Reports

Submarine Seepage of Natural Gas in Norton Sound, Alaska

Abstract. *Unusual concentrations of dissolved two- to four-carbon alkanes were observed in the waters in Norton Sound in a localized area approximately 40 kilometers south of Nome, Alaska, in 1976. The hydrocarbons were identified in the near-bottom waters downcurrent for more than 100 kilometers from a sea-floor point source. Preliminary dynamic modeling estimates of the initial gas phase composition predict methane/ethane and ethane/propane ratios of 24 and 1.7, respectively, assuming the hydrocarbons were introduced by bubbles. The low ethane/propane ratio is indicative of gas from a liquid petroleum source rather than from nonassociated or biogenic natural gas. Preliminary data on the structural geology of Norton Basin lend support to the interpretation based on the hydrocarbon plume. Unconformably truncated strata dip basinward from the seep locus; acoustic anomalies and numerous steeply dipping faults in the immediate vicinity of the seep are corroborating evidence that shallow gas- or petroleum-charged sediments and strata coincide with avenues for migration of mobile hydrocarbons to the sea floor. These factors, taken in concert with the sedimentological regime, the recent revision (increase) of basin depth estimates, and the highly localized hydrocarbon source, strongly suggest a thermogenic rather than a recent biogenic origin for these gaseous compounds.*

Environmental studies of the waters of the Alaskan outer continental shelf include measurements of the distribution and abundance of the low-molecular-weight aliphatic hydrocarbons (*1*) to evaluate their efficacy as indicators of natural and induced pollution by petroleum hydrocarbons. Because the saturated low-molecular-weight hydrocarbons (C_1 to C_4) are present in significant amounts in most natural gases and crude oils (*2*) and because they are relatively soluble in natural waters (*3*), these components have been used extensively to monitor and document the introduction of petroleum-related hydrocarbons into the ocean from production, shipping, and transfer operations (*4–7*). In addition, the ease with which these particular hydrocarbons can be surveyed has led to their use as an adjunct exploration tool for the detection of submarine gas or oil seeps (*8*).

Although many submarine petroleum seeps have been reported (*9*) few have been well documented, partially because of observational problems associated with the marine environment and partially because offshore petroleum exploration has thus far yielded few public data (*9*). Very few of the marine seep regions that have been identified and reported have been studied in detail, the major exception being the large seep swarm observed near Coal Oil Point in the Santa Barbara Channel (*10*). A few of the numerous gas seeps that have been identified in the northern Gulf of Mexico have been studied chemically, as reviewed by Bernard *et al.* (*7*).

In this report, we discuss our findings of relatively high concentrations of C_2 to C_4 alkanes in Norton Sound, a large shallow bay south of Seward Peninsula. The dissolved hydrocarbons were analyzed by He extraction and gas chromatography by a modification of a procedure originally developed by Swinnerton and Linnenbom (*11*). Briefly, the procedure is as follows. Discrete water samples were taken from predetermined depths in 10-liter Niskin samplers attached to a rosette sampler. The volatile hydrocarbons were removed from 1-liter portions of seawater in a stream of ultrapure helium and concentrated on a column of activated alumina maintained at −196°C. After the cold trap was warmed to 100°C, the volatilized components were chromatographed on a polymer bead (Porapak Q) (*12*) and detected sequentially with a flame ionization detector as they emerged from the column.

Historic petroleum seeps and shows. Onshore oil shows and marine seeps have been reported at several places along the shores of Norton Sound (Fig. 1). Prospecting for oil was carried out at Hastings Creek near Cape Nome in 1906 (*13*). Two wells were drilled; one showed a trace of oil and the other encountered flammable gas at 37 m in nonmarine coal-bearing rocks (*13, 14*). The gas pressure was sufficient to blow a 550-kg stem 23 m up the hole. Cathcart (*13*) also mentions oil-like films on the lagoons near Nome and Cape Nome, and a beach foam resembling paraffin which was brought in by the onshore (southerly) winds.

Other oil seeps have been reported at the mouth of the Inglutalik River on Norton Bay (*14, 15*), and 32 km northwest of Nome in the Sinuk River Valley, which may be underlain by infolded, unmetamorphosed Cretaceous or Tertiary rocks (*14*). An outcrop of middle Cretaceous oil shale has also been reported on Besboro Island in Norton Sound 40 km northwest of Unalakleet (*14*).

Geologic setting. The geology of Norton basin, the sedimentary prism beneath Norton Sound, has been discussed by Scholl and Hopkins (*16*), Grim and McManus (*17*), Nelson *et al.* (*18*), Walton *et al.* (*19*), Tagg and Greene (*20*), Moore (*21*), and others. Reconnaissance seismic reflection survey data suggest that the basin area is about 130,000 km^2 (*16*). The maximum basin depth has recently been estimated as approximately 5.5 km (*22*); the 100,000-km^3 volume calculated by Scholl and Hopkins (*16*) may therefore need to be increased by as much as 50 to 80 percent.

Seismic reflection profiles show the basin fill to consist of two major stratified units composing the main layered sequence (*16*) covered by a thin mantle of Quaternary deposits (*18, 20*). The major units are separated by an unconformity which lies at a depth of approximately 500 to 700 m near the basin axis. Greene and Perry (*23*) suggest that this unconformity represents a change in the rate of subsidence during middle or late Pliocene time, and Hopkins (*24*) notes that the Bering Land Bridge had been reestablished through most of the Pliocene. Acoustic basement is formed by strata which are probably analogous to the diverse older Paleozoic and Mesozoic rocks that occur on land around the basin margins (*25–27*).

Although Quaternary deposits everywhere cover the older Cenozoic and Mesozoic basin fill, some onshore outcrops and drill-hole data give clues to the nature of these deposits. Nonmarine coal-bearing strata of late Oligocene age are exposed on northwestern St. Lawrence Island (*23*), and several offshore holes drilled by the U.S. Bureau of Mines near Nome encountered marine sands and clayey silts of early Pliocene age at a subbottom depth of approximately 18 m (*16, 18*). Upper Miocene or lower Pliocene marine limestone was recovered from a dredge haul 30 km south of St. Lawrence Island, just outside the basin. Considering these facts and regional stratigraphic patterns, the basin fill probably consists of Upper Cretaceous and lower to middle Tertiary sedimentary rock in the lower major unit and upper Tertiary, Pliocene, and Pleistocene sedimentary rocks and sediments in the upper major unit. All direct evidence suggests that the lower unit is nonmarine, but the size of the basin is such that unseen transitions to marine facies could occur within this unit.

Strata of the lower major unit form a broad synclinorium whose principal axis trends generally east-west. The beds of the upper unit are more nearly flat-lying above the angular unconformity. Normal faults occur in many places around the basin periphery (*16, 17, 23*). Some faults form scarps on the sea floor (*17*), and some offsets at the acoustic basement surface can be correlated with fault traces (*16*).

Single-channel reflection data were gathered in 1967 on a jointly sponsored cruise by the U.S. Geological Survey and the University of Washington (*17*) and in 1969 by the University of Washington and the National Oceanic and Atmospheric Administration (then the Environmental Science Services Administration) (*19*). Two track lines passed near the seep location and are depicted in Fig. 1. The reflection records are reproduced in Fig. 2 and show the southward dip toward the basin axis of the lower unit of the main layered sequence. The southward dipping unconformity separating the upper and lower units rises to within 60 to 70 m of the sea floor in the vicinity of the seep; 10 km north of the seep it is covered by only 10 to 15 m of Quaternary sediment where it passes over an anticlinal crest and dips to the north. The basin fill is more than 1.2 km thick beneath the seep site, although the acoustic basement signature is difficult to discern.

Several steeply dipping normal faults can be seen on the reflection records in the vicinity of the seep. Some of these faults displace only the strata of the lower unit and may be growth faults associated with basin subsidence. More recent geophysical work by the U.S. Geological Survey also indicates the existence of a northwest-trending near-surface fault near the seep (*28*).

Table 1. Dissolved hydrocarbon concentrations within 5 m of the bottom near the locus of the seep (station N18F; 64°07.3′N, 165°29.5′W) are compared to similar measurements at station N13 (63°59.7′N, 165°29.7′W), approximately 15 km to the south.

Station	Depth (m)	Concentration of dissolved hydrocarbon (nl/liter)							$\frac{C_{2/0}}{C_{2/1}}$	$\frac{C_1}{C_2 + C_3}$
		Methane	Ethane	Ethene	Propane	Propene	Isobutane	*n*-Butane		
N18F	17	525	9.6	1.5	3.3	0.4	0.5	0.6	6.4	50
N13	17	219	0.3	1.2	0.2	0.4	<0.03	<0.03	0.2	413

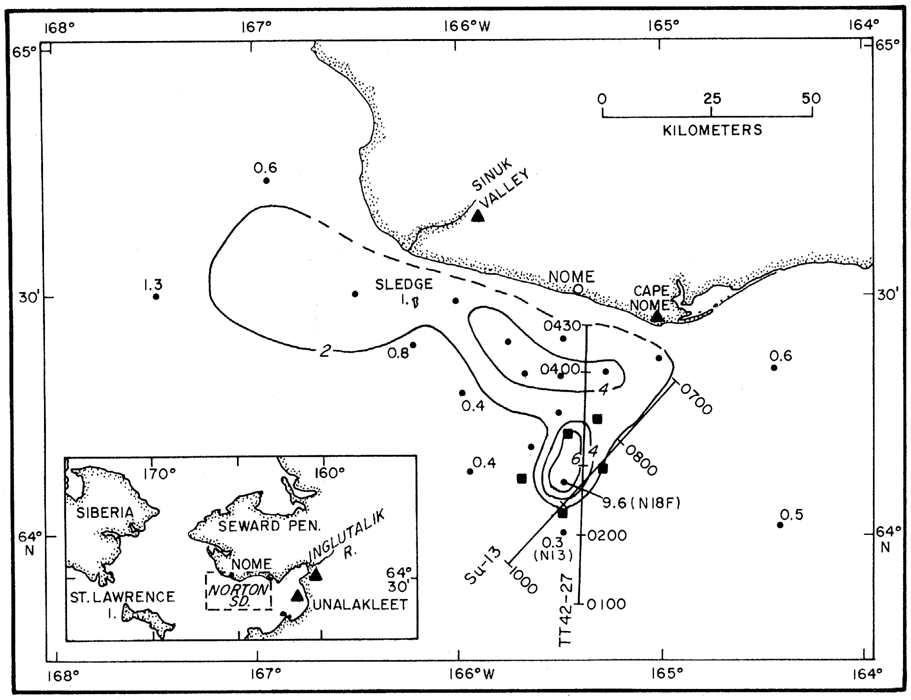

Fig. 1. Distribution of ethane (nanoliters per liter, standard temperature and pressure) within 5 m of the bottom of Norton Sound in September 1976. Station N18F is the nearest approach to the seep locus; station N13 is the control station. The grid was occupied on two separate occasions: (●) 13 September and (■) 23 September. Station N18F was visited on both occasions, although because of imprecise navigation, the 23 September occupation was approximately 4 km to the northwest. The concentration of ethane at this time was 4.8 nl/liter, or approximately 50 percent of that observed on 13 September. Also represented are the seismic reflection tracks with reference time ticks, and the locations of onshore petroleum seeps and shows (▲).

Acoustic responses which may be reflector pull-downs or abrupt changes in reflectivity on the two records suggest the presence of low-velocity gas-charged sediment within 100 to 200 m of the sea floor. The many faults, the basinward dipping strata truncated by an unconformity, and the acoustic anomalies all indicate that the geology in the area of the seep is compatible with a model of hydrocarbon fluids seeping toward the surface from deep sources.

Results. Relatively high concentrations of C_2 to C_4 alkanes were observed approximately 40 km south of Nome in water 20 m deep. Shown in Fig. 1 is the distribution of ethane in near-bottom water; concentrations of ethane reached 9.6 nl/liter near the locus of the seep, about 20 times the background levels observed just south and east of the seep location. The maximum concentration of propane was 3.3 nl/liter, whereas the levels of iso- and *n*-butane reached 0.5 nl/liter. These concentrations also are at least ten times ambient levels (Table 1).

The plume of ethane-rich waters appears to advect north toward the coast from a point source on the sea floor. A weak north-flowing current (less than 10 cm/sec) was measured near the seep several weeks after the chemical observations (*29*). The ethane-bearing waters spread westward past Sledge Island to at least 168°W longitude, a pattern in accord with the general cyclonic circulation that was observed in outer Norton Sound during late summer (*29*).

The "puff" structure of the plume shown in Fig. 1 may reflect multiple sources, episodic seep activity, or possible short-term fluctuations of the mean circulation. The second of these seems most probable (*9*); short-term meteorologically induced fluctuations in the mean circulation cannot be discounted.

Gas bubbles or surface slicks were not visually observed. However, much of the sampling was conducted during hours of darkness.

Discussion. A summary of the observed dissolved hydrocarbon composition near the locus of the seep (station N18F) is compared to similar data from a typical station 15 km to the south (Table 1). The relatively high concentrations of ethane, propane, and butanes are unusual features of this gas seep, along with the preponderance of alkanes over alkenes.

Natural gases originate in a variety of ways and show a wide range of chemical compositions. Methane of microbial origin (marsh gas) is widespread, of shallow origin, isotopically light, and initially accompanied by no more than trace quantities of the heavier homologs of methane. Methane from "dry gas" accumulations not associated with liquid petroleum may be of deeper origin, a product of thermochemical coalification of deeply buried sedimentary organic matter containing less than 6 percent hydrogen by weight (*30–32*). Methane from thermogenic dry gas accumulations tends to be isotopically heavier than bacterial methane and can be accompanied by variable amounts of the higher-molecular-weight alkanes, ranging from trace amounts upward to about 1 to 2 percent. With increasing contents of higher homologs and other more complex hydrocarbon compounds, natural gases from dry gas deposits grade into "wet gases," gas-condensate systems, and the gases associated with crude oil accumulations, either in gas-phase "gas caps" or in natural solution with the oil.

The relatively deficient methane content of the gases exsolved from Norton Sound waters is of special diagnostic interest. Several factors operating separately or in concert might cause the conspicuous methane deficiency: (i) seep gases are naturally deficient in methane relative to the more complex hydrocarbons; (ii) fractionation occurred during migration from deep source beds; (iii) selective microbial oxidation occurred, either in the sediments or in the water column; or (iv) the components of the seep gases were physically fractionated while dissolving. In the first case, nitrogen or carbon dioxide would presumably make up the bulk of the seep gas, although such compositions are relatively uncommon (*33*). Selective fractionation of the hydrocarbons during migration through the sediment column is possible, but we are not able to assess the significance of the process at this time. Similarly, preferred microbial oxidation of methane is possible, either in the surficial layers of the sediments or in the overlying water; however, if the flux of the seep gases is high, this fractionation mechanism would be minimal.

The fractional solution mechanism affords an explanation for the hydrocarbon ratios observed. Schink *et al.* (*34*) have shown, using a simple stagnant-film boundary-layer model, that gaseous hydrocarbons injected into seawater by bubbles are fractionated between the gas and aqueous phases according to their partial pressures, solubilities, and molecular diffusivities. Although we have no information at present on the hydrocarbon flux, the bubble size frequencies, or even the appropriateness of the stagnant-film model in this instance, a few qualitative statements are possible. If the depth of water is shallow and the bubbles consequently large, only a small amount of gas actually dissolves before the bubble escapes to the atmosphere. For example, the model profiles presented by Schink *et al.* (*34*) show that for large bubbles (radius > 0.14 cm; mass > 30 μg) and shallow depths (<30 m), less than 0.5 percent of the mass is lost for each meter of water column traversed. If we consider only the lower 10 m of the water column, less than 5 percent, and probably much less, of each component would be transferred to the dissolved state, depending on the actual surface/volume ratios of the bubbles. The time required to achieve equilibrium between the water and the gas bubbles also depends on the current strength over the seep.

The waters of Norton Sound are grossly undersaturated in the C_1 to C_4 hydrocarbons with respect to the pure component at hydrostatic pressures encountered (*35*). If pure methane gas bubbles were being released, the equilibrium concentration would be approximately 1×10^8 nl/liter, or a factor of 2×10^5 above the observed levels. Either the partial pressure of methane in the seep gas was exceedingly low or dissolution of methane and other hydrocarbons is relatively slight. High microbial oxidation rates also may exist, but our extensive measurements in other shelf areas of Alaska indicate that dissolved methane is oxidized slowly.

Although we have little information on the physical and chemical characteristics of the seep, some tentative assessment can be made of the probable proportions of methane, ethane, and propane in the seep gas. Using the equations of Schink *et al.* (*34*), the incremental increase in

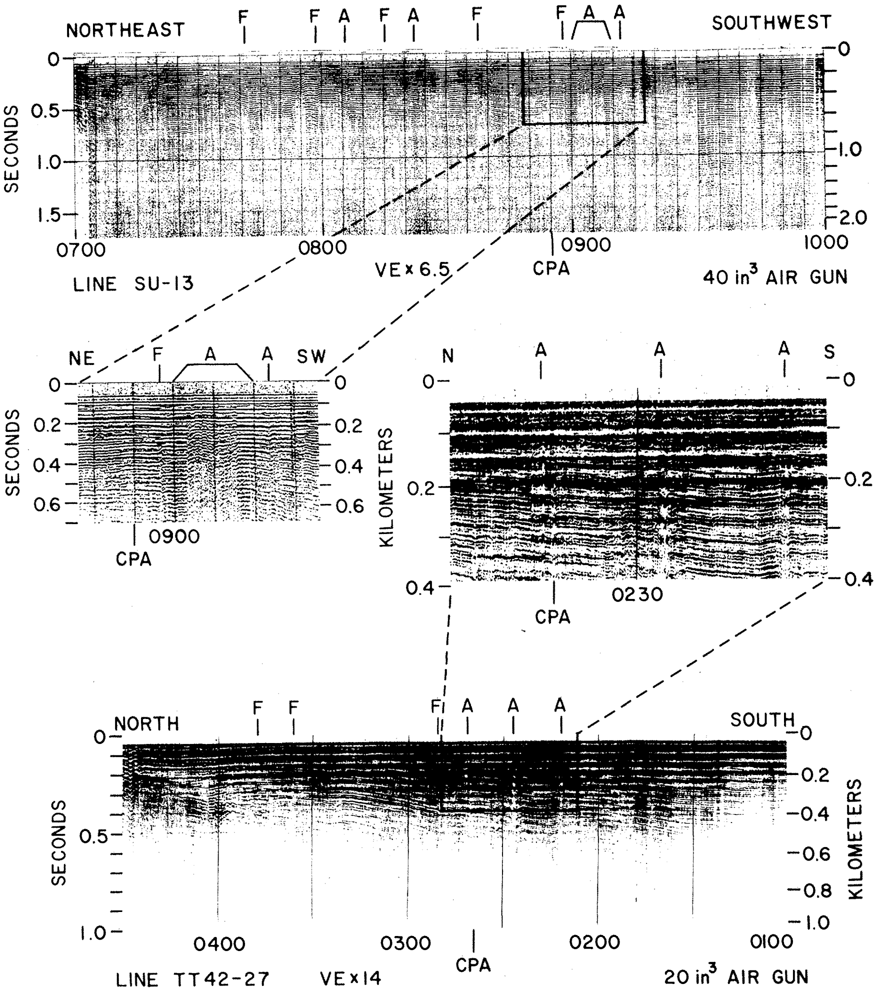

Fig. 2. Seismic reflection records obtained near the seep along track lines shown in Fig. 1. Line TT 42-27 is from the University of Washington 1969 cruise; Line SU-13 is from the NOAA 1969 cruise (*23*). Abbreviations: CPA, closest point of approach to seep site (station N18F); F, fault; and A, acoustic anomaly (reflector pull-down or reflectivity change) indicating possible gas-charged sediments.

the concentration ratio ($\Delta C_1/\Delta C_2$) for methane and ethane may be estimated as (36)

$$\Delta C_1/\Delta C_2 = (\alpha_1/\alpha_2)(D_1/D_2)(p_1/p_2) \quad (1)$$

To solve for the hydrocarbon partial pressure ratio in the gas phase (p_1/p_2), we adopted the solubility coefficients (α_i) presented by McAuliffe (3) and the molecular diffusivities (D_i) of methane, ethane, and propane at 4°C given by Witherspoon and Bonoli (37). Measurements made by the latter authors showed that the ratios of the molecular diffusivities (D_1/D_2 and D_2/D_3) did not differ significantly from 1.24 in the temperature range 4°C to 20°C. In both instances, no corrections were made for the ionic strength of the water.

The incremental increases in the methane, ethane, and propane concentrations (ΔC_i) were estimated by comparing concentration levels obtained at the seep locus and at stations to the south and east to be 200, 9, and 3 nl/liter, respectively. High temporal and spatial variability hampered the estimation of incremental increases in methane concentrations; an upper limit is 200 nl/liter, although the concentrations at stations N13 and N18F suggest a difference closer to 300 nl/liter (Table 1). Substitution of these values into Eq. 1 yielded the following partial pressure ratios in the source gas: $p_{\mathrm{CH_4}}/p_{\mathrm{C_2H_6}} = 24$, and $p_{\mathrm{C_2H_6}}/p_{\mathrm{C_3H_8}} = 1.7$. The dissolved ethane/propane ratio in the near and far field of the dispersion plume was calculated by means of two-way linear regression analysis. The relationship between ethane and propane was found to be $C_{\mathrm{C_2H_6}} = 2.9\ C_{\mathrm{C_3H_8}} + 0.07$ ($N = 14$, $r = .983$). Accepting this ratio as indicative of the seep gase, the partial pressure ratio of ethane to propane would be 1.7, as calculated above. Interestingly, the analysis of the reservoir fluid from the Sadlerochit oil pool, Prudhoe Bay, also yields a mole percent ethane/propane ratio of 1.7 (38).

Nikonov (39) studied the compositions of more than 3500 gas and oil deposits in the Soviet Union and the United States and characterized various petroleum and gas provinces on the basis of their C_2/C_3 ratios. He observed that the C_2/C_3 ratio decreased systematically from 5 for natural dry gas to approximately 2 for gases of oil deposits. Ignoring any compositional fractionation that may have occurred during migration from the original source strata to the sea floor, Nikonov's interpretation suggests that the low C_2/C_3 ratio calculated here (1.7) is indicative of gases associated with oil deposits ($C_2/C_3 = 2$).

Although the concentrations of the C_1 to C_4 fraction in the vicinity of the seep are relatively high compared to levels observed immediately upstream, the concentrations remain well below theoretical saturation values. We believe that kinetic rather than compositional factors explain this, and suggest that solution equilibrium between a gas phase and the bottom waters of the Norton Sound is not even closely approached. Low abundances of the low-molecular-weight hydrocarbons are probably due to small or episodic seep activity, persistent horizontal currents over the seep, and the injection of relatively large bubbles as the result of shallow water depths (total pressure ≤ 3 atm).

Other diagnostic chemical characteristics of the seep hydrocarbons (station N18F) are compared with those from a nearby station (N13) in Table 1. The most striking feature is the ethane/ethene ratio and the ratio of methane to ethane plus propane. Because biogenic production of higher homologs of methane is low and olefins in mature petroleum are nearly absent, both these ratios are useful indicators of petroleum-derived hydrocarbons. The $C_1/C_2{+}C_3$ ratio has been used by Bernard *et al.* (7) and by others to distinguish biogenic from thermogenic hydrocarbon sources or mixtures in the Gulf of Mexico. Ratios less than 50 are considered to be indicative of thermogenic sources; higher ratios imply significant biogenic input (7). As Table 1 shows, the minimum ratio observed in Norton Sound is approximately 40 near the seep locus. Regional background levels are 400 or greater.

Similarly, the high ethane/ethene ratios in the area of the seep are indicative of the negligible input of the C_2 unsaturated hydrocarbon. A comparison of the concentrations of ethene and propene at stations N13 and N18F reveals differences of only 0.3 and 0.0 nl/liter, respectively; these are not significant differences when sampling and analytical uncertainties are considered. Analyses of many samples from the near-bottom shelf waters of Alaska, including Norton Sound, have shown that the normal ethane/ethene ratio rarely exceeds 0.5.

In summary, the observed distributions of dissolved ethane, propane, and butanes, taken together with geological inferences on sediment accumulations, source material, and probable migration pathways for petroleum-derived hydrocarbons, suggest a possible thermochemical origin for the seep gas. Estimates of the probable C_2/C_3 mole ratio in the seep gas suggest that the hydrocarbon deposit from which the gas is leaking contains liquid petroleum in addition to natural gas, although the evidence at this point is circumstantial and equivocal. In future studies a broader range of hydrocarbon classes (heavy aliphatics and aromatics) should be investigated in both the water column and the bottom sediments. This should lead to a clearer understanding of the compositional complexity of the seep hydrocarbons, their probable source, their impact on the local marine biological community, and their possible implications regarding the prospect that Norton Basin might be a source for commercially exploitable petroleum.

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$$\Delta m = \frac{A P_t \alpha M D}{R T \Delta h} \Delta t$$

where A is the bubble surface area, P_t is the total gas pressure in the bubble (hydrostatic + surface tension), α is the Bunsen coefficient, M is the molecular weight of the component, D is the molecular diffusivity of the component in water, R is the gas constant, T is the absolute temperature, and Δh is the boundary film thickness. Since $\Delta m/M$ is equal to the concentration increase (ΔC_i) per unit time, the concentration ratio of two components is simply proportional to the respective partial pressures, solubilities (Bunsen coefficients), and molecular diffusivities as shown in Eq. 1.
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Water Vapor Maser "Turn-On" in the HII Region W3 (OH)

Abstract. *A line in the water vapor maser spectrum of the HII region W3 (OH) was observed to increase in brightness over an 8-day period and then decline to its original intensity over the following 4 weeks. The intensity variation can be explained by a simple maser model, with an impulse of energy suddenly applied. The observed time scale and energy output are consistent with a maser on the outskirts of a dust cocoon surrounding an O5 star, with a momentary "leak," lasting a day or two, supplying the necessary energy.*

Naturally occurring masers in interstellar clouds have been demonstrated for a number of different molecular transitions, the 18-cm OH lines and the 1.35-cm H_2O rotational line being the most intense examples (*1*). The masers are commonly found in ionized hydrogen (HII) regions where star formation is still in process, but are also found in association with late-type red giant stars. Both the OH and H_2O masers, when found in HII regions, have intense infrared sources (presumably protostars) in their proximity.

There is strong reason to believe that the masering phenomenon is short-lived and occurs early in the life cycle of a star. The H_2O masers in particular require high local gas densities ($\sim 10^{10}$ molecules of H_2 per cubic centimeter) in order to populate the rotational levels which lie roughly 450 cm^{-1} above the ground state. The total power output from the OH and H_2O masers in the radio line is an appreciable fraction of 1 solar luminosity ($\sim 10^{-4}$ to 1 $L_\odot$) and a copious source of pump energy is required. Typically, the masers consist of a cluster of individual "hot spots," each having an apparent size of approximately 1 astronomical unit (1 A.U. = 1.5×10^{13} cm) with the group spread over a total dimension of approximately 10^3 to 10^4 A.U. The group thus has a total dimension characteristic of the solar system. The pump mechanism has not been demonstrated, although infrared radiation and collisional pumping have both been proposed. The apparent size of each hot spot may not necessarily represent the true maser source size, and several authors (*2*) have shown that for simple, uniform models of H_2O masers, the true size of the masering region could be of the order of 50 times the apparent size. The H_2O masers, in particular, are observed to vary rapidly with time (*3*), and we report here the first complete "turn-on" sequence observed for an individual maser spot.

During the course of an observing run with the 120-foot (37-m) radio telescope of the Haystack Observatory in Westford, Massachusetts, the increasing intensity of a line in the H_2O spectrum of the HII region W3 (OH) (associated with the larger HII complex IC1795) was noted and was monitored closely for a 10-day period. The Haystack telescope then became less available, but the 26-m telescope of the Naval Research Laboratory (NRL) at Maryland Point was used at frequent intervals for the next 4 weeks, allowing a complete set of observations to be brought together.

The Haystack antenna was equipped with a left circularly polarized Cassegrain feed and a traveling wave maser preamplifier having a system temperature in the range 100° to 200°K. The sensitivity of the antenna at a wavelength of 1.35 cm is 14 jansky of total flux density per degree Kelvin of antenna temperature (1 jy = 10^{-26} watt m^{-2} $hertz^{-1}$). The spectrometer comprised a 1024-channel autocorrelator which with Hanning weighting of the autocorrelation function provided a velocity resolution

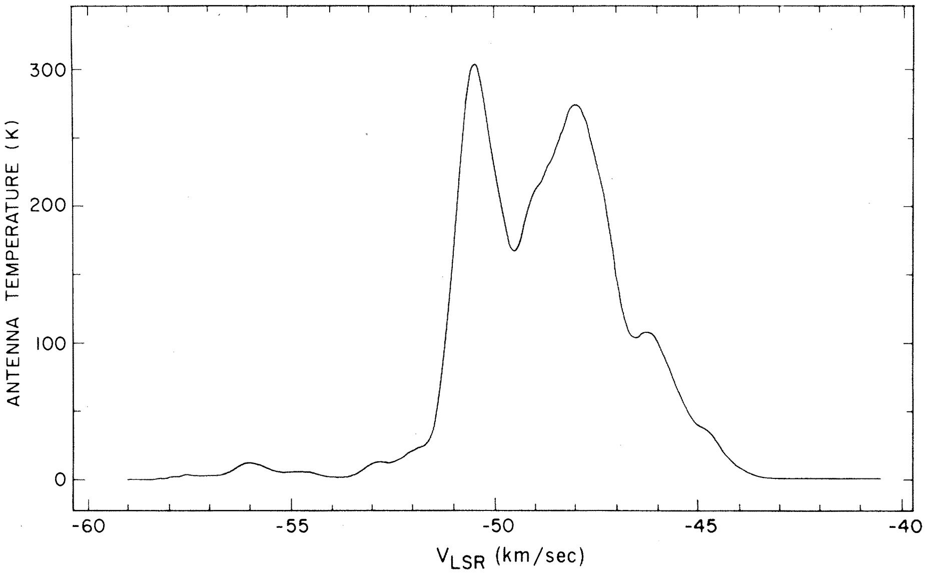

Fig. 1. Antenna temperature plotted as a function of the velocity with respect to the local standard of rest, assuming a rest frequency of 22,235.080 Mhz, for the source W3 (OH). The spectrum was taken on 13 May 1977 and represents a total of 3 minutes of integration time and an effective velocity resolution of 0.066 km/sec. The strongest line is the −50.4 km/sec feature; the next strongest is the −48 km/sec feature, on whose shoulder the −46 km/sec feature is visible.