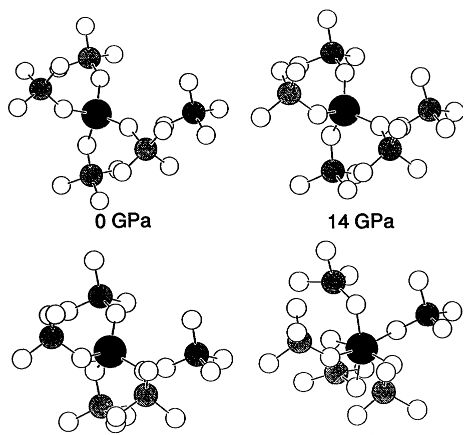

Fig. 4. The local structure about a typical Al atom in $AlPO_4$ at several pressures. The coordination number of an aluminum atom is indicated by the lines to oxygen atoms corresponding to lengths of 2.2 Å or less.

is the crystallinity of the sample fully restored, but its original orientation is also preserved. Details of the recovery mechanism can be examined through the analysis of bond angles, as presented above. The path following decompression retraces that of the compression (Fig. 3). Both the O–Al–O and the O–P–O angle distributions narrow and eventually return to tetrahedral angles in such a way that the tetrahedral helices unwind to their original positions. The PO_4 groups, which alternate with AlO_4 groups in the crystal, distort under pressure but remain largely four-coordinated. In the absence of diffusion, the relative positions of the atoms are effectively maintained in the disordered phase. When the pressure releases, the oxygens around the P atoms quickly relax back to the PO_4 tetrahedra. This process redirects the Al atoms back to the crystalline positions.

Several significant observations can be made from the theoretical investigation. The pressure-induced densified phase in $AlPO_4$ is not a random network but a solid that is disordered over the long range with considerable short-range order. Because of the lack of diffusion, pressure-amorphized materials would not, in general, have the same structure as quenched liquids. Attempts to correlate the structure of the disordered solid to that of high-density liquid may be misleading. The results obtained here can be generalized to other systems that exhibit structural memory effects. The presence of strongly covalently bound units that preserve their coordinations is essential, as, for example, the SO_4^{2-} in $LiKSO_4$ and the guest molecules in clathrate hydrates and clathrasils. In clathrate hydrates or clathrasils (*8*), the guest molecules remains intact, and therefore their pressure-induced phase transitions are reversible. This behavior is in contrast to that observed in closely related materials, ice Ih (*5*) and α-quartz (*6*).

REFERENCES AND NOTES

1. Y. Waseda, *Structure of Non-Crystalline Materials: Liquids and Amorphous Solids* (McGraw-Hill, New York, 1980); S. R. Elliot, *Physics of Amorphous Materials* (Wiley, New York, ed. 2, 1990).
2. W. H. Zachariasen, *J. Am. Chem. Soc.* **54**, 3841 (1932); R. Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983).
3. I. Amato, *Science* **252**, 1377 (1991); P. Gaskell, M. C. Eckersley, A. C. Barnes, P. Chieux, *Nature* **350**, 675 (1991).
4. B. E. Warren, *X-Ray Diffraction* (Addison-Wesley, Reading, MA, 1969).
5. O. Mishima, L. D. Calvert, E. Whalley, *Nature* **310**, 393 (1984); E. Whalley, O. Mishima, Y. P. Handa, D. D. Klug, *Ann. N.Y. Acad. Sci.* **484**, 81 (1986); J. S. Tse and M. L. Klein, *Phys. Rev. Lett.* **58**, 1672 (1987).
6. R. J. Hemley, A. P. Jephcoat, H. K. Mao, L. C. Ming, M. H. Manghnani, *Nature* **334**, 52 (1988).
7. A. Jayaraman, D. L. Wood, R. G. Mains, Sr., *Phys. Rev. B* **35**, 8316 (1987); M. B. Kruger and R. Jeanloz, *Science* **249**, 647 (1990).
8. Y. Fujii *et al.*, *J. Phys. C* **18**, 789 (1985); S. Sugai, *ibid.*, p. 799; H. Sankaran *et al.*, *Phys. Rev. B* **38**, 170 (1988); M. B. Kruger *et al.*, *J. Chem. Phys.* **91**, 5910 (1989); Y. P. Handa, J. S. Tse, D. D. Klug, E. Whalley, *ibid.* **94**, 623 (1991); J. S. Tse, D. D. Klug, J. A. Ripmeester, in preparation.
9. J. S. Tse and D. D. Klug, *J. Chem. Phys.* **95**, 9176 (1991); S. Tsuneyuki, M. Tsukada, H. Aoki, Y. Matsui, *Phys. Rev. Lett.* **61**, 869 (1988).
10. J. S. Tse and D. D. Klug, *Phys. Rev. Lett.* **67**, 3559 (1991).
11. J. R. Chelikowsky, H. E. King, Jr., N. Troullier, J. L. Martins, J. Glinnemann, *ibid.* **65**, 3309 (1990); J. R. Chelikowsky, H. E. King, Jr., J. Glinnemann, *Phys. Rev. B* **15**, 10866 (1990).
12. S. Nosé, *J. Chem. Phys.* **81**, 511 (1984); ——— and M. L. Klein, *Mol. Phys.* **50**, 1055 (1983).
13. B. W. H. van Beest, G. J. Kramer, R. A. van Santen, *Phys. Rev. Lett.* **64**, 1955 (1990).
14. H. Sowa, J. Macavei, H. Schulz, *Z. Kristallogr.* **192**, 119 (1990).
15. M. B. Kruger and R. Jeanloz, *Eos* **70**, 1385 (1990).

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Bulk Chemical Characteristics of Dissolved Organic Matter in the Ocean

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Dissolved organic matter (DOM) is the largest reservoir of reduced carbon in the oceans. The nature of DOM is poorly understood, in part, because it has been difficult to isolate sufficient amounts of representative material for analysis. Tangential-flow ultrafiltration was shown to recover milligram amounts of >1000 daltons of DOM from seawater collected at three depths in the North Pacific Ocean. These isolates represented 22 to 33 percent of the total DOM and included essentially all colloidal material. The elemental, carbohydrate, and carbon-type (by ^{13}C nuclear magnetic resonance) compositions of the isolates indicated that the relative abundance of polysaccharides was high (~50 percent) in surface water and decreased to ~25 percent in deeper samples. Polysaccharides thus appear to be more abundant and reactive components of seawater DOM than has been recognized.

DISSOLVED ORGANIC MATTER (DOM) in the oceans is important in the global carbon cycle (*1*), supports heterotrophic activity (*2*), and affects the penetration of light and exchange of gases at the sea surface (*3*). Despite its importance, relatively little is known about the composition and reactivity of marine DOM because of the lack of suitable methods for its isolation from seawater. Direct biochemical analyses of DOM in seawater typically account for less than 15% of the total mixture (*4*, *5*), and many techniques that would provide more comprehensive structural information, such as nuclear magnetic resonance (NMR) and infrared spectroscopy, require the isolation of DOM from the much more abundant salts in seawater. The conventional method for isolation has been adsorption of acidified DOM onto nonionic XAD resins (*6*). However, this method typically recovers a small fraction (5 to 15%) of the total DOM in seawater, requires large manipulations of pH during isolation, and is selective for hydrophobic constituents.

In contrast, tangential-flow ultrafiltration concentrates organic molecules primarily on the basis of size rather than chemical properties (*7*) and requires no pH adjustments that may change chemical associations and structures. Ultrafiltration therefore appears to be a more appropriate method for isolating a representative fraction of DOM than adsorption on XAD resins. In this report we describe the

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Table 1. Hydrographic data for samples collected at Station ALOHA (22°45.0'N, 158°00.0'W) and the concentrations of dissolved organic carbon (DOC), percentages of DOC recovered using tangential-flow ultrafiltration, and weight percentages of organic carbon (Wt%OC) in the recovered isolates as determined by direct-injection, high-temperature catalytic oxidation (HTCO) and the dry weights of the recovered isolates and by flash combustion of dried powders in a CHN analyzer.

Depth (m)	Salinity (per mil)	Temperature (°C)	Dissolved O_2 (μM)	DOC (μM)	Volume (liters)	% DOC recovered	% initial* DOC	Wt%OC† HTCO	Wt%OC† CHN
10	34.960	23.28	222.2	82	200	33	110	7.37	5.95
765	34.309	4.72	31.8	38	200	25	118	2.17	1.70
4000	34.684	1.46	154.2	41	200	22	106	1.96	1.77

*% Initial DOC = 100 ($DOC_{concentrate}$ + $DOC_{ultrafiltrate}$)($DOC_{initial\ water}$)$^{-1}$. †Sea salts were not completely removed during diafiltration resulting in weight percentages of organic carbon that are lower than those expected (~45%) for pure organic matter.

bulk chemical properties of DOM isolated by tangential-flow ultrafiltration from three depths in the open North Pacific Ocean.

Samples were collected during April 1991 from Station ALOHA (22°45'N, 158°00'W) located about 100 km north of Oahu, Hawaii. Hydrographic and basic chemical and biological parameters have been monitored at this station since 1988 (*8*). We collected water samples in Niskin bottles fitted with Teflon-coated closure springs using a 24-bottle rosette. Samples for ultrafiltration (200 liters) were collected from three depths, 10, 765, and 4000 m, corresponding to the surface, oxygen-minimum, and deep waters (Table 1).

Immediately following collection, we pumped water samples through 0.2-μm pore size, prerinsed Nuclepore polycarbonate filters and subsequently through 1000-dalton cutoff (~1-nm pore size) spiral-wound polysulfone filters using an Amicon DC10L ultrafiltration system. Total processing time for each sample was ~12 hours. Dissolved organic carbon (DOC) is operationally defined here as all organic carbon passing a 0.2-μm pore size filter and therefore includes all colloids <0.2 μm. We measured concentrations of DOC by a high-temperature oxidation method (*9*) in which a Shimadzu TOC 5000 analyzer was used (*10*). Concentrations of DOC and volumes of water were recorded for the initial water, the ultrafiltered concentrate, and the ultrafiltrate so that a mass balance of DOC could be established (*11*). Most sea salts were removed from ultrafiltered concentrates by diafiltration, and the samples were stored frozen for transport to the laboratory. Samples were dried under vacuum in a Savant SpeedVac concentrator.

The concentration of DOC in surface water (82 μM) was approximately two times as large as concentrations in oxygen-minimum and deep waters (Table 1). DOC profiles of this magnitude and shape have been observed at many ocean sites and interpreted to reflect the presence of labile organic matter of planktonic origin in surface water that is absent from older water at depth. Mass balance calculations indicate that all of the DOC in initial water samples was accounted for in the ultrafiltered concentrates (>1000 daltons) and ultrafiltrates (<1000 daltons) (Table 1); thus, contamination and processing losses were minimal. We recovered 33, 25, and 22% of the total DOC from surface, oxygen-minimum, and deep waters (Table 1). The observed trend of a decrease in the >1000-dalton fraction from surface water to deep water suggests that material in the colloidal size range comprised an important part of the reactive components of DOM.

Our results on the size distribution of DOM are similar to those of Carlson *et al.* (*11*), who found that ~34% of the persulfate-oxidizable DOC (~88 μM) in North Atlantic surface waters was >1000 daltons. However, a recent investigation by Sugimura and Suzuki (*9*) in the Northwestern Pacific Ocean indicated that ~85% of the total DOC (~290 μM) in surface waters was >1800 daltons. Similarly, these investigators found that ~85% of the total DOC (~95 μM) in Northwestern Pacific deep water (4000 m) was >1800 daltons (*9*). Such large differences between studies are beyond the range expected for natural variability, especially for two samples from 4000-m depth in the North Pacific Ocean, and suggest that there are systematic biases in DOM measurement or characterization. Because of uncertainty about the accuracy of seawater DOC measurements (*5, 9*), we also independently determined the organic carbon content of the ultrafiltered DOM (UDOM) by flash combustion (~1100°C) of the dried powder in a Carlo Erba 1106 CHN analyzer of the type used to quantitatively combust a wide variety of carbonaceous substances. The weight percentages of organic carbon measured were 10 to 25% lower than those calculated from the total DOC content (Shimadzu analyzer) and mass of the isolated samples (Table 1). Thus, we found no evidence for low DOC measurements that could be attributed to incomplete oxidation of the higher molecular weight or colloidal components of our DOM samples.

The atomic C/N values of the UDOM were lowest (15.3) in surface water and highest (22.5) in oxygen-minimum water (Table 2). These values lie in the middle of the range of 10 to 25 determined for bulk seawater DOM with the use of wet oxidation methods (*4, 5*). Humic substances isolated from the Pacific Ocean are carbon-rich [C/N ratio ≈34 (*12*)] relative to our UDOM samples; this difference reflects the bias of XAD resins against more polar nitrogen-containing DOM. Concentrations of dissolved organic nitrogen (DON) in the >1000-dalton size fraction (0.4 to 1.8 μM; from Tables 1 and 2) agree with concentrations determined recently for total DON (2 to 6 μM) in the North Pacific Ocean with the use of both high-temperature combustion (1100°C) and ultraviolet oxidation methods (*13*) and agree as well with average concentrations of total DON (5 to 8 μM) reported for these same water samples (*14*). These measurements are at odds, however, with other recent estimates of DON concentrations and C/N values for marine DOM. Suzuki and colleagues (*9, 15*) reported average C/N values near 7 for the total DOM in surface and deep waters of the Northwestern Pacific Ocean and concentrations of higher

Table 2. Atomic C/N ratios from elemental analysis and area percentages of the major ^{13}C NMR peaks for DOM isolated by ultrafiltration. Functional group assignments are: C–C, carbon singly bonded to carbon; C–O, carbon singly bonded to oxygen; O–C–O, carbon singly bonded to two oxygens; C=C, carbon doubly bonded to carbon; O–C=O, carboxyl and ester carbon; C=O, carbonyl carbon.

Depth (m)	C/N	C–C (%)	C–O (%)	O–C–O (%)	C=C (%)	O–C=O (%)	C=O (%)
10	15.3	26	43	11	7	13	3
765	22.5	32	24	5	21	14	4
4000	19.6	27	19	6	19	15	5

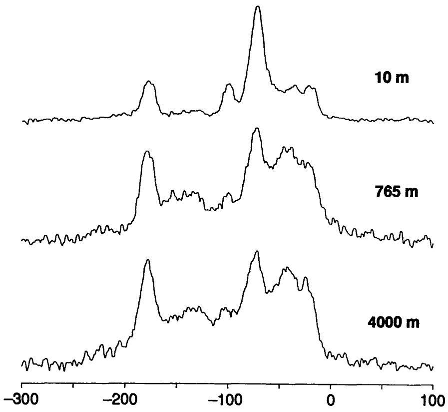

Fig. 1. Conventional CP/MAS ^{13}C NMR spectra of DOM isolated by ultrafiltration (>1000 daltons) from surface water (10 m), oxygen-minimum water (765 m), and deep water (4000 m) at 22°45'N, 158°00'W in the Pacific Ocean.

molecular weight (>5000 daltons) DON that were 20 to 70 times as large as our estimates for DON >1000 daltons. As discussed above, these large differences are beyond those expected for natural variability.

Structural features of the isolated DOM were investigated by cross polarization–magic angle spinning (CP/MAS) ^{13}C NMR (*16*). The ^{13}C NMR spectrum of the UDOM from surface water shows a dominant peak at 72 ppm and lesser peaks at 21, 40, 100, and 176 ppm (Fig. 1). Carbohydrates are the major family of biomolecules producing C–O resonances at 72 ppm and O–C–O resonances at 100 ppm. Unsubstituted alkyl carbons, such as methyl and methylene carbons, and amine carbons give rise to resonances between 0 and 50 ppm, and carboxyl, ester, and amide carbons produce resonances around 176 ppm.

Major compositional differences were apparent between UDOM from surface water and UDOM from oxygen-minimum and deep waters (Fig. 1). Integrated areas for C–O and O–C–O resonances indicate that there was a sharp decrease in the relative abundance of carbohydrate carbon from 54% in the UDOM from surface water to 29 and 25% in UDOM from oxygen-minimum and deep waters (Table 2). Surface-water UDOM had a threefold lower relative abundance of aromatic or olefinic carbons (in 110 to 160 ppm) than UDOM from deeper waters (Table 2). On the basis of these data and the vertical distribution of radiocarbon in DOM in the North Pacific Ocean (*17*), which indicates that labile and refractory components of DOM coexist in surface water, whereas refractory components dominate in deeper waters, it appears that high molecular weight polysaccharides (>1000 daltons) made up an important part of the labile DOM in surface water. Estimates of carbohydrate concentrations in the colloidal size fraction (1 to 200 nm) of DOM ranged from ~14 μM C in surface waters to ~2 μM C in deeper waters (Fig. 2).

The main structural features of the surface-water UDOM were very different from those of humic substances isolated by hydrophobic adsorption from seawater. The UDOM from surface water was rich in carbohydrates, whereas XAD-isolated humic substances are rich in unsubstituted alkyl and carboxyl carbons (*18*). Moreover, structural features of XAD-isolated DOM revealed by ^{1}H- and ^{13}C-NMR depict a material that is compositionally invariant with oceanic environment (*18*) and depth (*19*); these characteristics suggest that the XAD-isolated DOM is composed primarily of the older, more refractory components of DOM. There are, however, some similarities between the structural features of UDOM and humic substances from deep water. Both of the isolated fractions contained a significant aromatic or olefinic component and similar carboxyl contents, but the deep-water UDOM sample was enriched in carbohydrate and depleted in unsubstituted alkyl carbon relative to deep-water humic substances (*19*).

We also determined the carbohydrate content of the UDOM samples using a modified MBTH assay (*20*) to confirm the ^{13}C-NMR carbohydrate estimates. In the modified MBTH assay hydrochloric acid was replaced with sulfuric acid to more completely hydrolyze resistant polysaccharides, such as cellulose and chitin (*21*). The modified MBTH assay indicated that carbohydrates accounted for 49, 18, and 19% of the total C in surface, oxygen-minimum, and deep-water UDOM samples. The similarity between these data and those determined by ^{13}C-NMR confirms our estimate of carbohydrates in the UDOM samples and indicates that the modified MBTH assay yielded reasonably accurate estimates of total carbohydrate content.

Because ~70% of marine DOM was <1000 daltons (<1 nm), we do not know if the composition of the UDOM was representative of the total DOM. We used the modified MBTH assay to determine the total dissolved carbohydrate concentrations in the seawater samples collected for ultrafiltration. The modified MBTH assay yielded total dissolved carbohydrate concentrations of 27, 13, and 7 μM C in surface, oxygen-minimum, and deep-water samples (Fig. 2). These dissolved carbohydrate concentrations corresponded to 33, 34, and 17% of the total DOC, and were similar to those in the UDOM samples. Thus, ultrafiltration recovered a representative fraction of the MBTH-reactive carbohydrates from seawater.

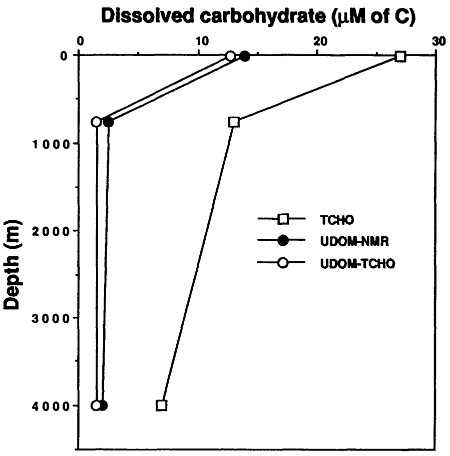

Fig. 2. Concentrations of dissolved carbohydrates in ultrafiltered DOM as determined by ^{13}C NMR (UDOM-NMR) and a modified MBTH assay (UDOM-TCHO) and the concentrations of total dissolved carbohydrates as determined by using the same modified MBTH assay (TCHO).

Our measurements of total dissolved carbohydrate concentrations are higher than most earlier estimates, which indicated that carbohydrates accounted for 10 to 15% of the total DOC measured by wet oxidation methods (*5, 22*) although values as high as ~35% were reported for the Caribbean Sea (*23*). We believe that the higher concentrations of carbohydrates measured with the modified MBTH assay result from the more complete hydrolysis of structural polysaccharides (*21*), which, as we have shown, appear to be abundant in the upper ocean.

The application of tangential-flow ultrafiltration to seawater samples has allowed a broad chemical characterization of a relatively large fraction of marine DOM, including all colloidal material. Compared to conventional hydrophobic adsorption techniques, ultrafiltration is less chemically selective and capable of recovering a greater portion of DOM. Our initial characterizations indicated that the concentration of the >1000-dalton size fraction of seawater DOM is one-tenth of that indicated by Suzuki and colleagues (*9, 15*) and that the C/N values are two to three times as large. Despite these differences, we concur that high molecular weight components of DOM are reactive and suggest that polysaccharides are dominant components of this reactive material, perhaps supporting much of the heterotrophic activity in the surface ocean. Use of ultrafiltration to recover DOM from seawater for experimental manipulations and detailed molecular-level characterizations will help resolve the above differences and provide a new understanding of the sources and reactions of the organic molecules composing this major carbon reservoir.

REFERENCES AND NOTES

1. W. F. Post *et al.*, *Am. Sci.* **78**, 310 (1990); J. I. Hedges, *Mar. Chem.*, in press.
2. L. R. Pomeroy, *Bioscience* **24**, 499 (1974); F. Azam *et al.*, *Mar. Ecol. Progr. Ser.* **10**, 257 (1983).
3. E. Goldberg and A. Bard, *Appl. Geochem.* **3**, 3 (1988).
4. P. J. Williams, in *Chemical Oceanography*, J. P. Riley and G. Skirrow, Eds. (Academic Press, London, 1975), pp. 301–363.
5. P. M. Williams and E. R. M. Druffel, *Oceanography* **1**, 14 (1988).
6. E. M. Thurman, *Organic Geochemistry of Natural Waters* (Nijhoff/Junk, Dordrecht, the Netherlands, 1985), chap. 10.
7. M. Cheryan, *Ultrafiltration Handbook* (Technomic, Lancaster, 1986), chap. 1.
8. S. Chiswell, E. Firing, D. Karl, R. Lukas, C. Winn, *School of Ocean and Earth Science and Technology Technical Report 1* (University of Hawaii, Honolulu, 1990).
9. Y. Sugimura and Y. Suzuki, *Mar. Chem.* **24**, 105 (1988).
10. Analyses of DOC were made using a Pt catalyst (0.5% Pt on Al$_2$O$_3$ support) at 680°C. Samples were filtered (0.2-μm pore size), acidified (10% H$_3$PO$_4$) to a pH of $\sim$2, and purged for 5 min immediately before analysis with the same ultrahigh purity oxygen that was used to operate the TOC analyzer. The water blank (4 ± 2 μM C) and instrument blank (22 ± 3 μM C) were measured at the time of sample analysis [R. Benner and M. Strom, *Mar. Chem.*, in press].
11. D. J. Carlson, M. L. Brann, T. H. Mague, L. M. Mayer, *Mar. Chem.* **16**, 155 (1985).
12. K. J. Meyers-Schulte and J. I. Hedges, *Nature* **321**, 61 (1986).
13. T. W. Walsh, *Mar. Chem.* **26**, 295 (1989).
14. J. I. Hedges, B. A. Bergamaschi, R. Benner, *ibid.*, in press.
15. Y. Suzuki, Y. Sugimura, T. Itoh, *ibid.* **16**, 83 (1985).
16. Solid-state NMR spectra were obtained using a Chemagnetics Inc. M-100 spectrometer. Conditions were chosen to insure that the NMR signal intensities quantitatively represented the carbon types observed in the samples [M. A. Wilson, *NMR Techniques and Applications in Geochemistry and Soil Chemistry* (Pergamon, Oxford, 1987)]. Approximately 50,000 transients, having pulse delays of 1 s, sweep widths of 14 kHz, contact times of 1 ms, and 90° ^{1}H pulses of 5.8 s were acquired at a field strength of 2.35 Tesla.
17. P. M. Williams and E. R. M. Druffel, *Nature* **330**, 246 (1987).
18. D. H. Stuermer and J. R. Payne, *Geochim. Cosmochim. Acta* **40**, 1109 (1976); R. B. Gagosian and D. H. Stuermer, *Mar. Chem.* **5**, 605 (1977); G. R. Harvey, D. A. Boran, L. A. Chesal, J. M. Tokar, *ibid.* **12**, 119 (1983); M. A. Wilson, A. H. Gillam, P. J. Collin, *Chem. Geol.* **40**, 187 (1983); R. Malcolm, *Anal. Chim. Acta* **232**, 19 (1990).
19. J. I. Hedges, P. G. Hatcher, J. R. Ertel, K. J. Meyers-Schulte, *Geochim. Cosmochim. Acta*, in press.
20. C. M. Burney and J. McN. Sieburth, *Mar. Chem.* **5**, 15 (1977).
21. J. D. Pakulski and R. Benner, in preparation.
22. C. M. Burney, K. M. Johnson, D. M. Lavoie, J. McN. Sieburth, *Deep-Sea Res.* **26A**, 1267 (1979).
23. C. M. Burney, P. G. Davis, K. M. Johnson, J. McN. Sieburth, *Mar. Biol.* **67**, 311 (1982).
24. We thank the scientists, captain, and crew on the R.V. *Alpha Helix* for assistance collecting water samples and D. Karl and R. Lukas for providing logistical support. We are grateful to M. Strom for assistance with DOC measurements and ultrafiltration experiments. We also acknowledge J. Schmoyer for help with integration of the NMR spectra. This research was supported by grants from the National Science Foundation (BSR 8910766 and OCE 9102407 to R.B. and BSR 8718423 and OCE 9102150 to J.H.). Contribution 830 of the University of Texas Marine Science Institute and contribution 1918 of the University of Washington School of Oceanography.

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Percolation Theory, Thermoelasticity, and Discrete Hydrothermal Venting in the Earth's Crust

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As hydrothermal fluid ascends through a network of cracks into cooler crust, heat is transferred from the fluid to the adjacent rock. The thermal stresses caused by this heating close cracks that are more or less vertical. This heating may affect network connections and destroy the permeable crack network. Thermoelastic stresses caused by a temperature difference of ~100°C can decrease the interconnectivity of a crack network to the percolation threshold. If the temperature is slightly less, thermoelastic stresses may focus the discharge in hydrothermal systems into discrete vents.

FLUID CIRCULATION IN HYDROTHERMAL systems is controlled by the distribution of rock permeability in space and time. In igneous and metamorphic rocks the permeability is controlled by fractures (*1*), and discharge in both continental and submarine hydrothermal systems appears to be localized by fault zones (*2*). On land, the fault-controlled discharge may emerge as discrete warm or hot springs; at mid-ocean ridge crests, high-temperature discharge occurs through orifices ≈10 cm in diameter as sulfide-laden black smoker plumes with a temperature ≈350°C (*3*).

It is not clear how hydrothermal upflow in a fault zone is focused into discrete vents or what factors control the spacing of vents along the fault zone. Deposits of silica and other minerals are common in hydrothermal systems, and it is generally believed that such deposits clog fractures and decrease permeability at shallow levels in hydrothermal systems (*4*). However, quantitative analysis of this process is extremely difficult. Models of porosity reduction due to chemical deposition suggest that the process is inefficient (*5*). It may be that chemical deposition alone may not cause flow to be focused into discrete vents.

In this report, we examine the role of thermoelastic stresses in a hydrothermal upflow zone as a mechanism for focusing. The conceptual picture (Fig. 1) is that, as hydrothermal fluid heated at depth ascends into the cooler, shallow crust, heat is transferred from the fluid in the cracks to the adjacent rock. Because the heated zone is always surrounded by cooler areas, this heating imposes horizontal thermal stresses on the rock that can close cracks. If enough crack connections are destroyed so that the crack network falls to near the percolation threshold, then only a few pathways would be open to the surface and the flow would be directed through them. We derive an expression for the closure of cracks by thermoelastic stresses and then estimate how much heating is required to decrease the interconnectivity of the crack network to the percolation threshold. Thermoelastic stresses may act in concert with chemical deposition to focus the flow into discrete vents.

Earlier work (*6*) showed that, if hot fluid flowed in a single, planar fracture 1 mm wide, the fracture could close within 0.5 year because of thermal expansion of the adjacent rock. Lowell (*7*) extended this result to a set of parallel planar fractures of uniform width and spacing. However, critical questions remain concerning thermoelastic effects in rocks containing a random crack network.

The sizes, orientations, number density, aspect ratios, and other properties of cracks in hydrothermal systems are uncertain. We therefore use an order of magnitude analysis to examine the role of thermoelastic effects in discharge zones and make a number of simplifying assumptions that are consistent with this approach. We assume that (i) for calculating the influence of thermoelastic stresses, each crack can be treated as separate but located in a rock volume with some effective elastic properties; (ii) the three-dimensional (3-D) cracks have the shape of a thin spheroid described in terms of an aspect ratio $x = a/b$, where a is the small semi-axis and b is the large one; (iii) the thermoelastic stress field on the cracks has two equal

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