

mediately above the experimental chamber permitted the supply to the chamber to be switched rapidly from one source to the other with negligible change in flow. The operation of these valves, the presentation of visual stimuli through the walls of the chamber, and the recording of responses were executed automatically by relay equipment.

The goldfish, weighing 4 to 6 g, was placed in the chamber, which was immediately sealed, filled with water, and freed of all air bubbles. It was trained for two procedures which alternated every 15 minutes throughout each daily 2-hour session. In the first procedure, each response of breaking the light beam was followed by a 15-second period in oxygenated water, at the end of which the water in the chamber reverted to the deoxygenated supply until the next response. A red light was illuminated to the right of the chamber while this procedure was in effect. In the second procedure the water in the chamber was deoxygenated until 20 seconds had elapsed without the occurrence of a response. Each response postponed the onset of oxygenated water for 20 seconds. At the end of 20 seconds without a response, oxygenated water was introduced for 15 seconds. A green light to the left of the chamber signalled that this procedure was in effect.

The three fish used showed steady responding within the first 10 minutes of the training. The rate of responding rose to a maximum over the first 5 to 7 days and then fell gradually to a steady intermediate level over a period of 20 days. Regular responding was maintained for as long as the fish were subjected to these procedures, in some cases for several months of daily experimentation.

The fish initially responded at an inappropriately high rate at the beginning of the 15-minute periods during which responding postponed reinforcement. Then, toward the end of these periods, the rate declined and reinforcements began to occur. After several sessions, these inappropriate responses disappeared, and the performance came under the control of the two stimulus lights. The fish then swam quietly with little movement toward the light beam. The mean response rates on the two procedures showed no overlap within an experimental session after the first few days of training. Figure 2 shows the medians of the daily mean rates for three fish after their rates of responding had stabilized.

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The fish showed a systematic tendency to respond at a higher rate in the first 15 minutes of the daily session. This may be associated with the brief exposure to air during transfer from the aquarium to the chamber, and with the increase in metabolic rate associated with handling. The decline in rate of responding during the first 20 to 30 sessions may arise from long-term habituation to restraint or from acclimation to lower oxygen tensions (2).

This experiment demonstrates that the goldfish is capable of regulating its respiratory environment by means of acquired behavior, and that this behavior can be brought under rather precise stimulus control. It provides a technique well adapted to studies not only of the behavioral effects of respiratory agents but also of many other physiological variables associated with the immediate environment of the fish (3).

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### Biological and Oceanographic Observations under an Antarctic Ice Shelf

**Abstract.** Animal life has been shown to exist under the Ross Ice Shelf, from samples obtained with bottom-sampling equipment through naturally occurring cracks in the permanent shelf ice. An abundant fauna, comprising at least nine phyla, was found on a mud and rock bottom. This fauna differs somewhat from that found under nearby seas periodically covered with sea ice 2 to 3 meters thick.

During November and December 1961 the White Island and Koettlitz Glacier regions of the Ross Ice Shelf, Antarctica (1) (Fig. 1), were examined, and sampling of the bottom marine fauna beneath a floating ice shelf was accomplished for the first time. These regions were chosen as investigation sites because of the presence of Weddell seals, *Leptonychotes weddelli* (Lesson). The presence of seals on the shelf ice suggests that direct

Table 1. Major zoological groups collected at White Island and Koettlitz Glacier.

Group	White Island	Koettlitz Glacier
Foraminifera	+	
Monaxonid porifera	+	+
Thecate hydroida	+	+
Athecate hydroida	+	
Alcyonacean alcyonaria	+	
Actiniaria	+	+
Nematoda	+	+
Branching ectoprocta	+	
Encrusting ectoprocta	+	+
Nereid polychaeta	+	
Sabellid polychaeta		+
Other polychaeta	+	+
Pycnogonida	+	+
Copepoda	+	
Isopoda		+
Tanaidacea	+	
<i>Orchomenella proxima</i>	+	+
Other amphipoda	+	
Patellacean gastropoda		+
Echinoidea spines		+

passages communicate with the ocean beneath.

White Island, a basaltic island located at latitude 78°10' S, longitude 167°20' E, is about 22 km from the open sea during the late antarctic summer. The shelf ice in this region varies in thickness from approximately 5 m at the seaward edge of McMurdo Sound to 70 m a few miles east of White Island. A narrow system of crevasses and disturbed shelf ice occurs along the northwestern coast of White Island and extends several miles northeast of the island. A more extensive crack system was found in the Koettlitz Glacier region, 78°13' S, 164°10' E, 28 km from the leading edge of the Ross Ice Shelf.

Three collecting sites were established. Collections from White Island were taken at depths of 43 and 75 m. All material from the Koettlitz area was taken at a depth of 40 m. A large number of thin ice platelets were present in the narrow White Island cracks, in some areas extending to a depth of 30 m. These ice platelets made it quite difficult to lower the collecting apparatus; however, successful use was made at all collecting sites of an orange peel grab 30 cm in diameter, cylindrical metal traps 15 by 60 cm, and Nansen bottles equipped with reversing thermometers. The absence of ice platelets at the Koettlitz Glacier site made it possible to pump several hundred liters of water and filter it through a plankton net with a mesh of 54 threads per inch. Oxygen and salinity determinations were made by standard oceanographic techniques (2).

The major zoological groups collected are listed in Tables 1 and 2, with temperature, salinity, and oxygen values where these are available.

The ocean floor off White Island consists of a heterogeneous mixture of yellowish-black basaltic muds, gravels, and rock. In contrast, bottom grab samples from the Koettlitz Glacier site indicated a bottom of yellow silty muds mixed with granitic and basaltic gravels and rock.

Traps, set seven times for periods of approximately 1 week, caught three species of gammarid amphipods at the White Island sites. One species, *Orchomenella proxima* (Chevreux), was caught by the thousands in traps at all sites; this species has been obtained in similar quantities under the sea ice at McMurdo Station. A small actiniarian (about 2 by 10 mm) occurred in concentrations of several hundred per

Table 2. Temperature, salinity, and oxygen values.

Date (1961)	Temperature (°C)	Salinity (0/00)	Oxygen (ml/lit.)
<i>White Island, 43 m</i>			
9 Nov.	-1.95		
15 Nov.	-1.95	34.78	6.28
21 Nov.	-1.94	35.14	
28 Nov.	-1.94	35.79	6.46
5 Dec.		34.70	6.39
23 Dec.		34.92	5.52
<i>White Island, 75 m</i>			
28 Dec.	-1.94	34.63	4.31
<i>Koettlitz Glacier, 40 m</i>			
28 Dec.	-1.92	34.72	3.61

square meter at the White Island 43- and 75-m sites.

The thick shelf ice presumably produces aphotic conditions in the waters below; consequently, a general absence of living plants would be expected (3). Eleven liters of water taken from the Koettlitz Glacier site on 28 December

1961 were filtered, and the residue was examined for chlorophyll content (4). No chlorophyll pigments were found. At White Island, ice crystals made it impossible to collect and filter large quantities of water. However, diatoms and flagellates were found in abundance, but only along the surface of the cracks, where they are probably of negligible importance as a source of food. Primary consumers existing under the Ross Ice Shelf must therefore depend largely on detrital material originating outside the boundaries of the shelf.

Before it can be determined whether characteristic faunas exist under antarctic ice shelves, many more collections must be made. However, a number of extremely common shallow-water animals found at McMurdo Station were absent from the White Island and Koettlitz Glacier collections, in particular the pelecypod *Limatula hodgsoni* Smith, the asteroid *Odontaster validus* Koehler, the nemertean *Lineus corrugatus* McIntosh, and the nototheniid fish *Trematomus bernacchii* Boulenger (5). Furthermore, at comparable depths at McMurdo Station there is no "mud-rock" bottom per se, but rather a thick layer of sponge spicules, pelecypod shells, serpulid and sabellid tubes, and debris. Many of these organisms will probably be found under ice shelves in future investigations; on the other hand, their absence in the studies reported here may indicate a real difference between the faunal composition under ice shelves and that under open polar seas periodically covered with thin sea ice.

The results of these studies show that marine organisms exist at least 28 km behind the leading edge of an antarctic ice shelf. More important, the studies show that sampling through cracks which penetrate antarctic ice shelves is a valuable technique for investigating this fauna (6).

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#### References and Notes

1. Antarctic ice shelves consist primarily of inland glaciers which have moved over the sea. Shelf ice can usually be readily distinguished from ice frozen from the sea (sea ice) because of the extreme contrast in thickness; however, in the McMurdo Sound region the Ross Ice Shelf gradates into the sea ice.
2. U.S. Navy Hydrographic Office Publ. No. 607 (1959).
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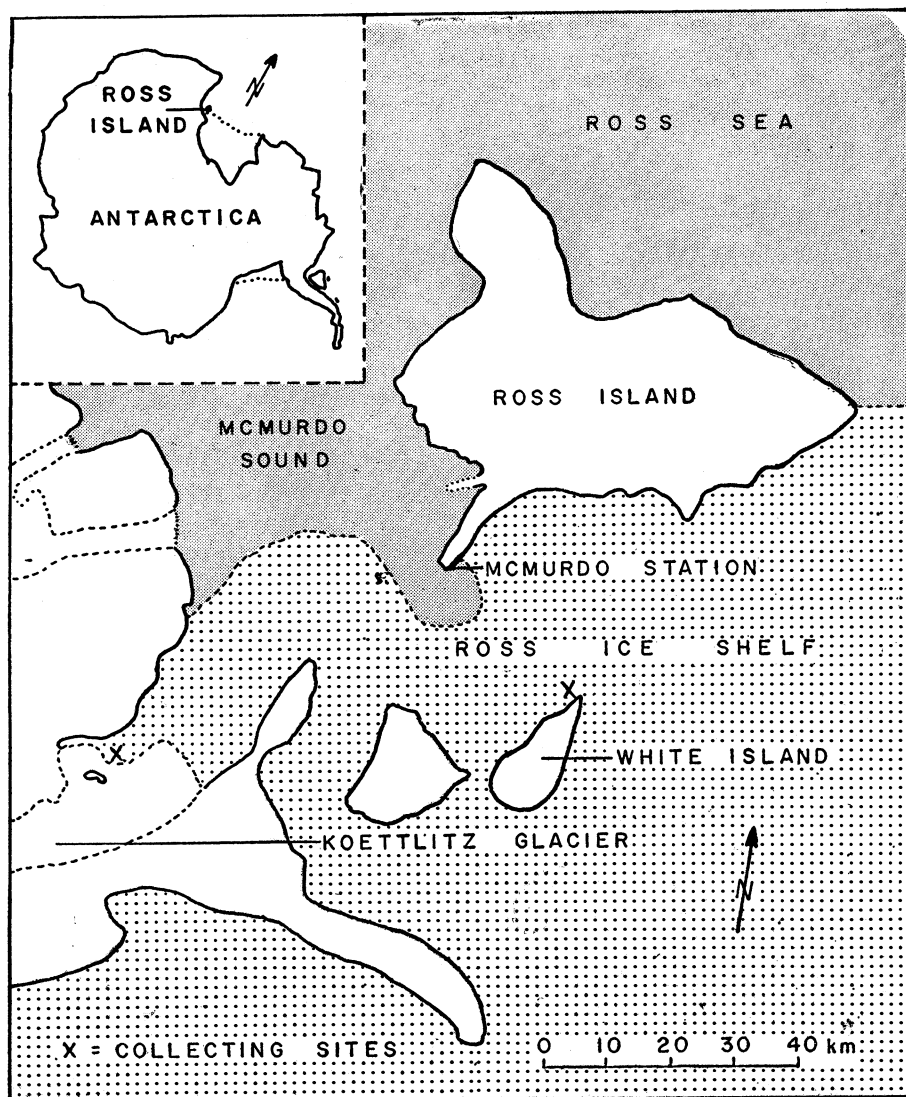


Fig. 1. McMurdo Sound and vicinity, Ross Sea, Antarctica.

4. J. D. H. Strickland and T. R. Parsons, *Bull. Fisheries Res. Board Can. No. 125* (1960).
5. Since this report was written, A. DeVries and G. Kooymans of Stanford University have notified us of the collection of *Trematomus* sp. at the Koettlitz Glacier site. They also report the water at this site to have been "soupy with plankton" in late January 1962.
6. We thank members of U.S. Navy Task Force 43, of U.S. Naval Air Development Squadron Six, and of the U.S. Antarctic Research Program for their cooperation. This project was supported by National Science Foundation grant No. G-13209.

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## Catalytic Dehydrogenation of Coal

**Abstract.** Coals were refluxed with palladium, ruthenium, and rhodium catalysts in high-boiling aromatic and heteroaromatic solvents. As much as 53 percent of the hydrogen in one coal was evolved as hydrogen gas. The yield of hydrogen varied with the rank of the coal and the nature of the solvent but was little influenced by the metal or catalyst support.

We report the first production of significant amounts of molecular hydrogen from coal by catalytic dehydrogenation. The results should help to elucidate the chemical structure of coal; and, since the amount of hydrogen obtained is surprisingly large, may lead to new uses for coal.

Several attempts have recently been made to estimate the hydroaromaticity of coal by dehydrogenation with sulfur (1) or iodine (2). The former method is open to question because of the complexity of the reactions taking place; indeed, it has been shown (3) that fully aromatic hydrocarbons are dehydrogenated by sulfur. The latter method is also uncertain, since little is known about the iodine dehydrogenation of model compounds.

We give here our results on the dehydrogenation of some vitrains (and related materials). A noble metal (palladium on calcium carbonate) was used as the dehydrogenating agent and a polycyclic aromatic compound such as phenanthridine was used as the solvent. This system offers the advantages that the hydroaromatic hydrogen is evolved as hydrogen gas, rather than as hydrogen sulfide or hydrogen iodide, and that the residual dehydrogenated vitrain is not contaminated, it being possible to remove the phenanthridine, calcium carbonate, and some of the palladium by treatment with hydrochloric acid. Phenanthridine was chosen because at its boiling point catalytic dehydrogenation usually proceeds at a rapid rate, and because it incorporates pyridine and phenanthrene structures, both of which

are good solvents for coal. The conditions chosen were such as to give aromatization of hydroaromatic compounds, with few side reactions (see below). A mixture of freshly ground -200 mesh coal (0.50 g), catalyst (0.55 g), and phenanthridine (7.50 g) was refluxed with stirring for 5 hours in a helium atmosphere. For most coals, the bulk of the gas was evolved during the first hour. The gases (largely hydrogen, with small amounts of carbon monoxide, carbon dioxide, and methane) were analyzed by mass spectrometry, and the hydrogen was calculated as percentage of the total hydrogen in the coal which was evolved as hydrogen gas. Appropriate blank corrections were made. The results are summarized in Table 1. The amount of hydrogen evolved varies with the rank of the coal, from 15 percent for lignite vitrain to a maximum of 30 percent for Pittsburgh seam (Bruceton mine) vitrain, and then to 12 percent for Pocahontas vitrain. Kerogen evolved as much gas during the fifth hour as during the first; longer reaction time would thus give a higher yield of gas. Gilsonite behaved similarly.

The data in Table 2 show that as solvents, 5,6-benzoquinoline and 7,8-benzoquinoline are somewhat less effec-

tive than phenanthridine (3,4-benzoquinoline); that phenanthrene yields less hydrogen than phenanthridine, 5,6-benzoquinoline, or 7,8-benzoquinoline; that platinum group metals other than palladium, and supports other than calcium carbonate, give similar results; and that a commercial chromia-on-alumina dehydrogenation catalyst is ineffective. The use of 2-azafluoranthene as solvent gives the largest yield of hydrogen (53 percent, or 9400 cubic feet of hydrogen per ton of coal) yet obtained from Bruceton vitrain; it is not known whether this increased yield is caused by the increased reaction temperature or by some specific effect of the solvent. The dehydrogenated vitrains are hard and brittle, which may be evidence that condensation and cross-linking reactions have taken place.

When dehydrogenated with phenanthridine and palladium on calcium carbonate, 9,10-dihydroanthracene and 1,2,6,7-tetrahydropyrene give somewhat less than the amount of hydrogen theoretically required for complete aromatization; acenaphthene and fluorene yield 0.32 and 0.27 mole of hydrogen per mole of hydrocarbon; and anthracene, pyrene, and 3-methylphenanthrene give no hydrogen. With 2-

Table 1. Dehydrogenation of vitrains and related materials by 30 percent palladium on calcium carbonate catalyst in the presence of phenanthridine at 347°C.

Substrate	Element in substrate (moisture- and ash-free) (%)		Percentage of total hydrogen in sample evolved as H <sub>2</sub>	Atoms of hydrogen removed per 100 carbon atoms
	Carbon	Hydrogen		
Vitrain, lignite, N.D.	67.9	5.5	14.6	14
Vitrain, Rock Springs, Wyo.	76.9	5.8	21.4	19
Vitrain, Pittsburgh, Pa.	83.3	5.4	29.7	23
Vitrain, Powellton, W. Va.	84.9	5.1	19.0	14
Cannel Coal, W. Va.	85.1	6.9	26.7	26
Vitrain, Pocahontas No. 3, W. Va.	90.1	4.6	12.1	8
Gilsonite (asphaltite), Eureka Mine, Utah	85.1	10.2	13.5	19
Kerogen (from Green River oil shale)	79.7	11.0	16.6	27

Table 2. Dehydrogenation of Pittsburgh vitrain with various catalysts and solvents.

Catalyst	Solvent*	Percentage of total hydrogen in sample evolved as H <sub>2</sub>	Atoms of hydrogen removed per 100 carbon atoms
30% Pd-CaCO <sub>3</sub>	2-Azafluoranthene	52.3	40
30% Pd-CaCO <sub>3</sub>	2-Azafluoranthene†	53.1	41
30% Pd-CaCO <sub>3</sub>	5, 6-Benzoquinoline	28.3	22
30% Pd-CaCO <sub>3</sub>	7, 8-Benzoquinoline	20.4	16
30% Pd-CaCO <sub>3</sub>	Phenanthrene	18.3	14
5% Pd-CaCO <sub>3</sub>	Phenanthridine	32.0	25
1% Pd-CaCO <sub>3</sub>	Phenanthridine	33.9	26
5% Pd-Al <sub>2</sub> O <sub>3</sub>	Phenanthridine	29.3	23
5% Ru-Al <sub>2</sub> O <sub>3</sub>	Phenanthridine	28.1	22
5% Rh-Al <sub>2</sub> O <sub>3</sub>	Phenanthridine	30.4	23
Cr <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	Phenanthridine	0	0

\* Reaction temperatures: 2-azafluoranthene, 384°C; 5,6-benzoquinoline, 349°C; 7,8-benzoquinoline, 339°C; phenanthrene, 333°C. † Solvent: vitrain ratio 25:1 instead of the usual 15:1.