the Fermi level. In crystalline graphite, the interaction between planes, although weak, causes the two bands to overlap slightly (40 meV). The result is that graphite is a semimetal with a low concentration of holes and electrons

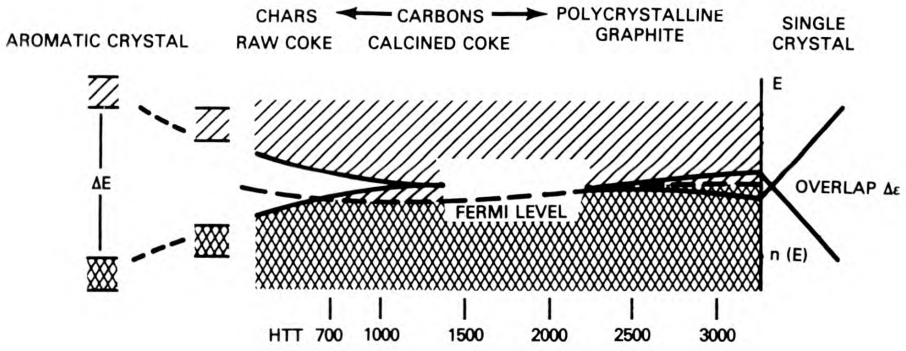

Figure 6. A schematic diagram illustration of the development of band structure in carbons as a function of heat treatment temperature. (Reference 19)

($n \sim 10^{-3}$/C atom) but with very large mobilities ($\mu \sim 1$ m^2/V sec) because of small effective masses ($m/mo \sim .06$ - $.004$) and reasonable scattering times. The result is good electrical conductivity $\sigma = n_e e\mu_e - n_h e\mu_h \sim 2 \times 10^6\ \Omega^{-1} m^{-1}$.

Chemical doping of the carbon — either by substitution of B for C in the hexagonal ring, by intercalation, or by attachment to an edge site — provides an effective mechanism to change the number of available charge carriers. The measurement of charge transfer in doped graphite has been inferred from a number of techniques. Band structure calculations for some simple intercalated three dimensional graphites have been calculated in detail.[1] A rigid band approximation appears to work reasonably well for phenomenological understanding. Within a rigid band model for the density of states, the chemical dopant simply contributes to (donor — Li, K, Cs, etc.) or extracts from (acceptor—AsF_5, Br_2, HNO_3, etc.) the conduction/valence band, respectively. This moves the Fermi level into a region of larger density of states (electrons for donor species, holes for acceptor). Electrical conductivity σ increases as the number of available carriers n increases. The resulting charged dopant is also presumed to contribute an additional scattering mechanism, decreasing the net scattering time τ and thereby lowering the mobility μ:

$$\frac{1}{\mu} = \frac{m}{e}\left(\frac{1}{\tau}_{\text{phonon-elec}} + \frac{1}{\tau}_{\text{defect}} + \frac{1}{\tau}_{\text{dopant}} + \frac{1}{\tau}_{\text{elec-elec}}\right).$$

On a percentage basis, doping changes the carrier density more significantly than scattering time until larger dopant concentrations are reached. This is thought to be the explanation for the peak in σ vs. intercalant concentration shown in Figure 1.

The transport properties of a material are largely determined through the carrier concentrations n and mobilities μ. A number of studies of PAN, mesophase pitch, and benzene decomposition fibers have examined the temperature dependences of conductivity σ, magnetoresistance p/p and/or thermoelectric power S in an attempt to determine the physical mechanisms dominating the transport. It is clear that defects and boundaries play a larger role in fiber than in crystalline graphite, but no study has definitely identified the physical mechanisms limiting fiber electron transport.

Mrozowski[19] recognized that doping of carbons could be a powerful tool for introducing large changes in carrier properties by small chemcial perturbations. Endo et al.[11] have shown this for the Br_2 residue compounds of their benzene decomposition fibers. We have demonstrated similar effects for Br_2 and and IC1 residue compounds of TP 4104B and GY-70 fibers (see Figure 7) in which the residual amount of halogen was maximized. It is possible to prepare residue compounds of fibers with lesser amounts of Br_2 or IC1; and this will be a significant tool in the investigation of fiber transport and in the role of dopants.

Fiber Mechanical Properties

As seen in Table 1, the tensile strength and Young's modulus for the a-plane of graphite are large compared to metals. These properties are related to the very strong C-C bonds formed in the sp^2 hexagonal network. The fact that the electrical properties derive from the p_π electrons and the mechanical properties from the sp^2 electrons gives one hope that chemical schemes found to alter the conductivity may not dramatically change the strength.

Carbon fiber strength and modulus are expected to depend on the formation of extended two dimen-

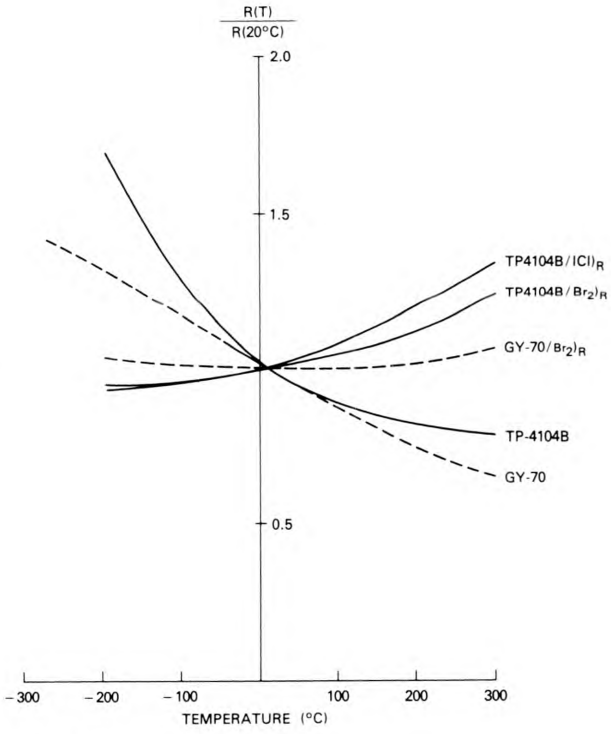

Figure 7. *The relative change in resistance versus temperature for TP-4104B (a mesophase pitch precursor) and GY-70 (a PAN precursor) fiber with and without intercalants. The residue compounds with Br{ and IC1 (designated by subscript R) were prepared by fully intercalating the fiber and pumping off any volatile material. Note the change to a positive TCR in the residue compounds.*

sional planes aligned parallel to the fiber axis. Studies of Young's modulus E in fibers and the data in Figures 3 and 4 confirm that expectation. The peaking and slight decrease in tensile strength above HTT ~ 1500 °C in Figure 4 is thought to be due to increased sensitivity to flaws.[9] As the tensile modulus becomes larger, the fibers behave increasingly like brittle materials. Stress becomes concentrated about structural flaws which act as nucleation centers for crack initiation. Once a crack is initiated, failure is catastrophic.

If the introduction of an intercalant or dopant into the carbon fibers results simply in charge transfer via the p_π electrons, then one would anticipate little change in the tensile modulus. However, swelling due to the physical insertion of the dopants may have some effect on modulus or strength by modifying the alignment of the "crystallite" c-axes. The swelling might be expected to have a larger effect on the tensile strength than on the modulus of the fiber, since differential expansion between more graphitized and lesser graphitized regions should exacerbate flaws.

Changes in mechanical properties due to the treatment of fibers with chemicals known to augment conductivity in graphite cannot be unambiguously identified by reference to the literature. The chemistry is often complex, with chemical etching possible as well as intercalation. There are no comprehensive studies to isolate these two effects, and each of the few available studies uses a different combination of fiber/chemical reagent. The results of chemical treatment by reagents known to intercalate graphite suggest that Young's modulus either is unchanged or increases somewhat. The effect on tensile strength is likely to be detrimental, but quantification is uncertain; a fact due in part to the difficulty of making the measurement. Tensile measurements made at NRL on graphite fiber/halogen residue compounds are shown in Table 4. These results suggest that no degradation of fiber strength occurs on residue compound formation.

Graphitized carbon fibers are susceptible to fracture if bent. Since the presently known techniques to improve fiber conduction (HTT and chemical modification) may reduce the tensile strength, the fragility problem may be serious. There are several possibilities that might reduce this difficulty. First, the fiber diameter d may be reduced. The radius of curvature R at which the fiber breaks is related to d and the tensile strength TS by:

$$R = \frac{d \times E}{TS}$$

Second, it has been observed by several groups[9] that smaller diameter fibers have increased tensile strengths. It is postulated that the outer shell of the fiber is more graphitized and carries most of the load. Smaller diameters augment the proportions of graphitized carbon and may also reduce the probability of flaws. Third, the susceptibility to failure of the highly graphitized fibers is dependent on flaws. As shorter fiber segments are tested, the tensile strength has been shown to approach 1% of the tensile modulus, even for heat treatment temperatures at 3000 °C. This observation demonstrates flaw sensitivity; the shorter the segment, the lower the probability of a flaw. Manufacturing techniques and surface treatment have been developed to achieve the present state-of-the-art; they can be improved further to reduce the incidence of critical flaws. Finally, one might imbed the fiber in a tough matrix material. Dieffendorf[2] has pointed out that this process is not a panacea because the fiber modulus is so much greater than that of available polymers. However, it is possible that a high strength matrix composite will hold broken fibers sufficiently close to retain good conductivity. It is also possible that a composite utilitizing electrically conductive polymers, such as polyacetylene which responds to the same dopants as the fibers, may be utilized to augment conduction between fibers.

TABLE 4. Tensile Strengths of Virgin Fibers and Residue Compounds

Fiber Treatment	Tensile Strength x 10^3 psi
TP 4104B	290 ± 40
(IC1)R	290 ± 40
(Br_2)R	280 ± 40
GY-70	280 ± 60
(IC1)R	220 ± 60
(Br_2)R	220 ± 60

Conclusions

Let us summarize the present state of understanding *viz a viz* the modification of carbon fiber electrical and mechanical properties. How good will carbon fibers be as electrical conductors? Graphitized carbon fibers, suitably modified by chemical dopants, have been made with p ~ 10$\mu\Omega$-cm and ambient stability. It is likely the p ~ 5$\mu\Omega$-cm can also be achieved since better fibers and dopant combinations are under investigation. However, since the best intercalated graphite has twice the resisitivity of Cu; on the basis of present knowledge, one should not expect that carbon fibers will ever have the resistivity of Cu.

A negative temperature coefficient of resistance (TCR) is valuable for electrical conductors because local heating will not lead to increased power loss. The TCR for virgin graphitized fibers is uniformly negative, but less so the more highly conductive the fiber. This trend is continued for the chemically doped fibers; the better the resistivity the more positive the TCR. However, the room temperature TCR for the most conductive closed fibers to date (TCR ~ 1-1.5x10^{-3}) is substantially lower than for Cu TCR ~4x10^{-3} or Al TCR ~4x10^{-3}.

The advantage of a carbon fiber over conventional metals lies in its high strength and low weight. The fiber tensile strength is significantly better than Cu, Al or even steels. However, fragility of the highly graphitized virgin and chemically doped fibers is and will be a problem. There are approaches to this problem that need be explored.

The chemical doping of a carbon fiber does increase its weight, but doping also increases the diameter. The two effects largely offset and leave the fiber density unchanged.

Finally, we must face the high cost of graphitized carbon fibers, presently about $1000/pound. One must remember that a pound of carbon fiber is the volume equivalent of four times that amount of a transition metal. However, fiber manufacturing technology must be improved to lower the cost. The largest contributing factor is the 3000 °C heat treatment temperature needed to achieve the higher orders of graphitization. The HTT requirements might be reduced by appropriate choice of precursor. It has been observed that graphitic "preorder" and graphitizability increases in the order pitch, rayon, PAN, and mesophase pitch. The latter is a relatively new material and it is reasonable to expect improvements in its manufacturing technology. The benzene decomposition technology is also relatively unexplored. An alternative way to reduce energy requirements to reach the 3000 °C temperature may be to heat the carbon fibers directly by passing electrical current through them or by RF inductive heating rather than by conventional furnaces.

Graphitized carbon fibers have a unique combination of strength, conduction and weight properties which can make them an important material for the Navy design engineer. There is reason to believe the desirable properties will continue to improve while costs will decrease. In the near term, intercalated graphite fibers probably will be useful only in selected applications, applications chosen so that the unique properties of the fibers will permit new design possibilities which offset the fiber cost. ■

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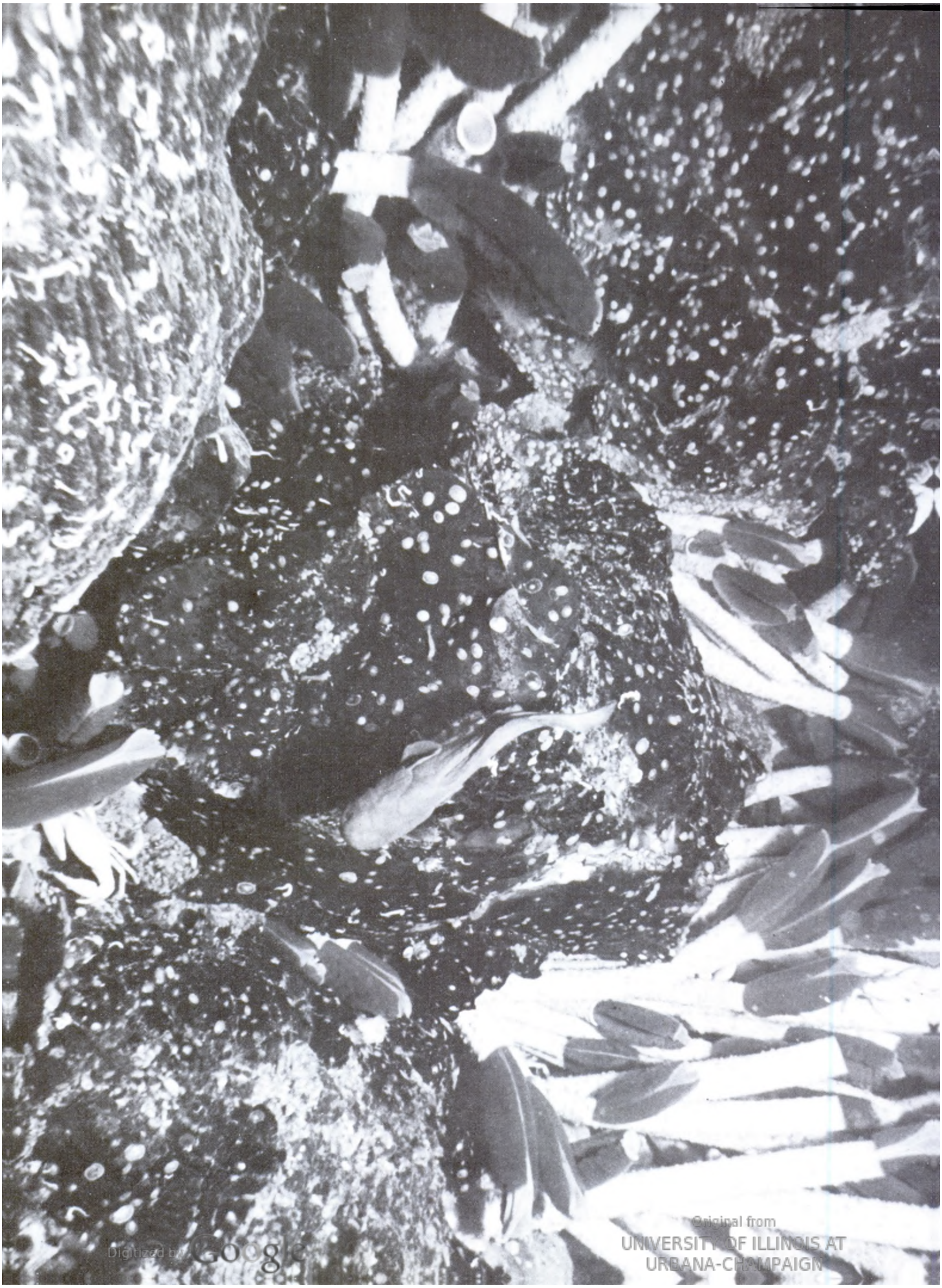


Ocean Chemistry:

Why is the Sea Salty and How Does It Vary?

By
Edward J. Green, John M. Edmond, Theodore T. Packard, Alberto Zirino, Jeffrey L. Bada, and John W. Farrington

The oceans contain all the elements of the periodic table. Their abundances are controlled by weathering of continental rocks, spreading of the ocean floor, and the complex biochemistry of life in the sea, as well as by man.

Introduction

The "salt" of seawater is a complex mixture of inorganic molecules and ions, trace nutrients necessary to fertilize the green crops of the oceans, and organic molecules resulting from life processes in the seas. This saline solution could be even more complicated than it is were it not for a simplifying factor known as "constancy of relative proportions." In 1819, A.M. Marcet presented a paper to the Royal Society in which he concluded that the various ions in the world ocean were present in nearly constant proportions and that only the amount of water was variable. This principle was confirmed by Wilhelm Dittmar's analysis of 77 samples of seawater collected on the worldwide cruise of *H.M.S. Challenger,* 1873-1877. Although the major components of seawater cannot be duplicated by dissolving one salt (it requires at least four pure compounds to account for 97% of seawater's dissolved solids), the oceans act as if sea salt were a simple substance. Surface waters get more saline where evaporation exceeds rainfall and river runoff and less salty where dilution occurs, but the ratios of sodium to magnesium and of chlorine to sulfur remain constant while the total solids dissolved in open seawater range from 3.3 to 3.7% by weight.

But this is true only for the ten or so most abundant elements in the seas. For these elements the oceans are well stirred; that is, the input rate (mostly from rivers) and the removal rate (largely by the creation of seafloor sediments) are slow compared to the mixing rate of the oceans. For the other eighty natural elements plus a few man-made radioactive species, the converse is true. Uptake of these elements by organisms is rapid compared to the rate at which the ocean mixes, so that local areas of depletion occur where biological production is active. Likewise in those deeper parts of the ocean where decomposition of biological detritus dominates, there is local enrichment of many trace elements.

It is convenient to categorize the dissolved constituents of seawater into four groups: the major elements; the trace nutrients (nitrogen, phosphorus, and silicon) which are known to be crucial to the growth of marine plants; the trace metals, many of which appear to behave as micronutrients; and organic compounds existing naturally and as man-made pollutants. Exciting areas of current research exist in all of these categories. We will consider some recent developments in each of them in turn.

Submarine Hot Springs

The scientific study of any natural system begins with the construction of what are called conservation equations. Familiar examples from chemistry and physics are the conservation of mass, energy, angular momentum, and spin pairing rules. In chemical oceanography one talks about flux balances—the amount of dissolved material entering the ocean every year from rivers, rain, and atmospheric dust must be balanced, at least over the long term, because from geological evidence it is known that there have been no major variations in the chemical composition of sea water over the last thousand million years. The ocean has never been as salty as the Great Salt Lake at one extreme or as fresh as Lake Superior at the other. In fact salinity variations much larger than we presently observe are quite unlikely to have happened.

When one inventories the river contribution to the ocean by compiling existing information of flow and composition, one finds that for a number of elements: magnesium, sulfur, potassium, sodium, chlorine; the amounts are much too large to be accommodated in the corresponding inventories of sediment removals. Various schemes have been advanced to get around this problem, but all have failed in the face of the evidence. Clearly discovery of a completely new and unforseen process which adds or subtracts various elements on a scale comparable to rivers and sediments—which in effect provides new terms in the conservation equation—represents a major scientific development. This is exactly what has happened.

Hydrothermal Activity at Oceanic Ridge Crests

This process involves large scale hydrothermal activity associated with the formation of new oceanic crust at ridge crests. At crests of the mid ocean ridges, new material almost identical to the lavas being erupted on Hawaii is being continually emplaced in thin sheets or dikes at an average rate of something like 4 cm/yr. This material is hot, near 1200 °C. Indeed it is the thermal expansion of the oceanic basement in the region of the spreading centers that makes them appear as ridges. However, as this material solidifies it cracks, producing a highly permeable environment. Volcanic islands such as Hawaii, Iceland, and the Azores show abundant examples of this effect on land. The result is that seawater can penetrate rapidly into very high temperature regimes. It often seems that seawater is about the most corrosive, reactive and generally insidious substance on the face of the earth. At four or five hundred degrees centigrade and several hundreds of atmospheres of hydrostatic pressure, these properties are even more pronounced. The hot rocks react rapidly with the incoming seawater, and as a result the compositions of both are transformed. The heated waters then ascend from the reaction zone and pour out at the sea floor as hot springs (Figure 1). Geophysical evidence,

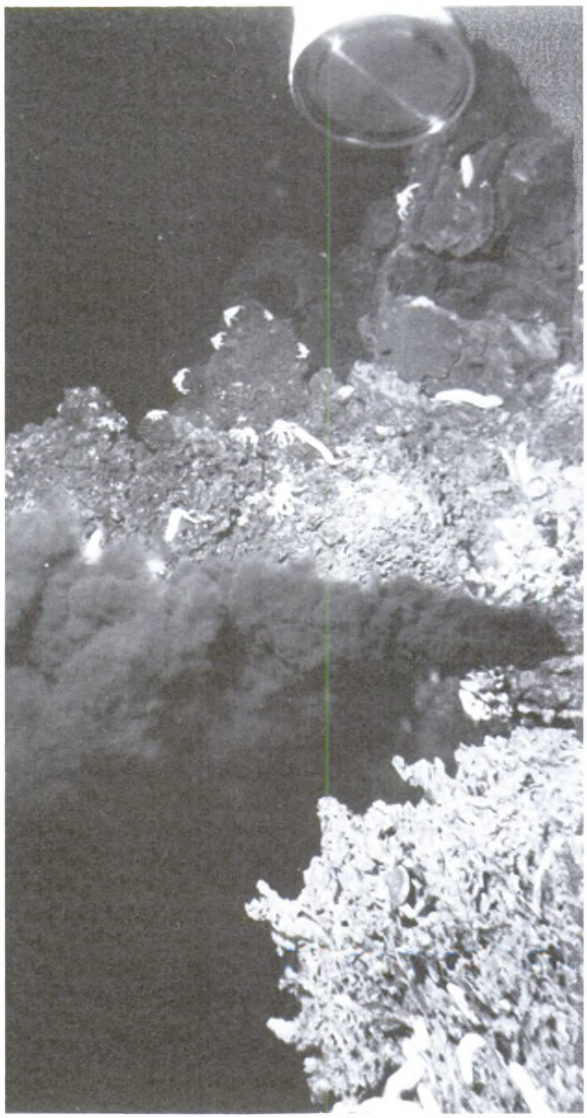


Figure 1. *"Black smoker" hydrothermal vent from the 21°N. oceanic ridgecrest area south of Baja, California. Here the hot waters are clear as they exit the rock fissure, but immediately turn black on contact with sea water due to precipitation of metallic sulfides.*

measurements of the temperature gradient and thermal conductivity of the sea floor, indicates that hot water removes by convection a large proportion of the heat from the newly emplaced crust. The total amount is about 5×10^{19} calories per year. To do this the flow of seawater through the reaction zone has to be about 1% of the total flow of rivers of the world. This fact, in combination with the pronounced chemical changes that occur during contact between the seawater and the hot rocks, makes ridge crest hydrothermal activity the "missing term" in the conservation equation.

Locating the Hydrothermal Vents

Finding these hot springs is something else again, just about as difficult as finding anything else on the deep sea floor. In fact it is "state of the art" in oceanography. First of all and perhaps most essential is a multibeam high resolution bathymetric survey of the segment of ridge crest targeted for exploration. Then a photographic survey is made of areas that look promising within the bathymetric survey. This survey is done using the Office of Naval Research (ONR)-sponsored ANGUS (Acoustically Navigated Geophysical Underwater Survey) deep sea camera system. Why photography? For once in oceanography, luck is on the side of the scientists. One by-product of the water-rock reactions is hydrogen sulphide (H_2S). Some bacteria can use the oxidation of H_2S as an energy source just as the more common ones oxidize organic carbon. Many filter feeding organisms live on bacteria. Hence the hot springs become oases of life on the sea floor. The bacteria metabolize the H_2S, and the clams, mussels, and worms eat the bacteria, establishing a unique food chain that is not linked to photosynthesis. The filter feeders grow to a very large size on the dark and otherwise barren sea floor and can be spotted by photographic reconnaissance (Figures 2 and 3). Curiously then, photography is the best way to find hot springs rather than detailed water temperature surveys. After all this preliminary work is done, scientists in the deep submersible Alvin dive on the vents and sample the shimmering fluids as they stream out of the sea floor. Other special instrumentation on the submersible allows retrieval of biological samples (Figures 4 and 5). Needless to say, the navigational requirements for all this are severe, and the level of coordination required is very high. It is remarkable that such a diverse battery of techniques developed independently, mainly by the Navy, provides the means for the discovery, exploration and sampling of hot springs along the oceanic ridge crest.

Hot Spring Chemistry

After collection, the samples are subjected to a broad range of chemical analyses. Nearly every element in seawater is affected by reactions of hot water with basalt and the characteristic chemistries of the different elements allow us to extrapolate into the conditions in the reaction zone itself. What we find is pretty amazing. Magnesuim and sulfur, two of the "problem elements" mentioned earlier, are removed from the hot waters, balancing the river input world wide. Minor and trace elements in normal seawater such as lithium, barium, managanese, iron, copper and nickle become major components. The waters are highly acid and loaded with H_2S. They are in fact ore-forming solutions.

This last factor is very significant. Not only do the hot springs provide a resolution for most of the problems of the oceanic mass balance, but they also

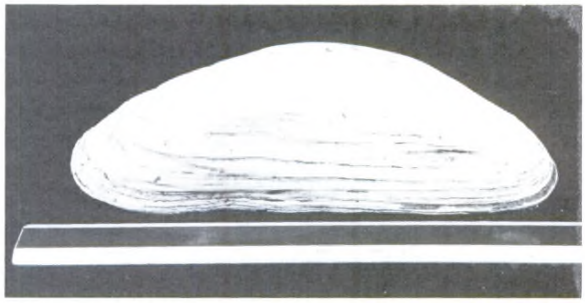


Figure 2. *Large clam from the abyssal seafloor at the Galapagos vent field.*

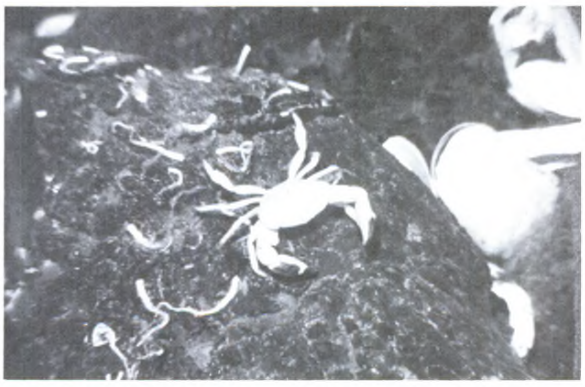


Figure 3. *This crab, about six inches (15 centimeters) across, seaworms, and dead clams were photographed by one of the expedition's chief scientists, Dr. Robert Ballard of the Woods Hole Oceanographic Institution, from the submersible Alvin. Dead clams quickly begin to dissolve in the acidic environment of the area.*

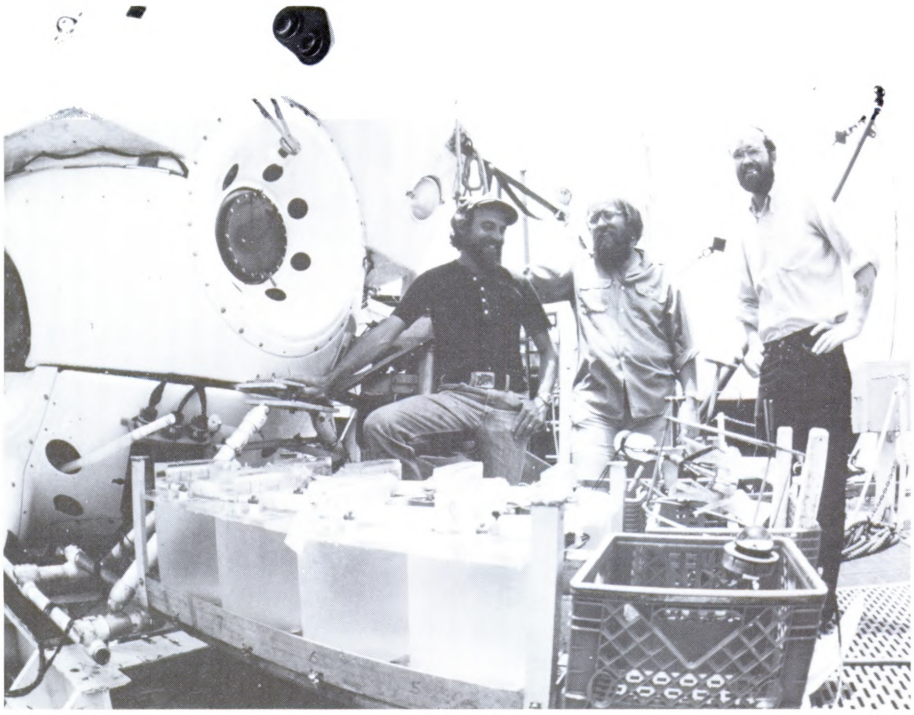


Figure 4. *The research submersible Alvin fitted with its hot springs water sampling system. Some of the expedition scientists with the Alvin are, left to right, Dr. Jack Dymond and Dr. Jack Corliss of Oregon State University and Dr. John Edmond of the Massachusetts Institute of Technology.*

Figure 5. *A mechanical arm outside Alvin collects samples of abyssal clams from an area called Clambake 1 by the scientists. This clam is about 12 inches (30 centimeters) long.*

are responsilbe for the various metal rich deposits found in ridge crest environments: pure manganese dioxide crusts, iron-manganese oxide sediments, and massive accumulations of iron-copper-zinc sulphides.

Work in this area is just beginning as the elaborate and expensive exploration program is slowly extended to more diverse ridge crest environments. A whole new area of chemical oceanography is opening up which will certainly lead to a more profound understanding of the age old problem: "Why is the sea salty?", or more precisely: "Why is it at the particular salinity it is?"

Aguajes and El Ninos in the Peru Current

As the floor of the ocean is yielding a better understanding of the sources and sinks for many of the major elements in seawater, so is research in the surface to mid-waters of highly productive areas expanding our knowledge of the biochemical role that certain trace components play.

The Upwelling Ecosystem

The sea off the coast of Peru is one of the most dynamic parts of the world ocean. It is a region of complex currents. A broad undercurrent runs south

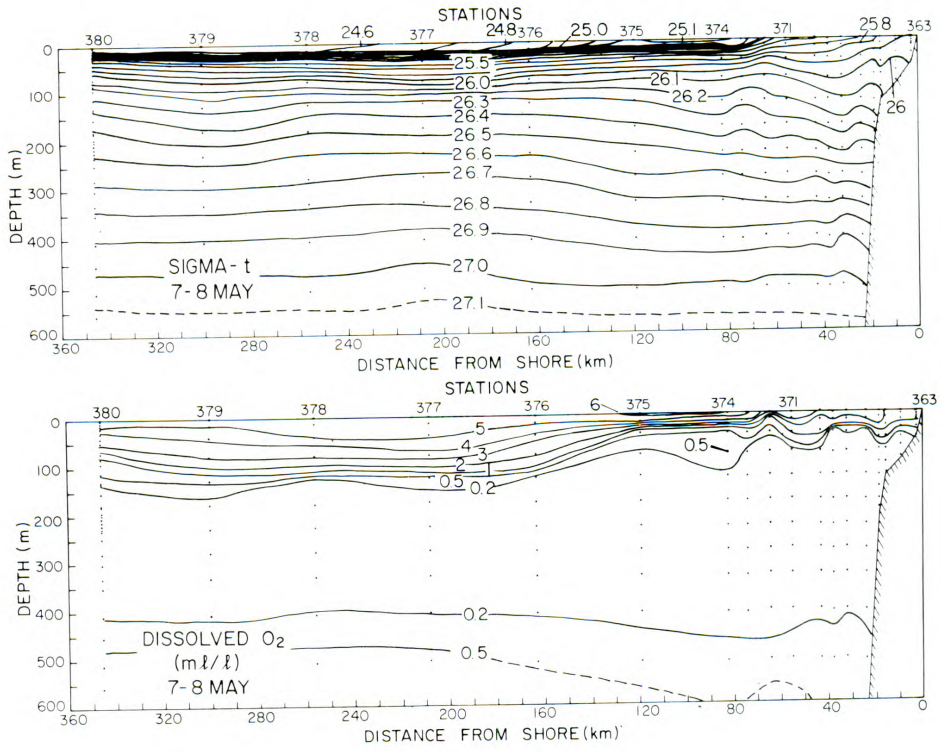


Figure 6. *Cross sections of the Peru Current at 15°S. latitude with the coast on the right. The sloping isopycnals in the upper 100m of the top panel reveal the upwelling. The downward sloping isopycnals at the shelf break indicate the presence of the Peru-Chili undercurrent. The oxygen minimum zone is shown in the middle of the lower panel. For 360 km offshore the seawater is stripped of oxygen between 150 and 400 m. In the coastal waters the oxygen is depleted as shallow as 75 m and sometimes by 50 m. It is in this oxygen minimum zone that microbes often turn to nitrogenous electron acceptors and ultimately to sulfate, so as to carry out their metabolic reactions. It was between 100 and 250 m at the shelf break that sulfied was first discovered in the open ocean water column in 1976.*

along the shelf towards Chile, and there are bands of surface currents that flow poleward or equatorward depending on the wind, time of year, and distance off shore. It is a region where red tide can cover the sea for 600 miles along the coast, where porpoises circle anchovy schools in living corrals, and where sea birds flock the skies by the millions. This intense biological activity results from extensive upwelling where cold, nutrient-rich waters rise to the surface and nourish larger blooms of oceanic plant life (phytoplankton) which in turn feed the anchovies, birds, and porpoises.

Aguajes and the Oxygen Minimum Zone

Below these rich surface waters the sea is also dynamic, but more with respect to its chemistry and biochemistry than its biology. Organic matter sinking from the surface layer supports large populations of microbes at mid-water depth that, by their utilization of dissolved oxygen, develop the oceans most intense oxygen-minimum zone (Figure 6). Due to their metabolism, there is no oxygen between 100 and 300 m depth, and the microbes are forced to couple their respiration to alternative electron acceptors (Figure 7). Their first choice after oxygen is nitrate (NO_3^-) (Figure 8 and 9), and successively as each chemical nitrogenous electron acceptor becomes scarce they turn to nitrite (NO_2^-), nitrous oxide (N_2O) and finally, when all the soluble combined nitrogen has been reduced to nitrogen gas, the microbes start reducing sulfate ($SO_4^=$). At this point, the end product, sulfide ($S^=$), starts to accumulate in the seawater column. This is disastrous for normal oceanic ecosystems because sulfide is toxic to fish, invertebrates and other higher organisms. As a result, these organisms are killed or otherwise excluded form the sea water column as the zone of sulfide bearing waters expands. Since the mid-water regions are relatively poorly inhabited, the effect of sulfide in the seawater is rarely noticed.

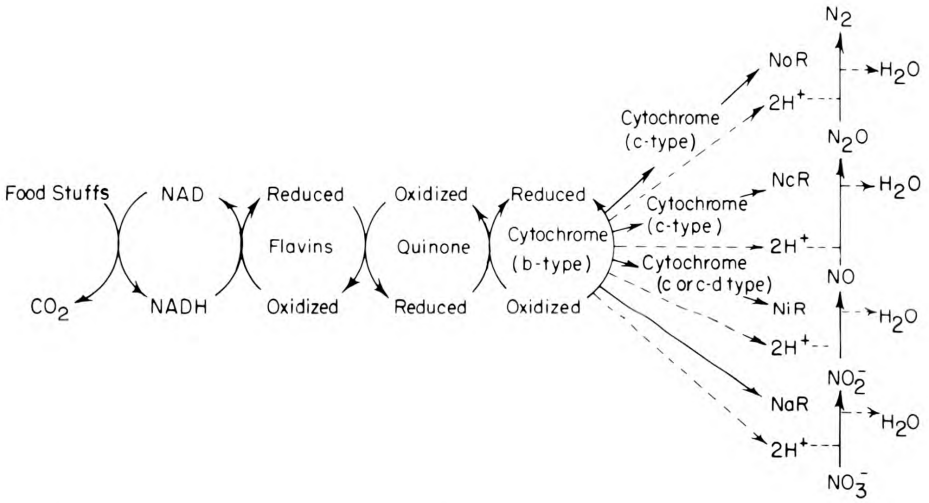


Figure 7. *The coupling between the microbial electron transport system (ETS) and the different reaction steps of denitrification. On the left, food stuffs are broken down to CO_2, and in the process they reduce a hydrogen transport molecule, NAD to NHDH. This initial reduction sets up a chain of oxidation-reduction reactions in the ETS with each carrier molecule being successively reduced and oxidized by its preceeding and following members of the chain. Depending on the availability of electron acceptors, there develop at cytochrome-b, different cytochrome branches to link the ETS to different reductases. If nitrate (NO_3^-) is available, then electrons are passed directly to the enzyme, nitrate reductase (NaR) which reduces NO_3^- to nitrite (NO_2^-). As in the oxygen consuming system the protons are transported separately after cytochrome b. If nitrate is no longer available in the surrounding seawater, the microbes turn successively to nitrite, nitric oxide (NO) and nitrous oxide (N_2O). For each of these reductions a unique cytochrome serves as the electron carrier, and a unique enzyme catalyzes the reaction. The enzymes are: nitrite reductase (NiR), nitric oxide reductase (NcR) and nitrous oxide reductase (NoR). The detailed chemistry of these carriers and enzymes is a topic of current ONR research.*

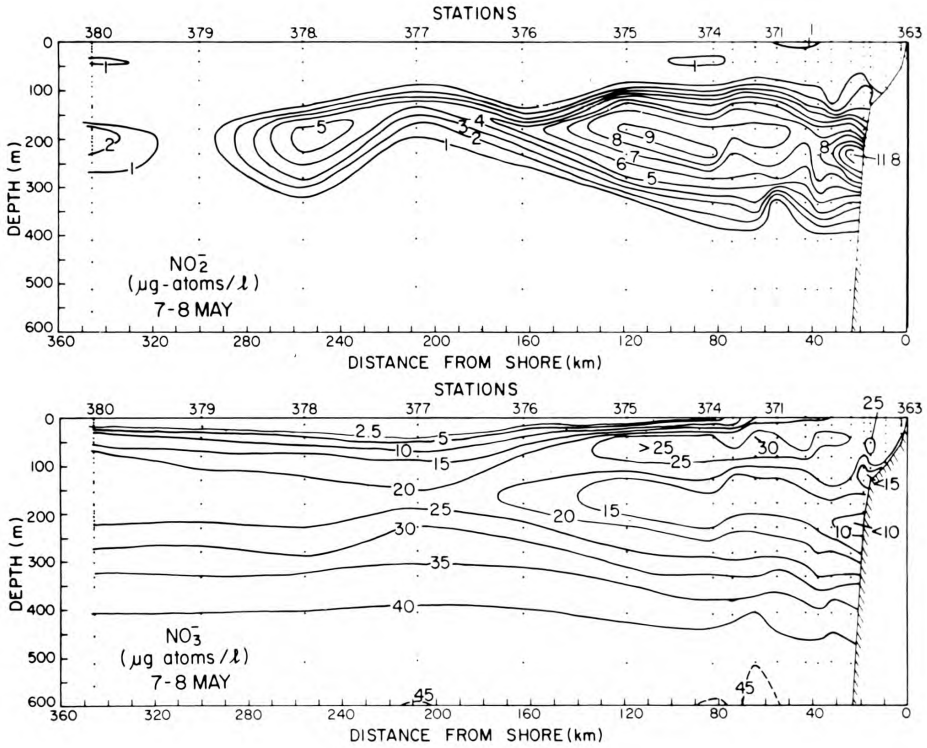


Figure 8. *Nitrite and nitrate cross sections of the Peru current, looking northwest, with the Peruvian coast at 15°S. latitude on the right. The large mid-water plume of nitrite in the upper panel respresents the intensity of microbial nitrate reduction. It is most intense close to the coast at 200 m. The impact on the mid-water concentrations is shown in the lower panel. Sulfate reduction starts soon after the combined nitrate and nitrite fall to zero.*

However, if the sulfide is upwelled into the surface, its presence is indicated by massive fish kills. Along the Peru coast this event is called an aguaje. In March 1976 a major aguaje occurred. The oxygen minimum zone off Peru exhaused its supply of nitrate, nitrite and nitrous oxide and began to reduce sulfate to sulfide. The sulfide-bearing water upwelled and fish kills occurred along the coast. Records of similar aguajes show that deep-water metabolic anomalies occur roughly every eight years, which is similar to the frequency of another marine disaster, El Nino.

El Nino and the Collapse of the Anchovy Fishery.

El Nino occurs when warm nutrient-poor equatorial waters flow along the Peruvian coast and bring torrential rains and floods to the land and starvation to the anchovy populations in the sea. The combination of destruction in the country side and the collapse of the anchovy fishery spells economic disaster for Peru. In the sea the catastrophe starts when the nutrient-poor equatorial waters replace the nutrient-rich Peru undercurrent waters. When this poor water is upwelled to the surface it fails to stimulate phytoplankton growth, forcing the anchovies to seek food elsewhere or starve. Many anchovies do starve; but even if some survive, they become too dispersed to be fished, so the fishery fails.

Teleconnections Between Equatorial Currents and Peruvian Coastal Chemistry

The control over the timing of aguajes and El Ninos is unknown. However, recent research has revealed a connection between these events and changes in atmospheric pressure, trade winds and oceanic currents along the equator. The sequence of events starts when a low pressure center over Indonesia

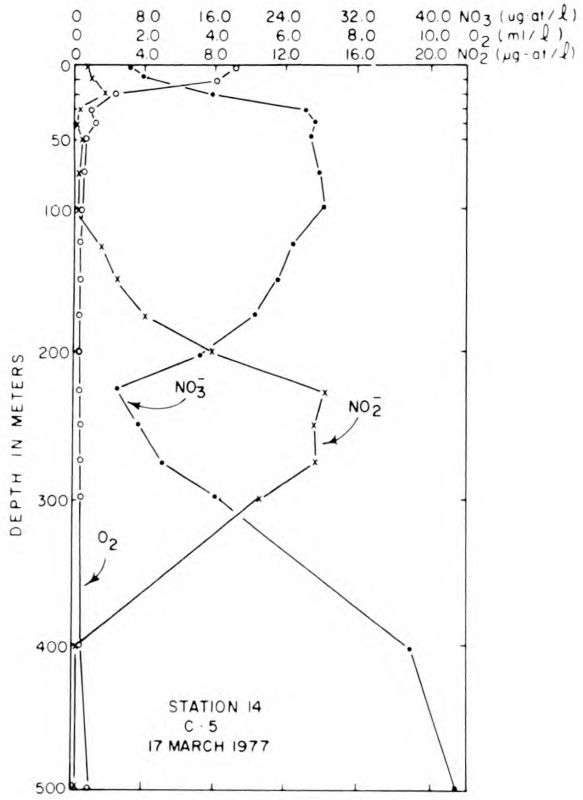


Figure 9. *A depth profile of oxygen, nitrate, and nitrite through the oxygen minimum zone at the shelf break off the Peruvian coast at 15°S. latitude. Between 200 and 300 m nitrate respiration, in which nitrate is reduced to nitrite, has begun. This is the first step in the denitrification process.*

shifts eastward. This results in stronger southeast trade winds over the equatorial Pacific, which strengthens the South Equatorial Current and which causes a thick warm-water lens to develop in the western Pacific. At the same time, while the eastern Pacific is stripped of its warm surface water, cold nutrient-rich water is upwelled, and the biological productivity is enhanced along the American coasts. Then the Indoesian low re-centers over Indonesia, the trade winds relax, and the excess warm water flows back toward the Americas. This transport is accomplished by a strengthened equatorial counter-current system. Tide guage records on Pacific Islands show clearly this itensified flow soon after the southeast trades relax. Upon reaching the Galapagos, this water is diverted north and south. Tide guages as far apart as Sitka, Alaska and Valparaiso, Chile record this event. Along the Peru coast, this warm water is seen as El Nino. The aguaje probably results as organic-rich high-density water subsides under the low-density advancing El Nino waters, stimulates metabolism in the oxygen minimum zone, and forces the microbial populations to utilize sulfate to meet their respiratory requirement.

Trace Metals in the Marine Environment

We have seen that it is convenient to divide the dissolved substances of the oceans into groups based on abundance. It is most interesting that each of these groups affects the phytoplankton differently. The abundant elements, collectively called the major constituents and consisting primarily of chlorine, sodium, sulfur, magnesium, calcium, potassium and carbon in their ionic (charged) forms, make up the "salt" in seawater and effectively exclude from the oceans those forms of life which cannot tolerate a salty environment. However, once this selection is made, the major constituents assume a passive role of secondary interest. The abudance of plant life—the annual plant crop, usually expressed in grams of carbon per meter square of oceans surface per year—is regulated by the minor constituents, those scarce substances without which there can be no growth.

Trace Metals as Limiting Nutrients or as Toxins

In the oceans as on the land, nitrogen and phosphorous in their mineral form have been recognized to be some of the scarce commodities, the so-called "limiting nutrients" essential to plant life. Certain trace metals, such as copper (Cu), zinc (Zn), maganese (Mn) and cobalt (Co) have also been shown to be essential for the growth of plants and are believed to be possible limiting nutrients in the open sea. However, Cu and some other metals may have a dual function in the sea; while they may be limiting nutrients at sub part per billion levels, they may also be toxic to algae at slightly more elevated concentrations. Indeed, Cu is an important commercial algicide commonly used in antifouling paints, and a great deal of it is released into the water by pleasure boats as well as commercial and military shipping. Other trace metals found in seawater, such as lead (Pb) and mercury (Hg), are not known to have any vital biological function and must simply be regarded as possible toxic pollutants.

How then does the chemical oceanographer differentiate between nutrient metal concentrations and toxic ones, or between natural, background levels of trace metals and subtle toxicity from pollution? And

how can this be done on an oceanic scale, working at the trace level, in a medium which contains a million-fold more interfering elements? Presently, the attack on this problem is two-pronged. First, ultrasensitive shipboard analytical techniques are being developed. As these new methods evolve they are being used to study the natural processes, both physical and biological which affect the concentrations of trace metals in the oceans.

Studies with New Instrumentation

Recent advances in automation technology have made it possible to develop electrochemical instrumentation which can carry out extremely difficult chemical analyses for trace metals in seawater totally unattended and with previously unattainable precision. An example of such an instrument is the trace element analyzer developed at the Naval Ocean Systems Center under ONR and Naval Material Command (NAVMAT) sponsorship (Figure 10). This microprocessor-based device samples a known volume of seawater from a continuous stream; acidifies it; carries out an electrochemical determination for Zn, Cd, Pb and Cu; adds a known amount of standard of each element; repeats the analysis; and calculates the concentrations of the elements in the original sample by comparing the electrochemical signal before and after the addition of the standard. A separate measurement for 3 or 4 metals is made every ten minutes, and concentrations in parts per billion are printed out on a strip of paper, along with date, the time of day and other remarks. A version of this instrument has been used in San Diego Bay to locate sources of Cu and Zn pollution. An interesting observation made during that work was that at a certain location in the bay, the trace metal content of the water varied precisely, but inversely, with the tides (Figure 11). This result clearly indicated that the outflowing bay water was significantly higher in trace metals than the incoming ocean water.

The presence of pollutants in the oceans can often be detected by the mathematical relationship between the trace element concentration and other nutrient variables. For example, in the open ocean, nutrient materials are taken up by the phytoplankton in the presence of sunlight and formed into organic materials. Subsequently, these nutrients are released into the water when the organic material is decomposed by bacteria. Thus we find that nutrient concentrations are low in the zone of photosynthesis, and that there is a distinct increase in concentration at depth (approximately 1000m) where they are released. The cycle begins anew when the nutrients are returned to the surface by vertical mixing. Figure 12 shows such a nutrient cycle. It has been observed that elements of biological origin in seawater are present in discrete ratios to each other, these ratios representing the fundamental and unalterable requirements of living tissue. When the concentrations of nitrogen (as nitrate, NO_3-) and phosphorous (as orthophosphate, $PO_4 - ^3$) in seawater are plotted versus one another on

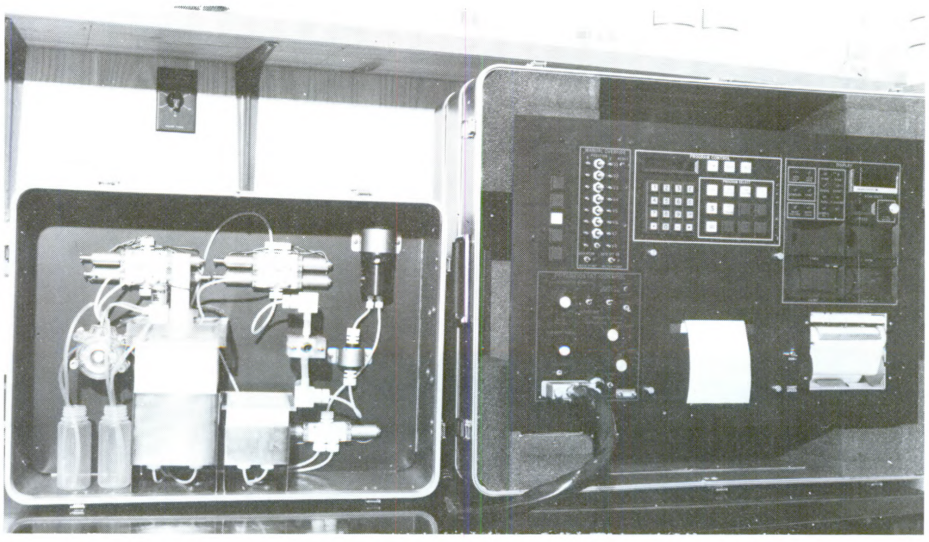


Figure 10. *Microprocessor controlled automated trace metal analyzer developed by Naval Ocean Systems Center.*

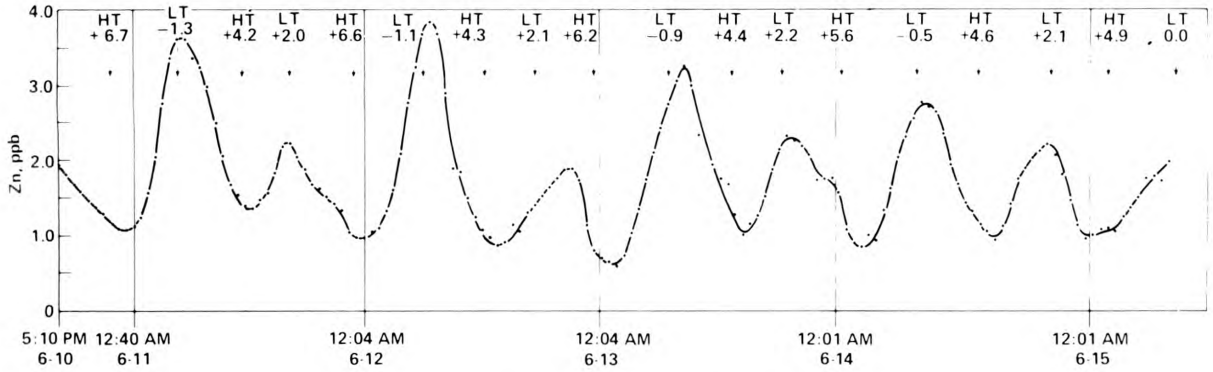


Figure 11. Zinc concentrations in San Diego Bay.

the same graph, it is found that between 15 and 16 atoms of nitrogen are present for every atom of phosphate. This ratio is maintained at virtually all depths (Figure 13), and is also found in the elemental composition of mixed phytoplankton populations. If the trace metals measured in seawater also come from this biogeochemical cycle, then it can be expected that they will also be found in discrete ratios, not only to each other but to nitrogen and phosphorous as well. Unfortunately, our present analytical expertise is insufficient to show such relationships conclusively. Nevertheless, the process of biogenic uptake at the surface and release at depth has already been identified for certain metals; and it is likely that more detailed information on trace element ratios will follow.

Occasionally, man-made pollution is easy to observe from the depth vs. concentration profiles of certain metals. Figure 14 shows three such concentration profiles in the ocean. The profiles are idealized to serve as examples. The first profile (A) shows that oceanic mixing will in time destroy a profile and give a homogeneous distribution of concentration with depth. Profile B indicates that if surface (biological) uptake is more rapid than deposition from, e.g. the atmosphere, then the concentration at shallow depths will be less than that within the body of the oceans. On the other hand, airborne pollution in excess of uptake will exhibit a high surface concentration (profile C). Since the mixing rate of the deep oceans is on the

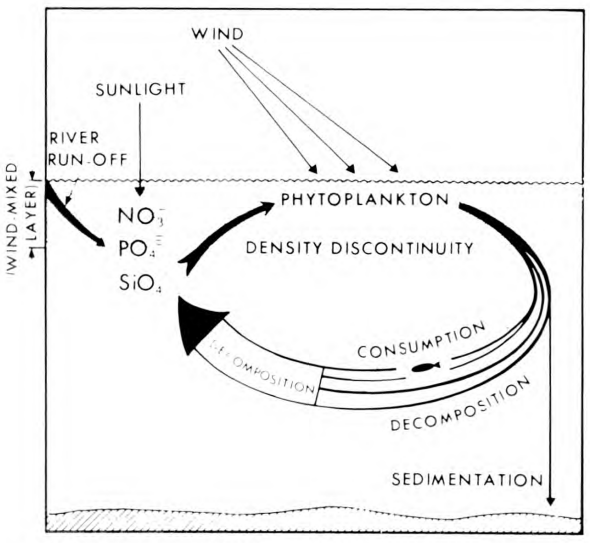


Figure 12. The cycle of oceanic micronutrients.

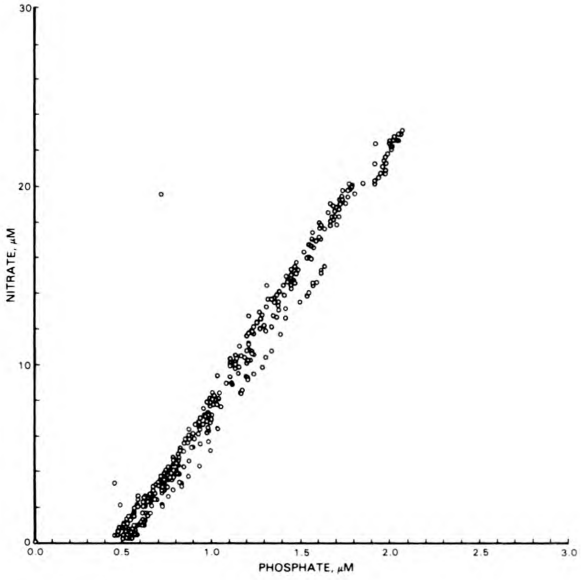


Figure 13. Nitrate concentration versus phosphate concentration in the upwelling region off of Monterey, California. The points fall on a slope of value slightly greater than 15. Data courtesy E.D. Traganza, Naval Postgraduate School.

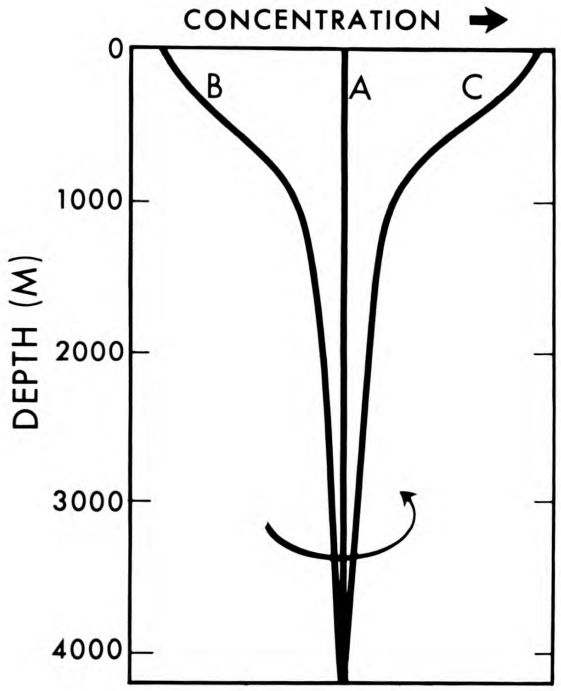


Figure 14. *Three profiles of concentration versus depth as they may occur in the oceans: A, the net surface input or depletion rate is slow compared to the vertical mixing rate; B, surface depletion is greater than the mixing rate; and C, surface input rate is greater than the mixing rate.*

order of a thousand years, profile defining processes must occur on a shorter time scale. Figure 15 shows some actual trace metal concentrations measured in the ocean in the last decade. Some of the elements shown, Zn, Cu and Ni, exhibit discrete concentration minima in the upper layers, an indication of uptake. This is not true for Pb and Hg which show high concentrations at the surface. Since both of these elements are known to be airborne pollutants, Pb from automobile exhausts and Hg from uncontrolled industrial projects, the observation leads us to suspect that the sampled area was contaminated by an anthropogenic discharge. In the future, research efforts towards the development of faster, more sensitive and precise instrumentation will allow the oceanographer to assay larger oceanic areas and will permit a more accurate determination of man's impact on the sea.

Dissolved Amino Acids

Marine chemistry traditionally has been concerned with investigations of the cycles and interactions of the inorganic components of seawater. In contrast, only limited studies have been carried out on the organic constituents. Therefore, the knowledge of processes involving organic compounds in the ocean is meager. Most previous studies of the organic chemistry of seawater have focused on measurements of total organic carbon. Few studies have concentrated on individual organic constituents of the oceans, and those that did often had severe contamination problems arising from the attempts to isolate small quantities of organic material from large volumes of seawater.

Importance of Trace Organics

It has been well documented that trace inorganic constituents are important components of both biological and chemical cycles in the oceans. Despite

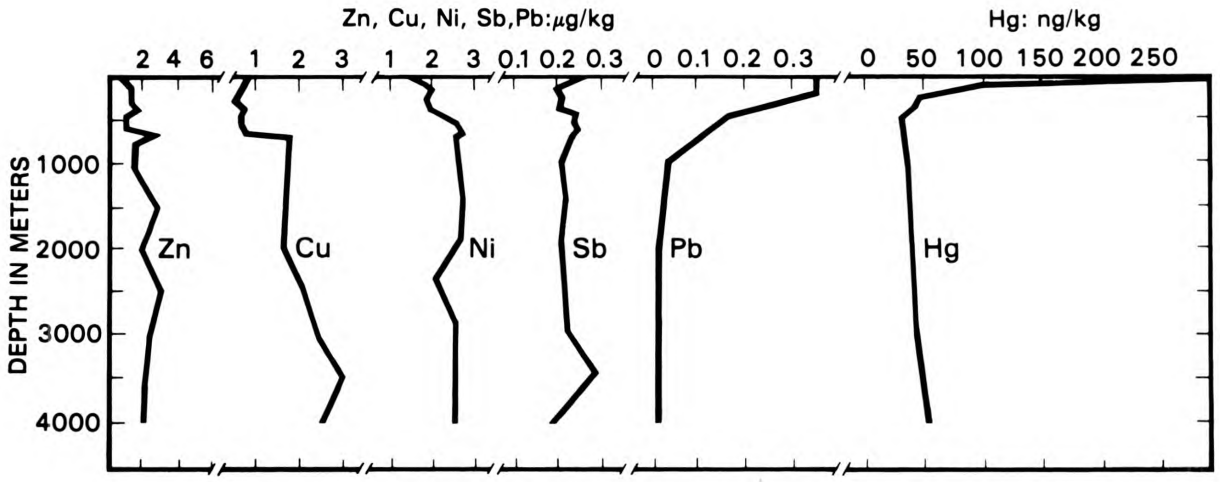


Figure 15. *Trace metal profiles measured in oceanic waters.*

the limited number of investigations of specific organic compounds in seawater, there is evidence that these components could be equivalent in importance to the inorganic constituents; for example, organic compounds in extremely low concentrations are known to induce feeding or sexual responses in a variety of marine organisms.

Amino acids are molecules that are essential to all forms of life on earth. Thus, studies of these compounds in the oceans could provide new insights into the cycle of important biological molecules in the sea. Investigations of *free* amino acids in the ocean reveal undetectable levels in deep waters, while surface waters have been found to contain very low concentrations of free amino acids. There are significant quantities of *combined* amino acids at all depths in the oceans; however, combined amino acids are bound in some sort of polymeric material and are released only upon boiling in strong acid. The concentration of combined amino acids is roughly ten times that of free amino acids. It was originally suggested that the source of these combined amino acids was simply bacteria that passed through the filter used in the initial seawater processing step. One way to verify or disprove this would be to determine the D/L amino acid ratios of the combined amino acids. Most amino acids can exist in two different isomeric or mirror image forms, called the "D" and "L" enantiomers (Figure 16). In most organisms, only the L enantiomers are found, with the exception of bacteria that contain several D-amino acids in their cell wall proteins. Thus, by measuring the D/L ratios of amino acids in the combined fraction, it was hoped to be able to demonstrate that this material was of bacterial origin.

The results of the D/L alanine measurements in the combined amino acid material are shown in Figure 17. As can be seen, the D/L alanine ratio increases with depth until it is very close to 1.0 below 500m. There is a possibility that this increasing ratio with depth in the ocean reflects a change in the bacterial population which, in deep water, has a D/L alanine ratio close to 1.0. However, it is unlikely that bacteria would incorporate D and L alanine in a proportion close to 1.0, which is the chemical equilibrium ratio for the enantiomers. Also deep water has been sampled at widely different locations, and the D/L alanine ratio never exceeds 1.0. It would seem highly likely that the various water samples would contain different bacterial populations that might have differing D/L alanine ratios in their cell wall proteins, and that they might have D/L ratios less and greater than 1.0. The fact that the measured D/L ratios do not exceed 1.0 suggests that we are observing a chemical process, not a biological effect.

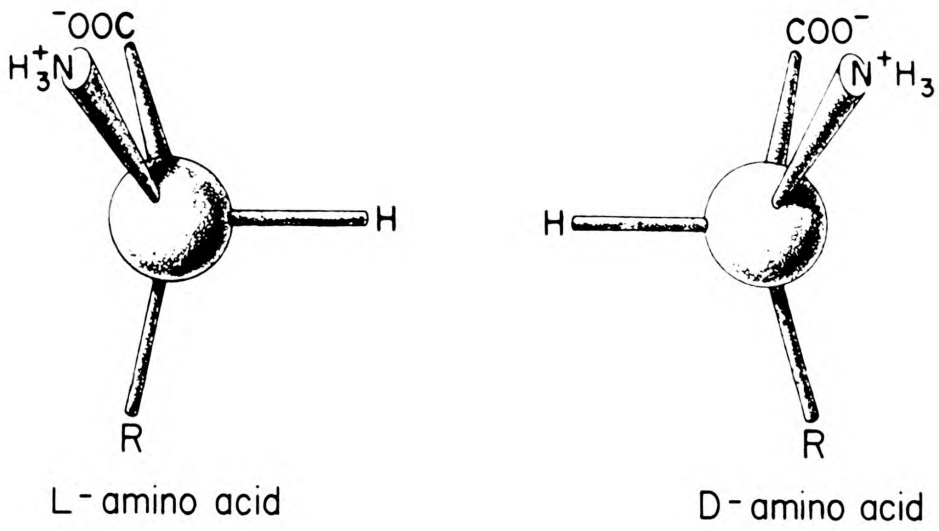


Figure 16. *Diagrammatic representation of the D and L enantiomers of amino acids. The "R" substituent is the variable that distinguishes the 20 different amino acids found in living organisms.*

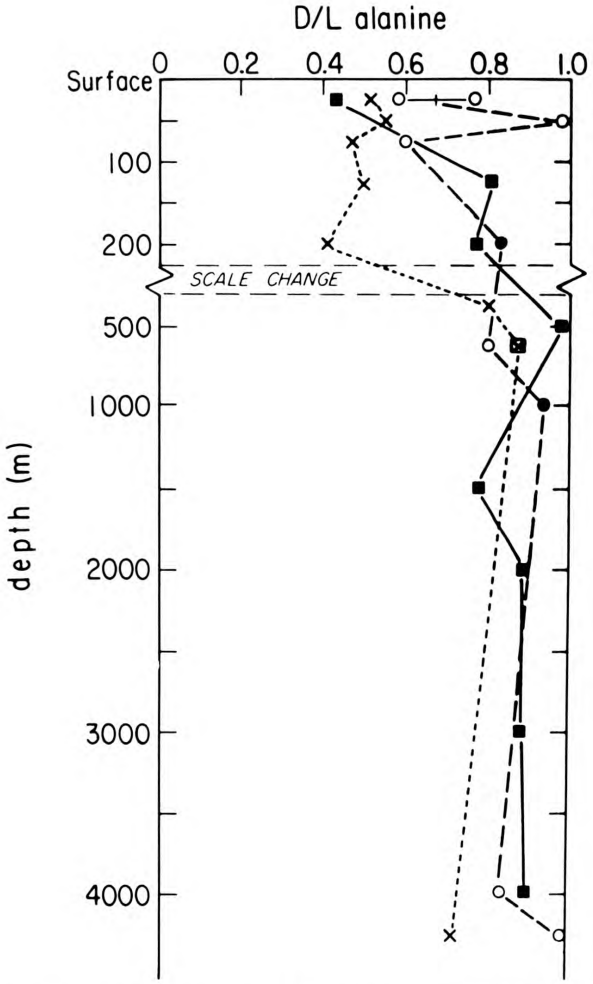


Figure 17. The results of the D/L alanine measurements for stations in the North Pacific gyre (o), 670 km southwest of San Diego (x), and 60 km off Peru (■). The results with symbols (●) and (⧓) are independent measurements carried out by Dr. K. Kvenvolden, U.S. Geological Survey, Menlo Park.

The Racemization Hypothesis

Another possibility that could explain the high D/L alanine in the "combined" amino acids in deep oceanic waters is that racemization has taken place. Racemization is a chemical reaction that converts a pure L-amino acid into a mixture containing equal amounts (a racemic mixture) of both D and L enantiomers. Racemization has been observed in a variety of fossil materials and in deep-sea sediments. However, estimates of the racemization rate in the ocean indicate it would require 100,000 years to produce a D/L alanine ratio approaching 1.0; this is much longer than the mixing times of the oceans. Also the relative rates of the various amino acid racemization reactions indicate that aspartic acid would be more rapidly racemized than alanine, which is not what is found for "combined" amino acids in the ocean.

The Serine Decomposition Hypothesis

An interesting possible explanation for the increase in the D/L alanine ratio with depth in the ocean is that a decomposition reaction of the amino acid serine takes place, producing alanine with a D/L ratio of 1.0. This serine decomposition reaction has recently been found to occur in the carbonate fraction of deep sea sediments. A check of this hypothesis is provided by the fact that the amino acid threonine can decompose via a pathway identical to that of serine, producting the amino acid alpha-amino-N-butyric acid (ABA) and that the ABA produced by this mechanism has a D/L ratio of 1.0. ABA is a nonbiological amino acid, and its presence in seawater therefore would be convincing evidence that the serine and threonine decomposition reactions occur in the ocean. It was recently found that ABA is present in seawater and that ABA concentration increases with depth. Moreover, the D/L ABA ratio in deep water was found to be 1.0.

This is one of the first indications that chemical alteration of dissolved organic compounds takes place in the ocean. Alteration reactions, such as the serine and threonine decomposition reactions, may cause the organic material in the ocean to be less biologically usable, and thus they could partially account for the fact that the bulk of the dissolved organic carbon in the oceans is of considerable age. Another important aspect of these amino acid studies is that the D/L enantiomeric "fingerprint" of oceanic combined amino acids has been established. Anthropogenic inputs would likely alter the indigenous D/L amino acid ratios in seawater. Thus in the future, measurements of the D/L amino acid ratios could be useful to ascertain whether human activities are affecting the amino acid balance in certain oceanic waters.

Hydrocarbon Pollutants

In addition to naturally occuring organic compounds, a number of man-made inputs can be detected. Several scientists have been studying the biogeochemistry of fossil fuel compounds in the environment. These studies are complementary to studies of lethal and sublethal effects of these compounds on

aquatic organisms. Biogeochemical studies provide information on the routes and rates of transfer, reactions, and reserviors of these compounds in the marine environment. For example, given an oil spill in a harbor, how fast will oil compounds mix into the water and move towards the mouth of the harbor? Where do marine organisms come into contact with the toxic components?

Petroleum is an extremely complex mixture of tens of thousands of compounds with a wide molecular weight range. This complex chemical soup is discharged into the aquatic environment, itself a complex chemical soup, and then acted on by a variety of physical, chemical, biological, and geological processes. A stylized representation of this is given in Figure 18 and is a composite of information gathered in the literature to date. Research is now focused on measuring the absolute and relative rates of these processes and reactions for different oil inputs and different environments, e.g. arctic and tropical. We already know from our own and other research that the absence of an oil slick does not mean the absence of petroleum compounds in the water, sediments, or organisms in an area. For example, some aromatic hydrocarbons which are toxic to marine life under certain conditions can still be detected in marsh sediments five years after an oil spill.

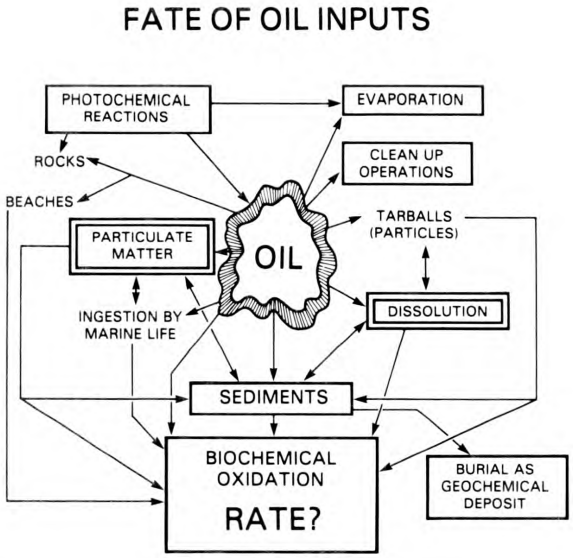


Figure 18. *Fate of oil inputs. Stylized representation gathered from many different studies.*

Fossil Fuel Inputs to the Oceans

Oil spills from ship or production accidents are only a small part of the input of fossil fuel compounds to the marine environment. Table 1, taken from a National Academy of Sciences study, *Petroleum in the Marine Environment,* published in 1975, illustrates this point. Note that normal operations of ships, including tankers, is a substantial source of fossil fuel compounds discharged to the oceans as are the discharges from rivers and from land operations where fossil fuel compounds are introduced by chronic releases which sum up to about 44 percent of the world inputs. For example, studies in the New York Bight area suggest that 4×10^3 tons of hydrocarbons per year are discharged to that area (Figure 19) by dumping of sewage sludge and harbor dredge spoils.

What about the future when oil becomes scarce? Will we have a reprieve from the input of fossil fuel compounds to the oceans? The answer to that is in part contained in the past. By studying hydrocarbons in cores of sediments deposited during the past 100 to 1000 years in near shore waters and lakes, several groups of scientists have shown that an historical record of fossil fuel use has apparently been preserved in sediments from several locations. The polynuclear aromatic hydrocarbon composition of the sediments had a signature which pointed to combustion processes as the major source of these compounds. The theory gaining general acceptance and being more rigorously tested is the following. Combustion of oil and coal for heating and power generation releases these compounds to the atmosphere. They then are deposited on land and on the ocean by rain and dry fallout. The material falling on land is partially remobilized and transported by runoff to coastal areas and to lakes. As fossil fuel consumption increased, the concentrations in the environment as reflected in the sediments also increased. Concentrations in sediments deposited in 1970 are sometimes ten to one hundred times higher than in sediments deposited in 1840 to 1890. Many of these compounds and their reaction products are carcinogenic or mutagenic. What are the long term effects of increasing environmental levels of these compounds on human health and on the viability of natural resource populations? These are questions that medical researchers and marine biologists have begun to investigate. The incredibly sensitive analytical techniques developed by marine organic geochemists will be invaluable in these studies. However, there is another very important application of marine organic geochemistry knowledge which is the responsibility primarily of the Department of Defense. It is not often discussed in scientific or general

TABLE 1. Estimate of petroleum and petroleum hydrocarbon inputs to the marine environment.

(Millions of Metric Tons Per Year)

	World
Normal operations	
Offshore Production[a]	0.02
Transportation[a]	
Load-on-top tankers	0.31
Non-load-on-top tankers	0.77
Dry docking	0.25
Terminal operations	0.003
Bilges bunkering	0.5
Coastal Refineries[a]	0.2
Coastal Municipal Wastes[a]	0.3
Coastal Non-Refinery	
Industrial wastes[a]	0.3
Urban Runoff[b]	0.3
River Runoff[b]	1.6
Atmosphere[c]	0.6
Natural Seeps[b]	0.6
Accidents[a]	
Offshore production	0.06
Tankers	0.2
Non-Tankers	0.10
	6.113

[a]*Estimate with high confidence rating.*
[b]*Estimate with modest confidence rating.*
[c]*Estimate with low confidence rating.*

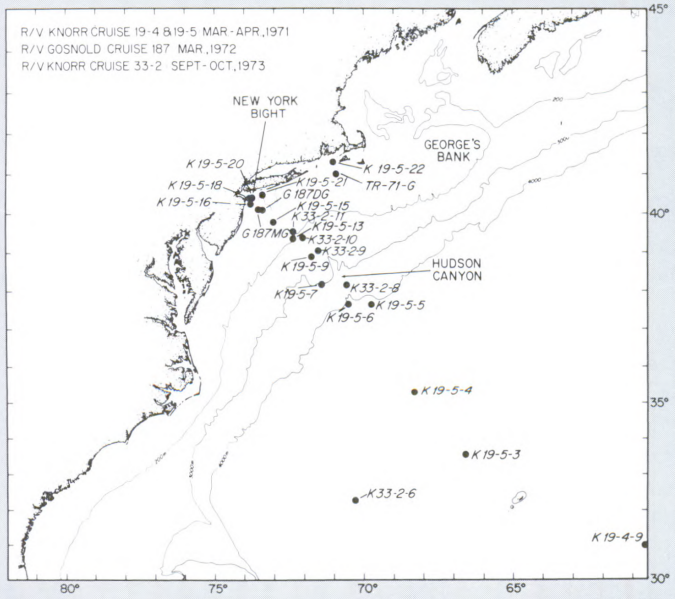
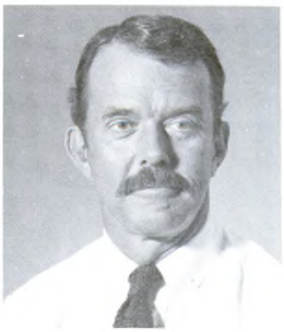


Figure 19. Station locations of surface sediment samples analyzed from biosynthetic and fossil fuel hydrocarbons.

public forums, perhaps because it is fervently hoped that the need for the application of the knowledge will never arise. This is the question of the movement of chemical warfare agents through local and global ecosystems and the ultimate fate of these chemicals—most of which are organic compounds. We must be prepared with an adequate body of knowledge about organic compounds in the marine and fresh water environments in case of accidental or intentional releases of chemical warfare agents by unfriendly powers or terrorist groups.

Navy Interests

The major operating area of the Navy is the open ocean. Ports and harbors with a wide range of marine environmental characteristics are also used extensively. To operate effectively, the Navy must possess a substantial knowledge of this marine environment; with this knowledge, the degree of operational effectiveness can be maximized. It is for this reason that the Office of Naval Research supports a diverse research program in the ocean sciences. In as much as oceanic chemistry occupies a central role in the understanding of the multifaceted marine environment, chemical oceanographic research forms a part of this Ocean Sciences Programs. The research provides insight into the processes and mechanisms that determine the chemical character of the sea. Therefore, it is directly applicable to solving specific problems of Navy relevance, such as the corrosion and deterioration of materials in the marine environment; the monitoring, assessment, and possible control of pollutants in the sea and harbors used by naval craft; the interchange of materials across the air-sea and sea-bottom boundaries, factors that determine in the air the characteristics of marine aerosols and influence weather, and at the sea floor affect bottom stability and sound reflectivity; the effect of chemical processes on the properties of sound transmission, absorption, and scattering in the oceans; and improved understanding of suspended matter controlling underwater visibility in seawater; and the use of tracers for the identification of water masses in studying ocean circulation and mixing mechanisms. There is also promise that marine chemists can develop useful military surveillance techniques in the future. All these Navy problem areas share a common basis in oceanic chemistry. ■

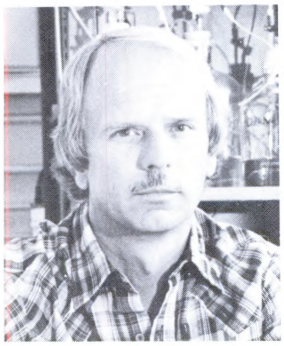


Dr. Edward J. Green *is Group Leader for Oceanic Chemistry and Biology, Environmental Sciences Directorate, Office of Naval Research, Naval Ocean Research and Development Activity. His research has focused upon dissolved gases in natural waters, but he has also published in the fields of solid-solution thermodynamics, geostatistics and electrotellurics. He serves on the UNESCO Committee on Global Investigations of Pollution in the Marine Environment and is a member of the Geochemistry Society, the American Geophysical Union, and the American Association for the Advancement of Science.*

Dr. John M. Edmond *is Professor of Marine Chemistry at the Massachusetts Institute of Technology. His research deals with the processes and mechanisms concerning the composition of oceanic and continental waters in space and time. He has also been in the forefront of research on the chemistry of deep sea hydrothermal vents. He is a member of the Geochemistry Society, the American Geophysical Union and the American Association for the Advancement of Science.*

Dr. Theodore T. Packard *is a principal investigator at the Bigelow Laboratory for Ocean Sciences in West Boothbay Harbor, Maine. His research is focused on enzymetically regulated chemical reactions in the ocean and especially how these reactions regulate the formation and maintenance of midwater oxygen minimum zones. He is a member of the American Chemistry Society and the American Geophysical Union.*

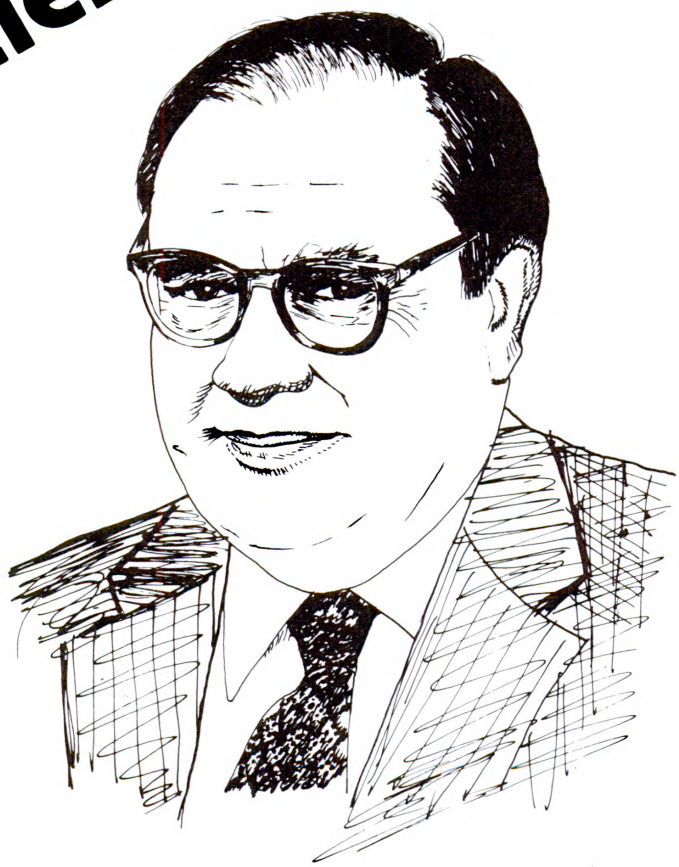
Dr. Alberto Zirino *heads the Marine Environmental Branch of the Naval Ocean Systems Center, San Diego. His doctoral work concerned electrometric measurements of trace metals in seawater, a subject to which he has continued to make important contributions. Dr. Zirino has acted as chief scientist on a number of oceanographic cruises. In addition to his duties at NOSC, he is Adjunct Professor of Chemistry at San Diego State University.*



Professor Jeffrey L. Bada *is a Professor of Marine Chemistry at the University of California, San Diego. He joined the Scripps Institution of Oceanography, La Jolla, in 1970. In 1979 he was chosen to be one of the first American scholars to participate in a scientific exchange program between the United States and the People's Republic of China. Professor Bada's research interests are concerned with the diagenesis of low molecular weight organic acids in nature as well as the biological and geochemical implications and applications of these reactions.*

Dr. John W. Farrington *is Senior Scientist at Woods Hole Oceanographic Institution and Director of the Coastal Research Center of that institution. His research has focused on the organic geochemistry of the oceans, particularly that of sediments and particulate matter. He is an internationally recognized expert on the biogeochemistry of the anthropogenic compounds in the marine environment. Dr. Farrington serves on numerous national boards and committees, including the U.S. National Academy of Sciences Steering Committee for Petroleum in the Maine Environment and the NAS Environmental Studies Board.*

profiles in science



Arthur L. Schawlow is the J.G. Jackson and C.J. Wood Professor of Physics at Stanford University and has been a contractor of the Office of Naval Research (ONR) for many years. His research is in the fields of optical and microwave spectroscopy, nuclear quadrupole resonance, superconductivity, and lasers. With Charles H. Townes, he is coauthor of a book, *Microwave Spectroscopy,* and of the first paper describing optical masers, which are now called lasers. For this latter work, Schawlow and Townes were awarded the Stuart Ballentine Medal of the Franklin Institute in 1962. [In the 1950's ONR supported the research of Townes which led to the development of the maser.]

In 1976, he was awarded the Frederick Ives Medal of the Optical Society of America in recognition of his pioneering role in the invention of the laser and his continuing research in the refinement of coherent optical sources and in the application of optics to science and technology.

Professor Schawlow received a Nobel Prize in 1981 for his contributions to the development of laser spectroscopy. He developed a means whereby lasers with very pure output radiation can selectively be tuned to interact with atoms. The precision of this method is so great that it can be used to test experimentally for the first time fundamental theories about matter itself.

Professor Schawlow is a member of the National Academy of Sciences, A Fellow of the American Academy of Arts and Sciences, past President of the Optical Society of America, and past President of the American Physical Society. ■

research notes

Universal Donor Red Blood Cells

Extensive national publicity has been given to a research report in *Science* (Vol. 215, 8 January 82) which describes the successful transformation of Type B red blood cells to universal-donor Type O blood cells and the first successful evaluation of these cells in humans. Individuals with Type A blood can donate only to a Type A recipient, and a Type B individual can donate only to a Type B recipient. However, an individual with Type O blood can donate to Types A, B, and O recipients with no subsequent transfusion reactions.

The research, conducted by Dr. Jack Goldstein of the New York Blood Center with funding from the Office of Naval Research (for which a patent application has been filed), used enzymatic modification of the type-determinant molecule on the red blood cell membrane to accomplish the transformation from Type B to Type O. Evaluation of samples of the transformed blood in three humans showed normal survival after 30 days.

The ability to provide a single universal donor type blood in military combat theaters would significantly improve logistical and processing requirements in military medicine. Efforts under this program are continuing in order to duplicate this process in the transformation of Type A to Type O blood. A different enzyme is needed for this process. The final objective of this program is to combine the type transformation process with long-term freeze preservation of the red blood cells in order to provide a long-term stockpiling capability for universal donor cells. The long-term freeze preservation capability also is a past accomplishment of the U.S. Navy funding. ■

(Arthur B. Callahan, ONR-Boston)

A New Look at Organizational Commitment

Traditionally, personnel turnover has been seen as an inevitable, if unfortunate, fact of life in organizations. The disruptive effect of a worker leaving the organization is compounded by the costs of recruiting, hiring, and training a replacement. The loss of skills and experience by the organization has made turnover an often-used negative indicator of organizational effectiveness. An updated and expanded analysis of the causes and consequences of personnel turnover is provided in a recent book by Richard Mowday, Richard Steers, and Lyman Porter, *Employee-Organization Linkages,* published by Academic Press. The book provides fresh insights into the nature of organizational commitment and examines the positive as well as the negative effects of turnover on both organizations and individuals. Viewing turnover as a symptom rather than a disease, the authors point out that turnover is also a process through which organizations replace discontented and ineffective employees, providing the organization with an opportunity to bring in new and potentially innovative workers. At the individual level, the beneficial effects of leaving an organization are often overlooked. The potential for self-advancement, new challenges, increased earnings, and improved individual-job match may come about only in a new organizational setting.

In addition to an analysis of the research on organizational commitment, an area in which the authors themselves have carried out significant original research, the book also provides suggestions for ways that managers can increase employees' commitment to the organization. The research reported in this book was supported by the Office of the Naval Research. ■

(David Stonner, ONR)

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