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An Overview of Gas Hydrates

by

I. Donald & K. Stillwell

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CONTENTS

	Page
SUMMARY	
INTRODUCTION	1
Definition	1
History	1
Physical properties	1
Conditions for the formation of gas hydrates	2
Inhibiting-factors	5
Production and drilling	9
OVERSEAS OCCURRENCE	9
Canada	9
USSR	12
AUSTRALIA & ANTARCTICA	12
CONCLUSIONS	15
REFERENCES	18
FIGURES	
1. Maximum length of molecules which form gas hydrates and the water to gas ratio in hydrate crystal	
2. Conditions for methane-hydrate formation	
3. Hydrate formation conditions of methane-propane mixtures	
4. Hydrate forming conditions for natural gas of various gravities	
5. Determination of gas hydrate zone	
6. Reservoir hydrate zone	
7. Mean atmospheric temperature in arctic regions of North America	
8. Geophysical logging characteristics of gas strata containing free gas, hydrate and formation water.	
9. Australia Average Minimum Temperature July	
10. Vertical distribution of temperature, O ₂ , Cl and H ₂ S in Lake Vanda Antarctica	
11. Location of sites drilled during leg 28 in Antarctic waters south of Australia and in the Ross Sea	

SUMMARY

Gas hydrates are natural gas and water combined as a solid crystalline solution under pressure and at temperatures above the freezing point of water. They were first encountered in the gas industry in 1934 when hydrate formation caused problems in gas pipelines. Discoveries of naturally occurring hydrates in Russia and Canada have sparked off renewed interest in the formation of hydrates and their significance in the petroleum industry. Their major significance lies in their ability to lock up vast amounts of gas in a small volume - 1.0 m³ of saturated hydrate may produce as much as 160.0 m³ of natural gas, measured at standard conditions.

Hydrate formation depends on the pressure, temperature, and composition of the gas. Methane, ethane and propane are the only hydrocarbons which readily form hydrates and then only in the presence of water, not ice. The ground surface has to be frozen to allow the temperature and pressure to reach conditions favourable for hydrate formation.

The Russian and Canadian reports detail natural hydrate accumulations in onshore sediments and offshore relict sediments within the arctic region.

Australian temperature conditions prevent the formation of hydrates, but reported gas finds offshore in the Ross Sea of Antarctic may hold promises of gas hydrate accumulations being found there.

INTRODUCTION

Reports of gas hydrates from overseas countries have led to this study of the possibility of hydrates occurring in Australia and its territories. The study is based only on a survey of readily available literature.

Definition

Gas hydrates are solid crystalline solutions of natural gas and water, formed under pressure in the presence of water.

History

Gas hydrates were discovered in 1823 by Faraday while he was liquifying chlorine in the presence of water. Hammerschmidt, in 1934, linked hydrates with the natural gas industry in his report on the problems of hydrate formation in gas pipelines.

In recent years several works have been published on the possibility of the formation of gas hydrates below the surface of the Earth. This possibility became reality in 1970, when the Russians reported finds in the Messoyakh field, Krasnoyarsk Territory, USSR.

These reports stimulated the Canadians into considering the possibility of hydrates occurring naturally in Canada, and, in 1972, two exploration wells being drilled by Imperial Oil, to test for hydrocarbons in the Mackenzie Delta, encountered significant quantities of gas in hydrate form.

Physical properties

Gas hydrates behave as solutions of gas in a crystalline solid, and their formation is physical rather than chemical. Their specific gravity ranges from 0.88 - 0.90 (Katz & others, 1959). The main framework of the hydrate is formed with water molecules, and the hydrocarbon molecules occupy the spaces in the water lattice. No strong chemical bonds exist between the hydrocarbon and water molecules. Therefore, the hydrocarbons are free to rotate within the spaces. The crystal lattice is

different to ice, since the ice lattice provides no spaces for hydrocarbon molecules.

Five molecules of oxygen joined by hydrogen bonds form rings, which when combined result in a dodecahedron that cannot be arranged in a packing system such that all the spaces are filled. The vacant spaces are filled by gas molecules of an appropriate size (Fig. 1), thus producing a crystalline structure. Of the hydrocarbon gases, only methane, ethane, and propane readily form hydrates, others being too large to enter the spaces in the lattice. When the pressure is released on hydrates, the gas comes out of solution, but the crystals remain as ice and do not change in appearance. The gas released during decomposition is generally at higher than formation pressure. Judge (1976) reports 1.0 m³ of saturated hydrate produces 160 m³ of natural gas and Sheshukov (1973) reports 1.0 m³ of saturated hydrate contains 0.9 m³ of water and 70 to 240 m³ of gas.

Conditions for the formation of gas hydrates

Initial temperature and pressure conditions for the formation of solid hydrates are represented in Figure 2. Important to note is the fact that an increase in pressure enables hydrates to form at higher temperatures. Liquid water must be present for hydrates to form. If there is an excess of gas to water in the reservoir during hydrate formation, a reduction in pressure will occur and prohibit further hydrate formation.

Composition of the gas affects conditions for hydrate formation; very small quantities of the larger hydrocarbons reduce the pressure required (Fig. 3). McCain reports that a mixture of 40% methane and 60% propane will form hydrates at pressures nearly as low as that for pure propane. However the hydrates will form at much higher temperatures than for pure propane. It appears that mixtures of methane and heavier hydrocarbons will retain the high hydrate forming temperatures of methane and approach the larger hydrate forming pressures.

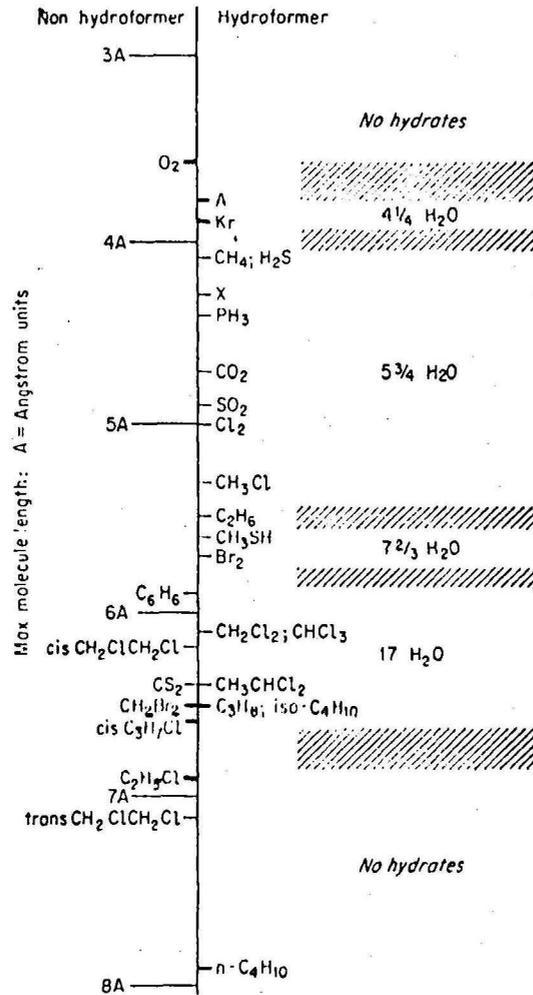


Figure 1. Maximum length of molecules which form gas-hydrates and the water-to-gas ratio in the hydrate crystal. Several molecules of the same maximum dimension which do not form hydrates are also given. (from Katz & others, 1959).

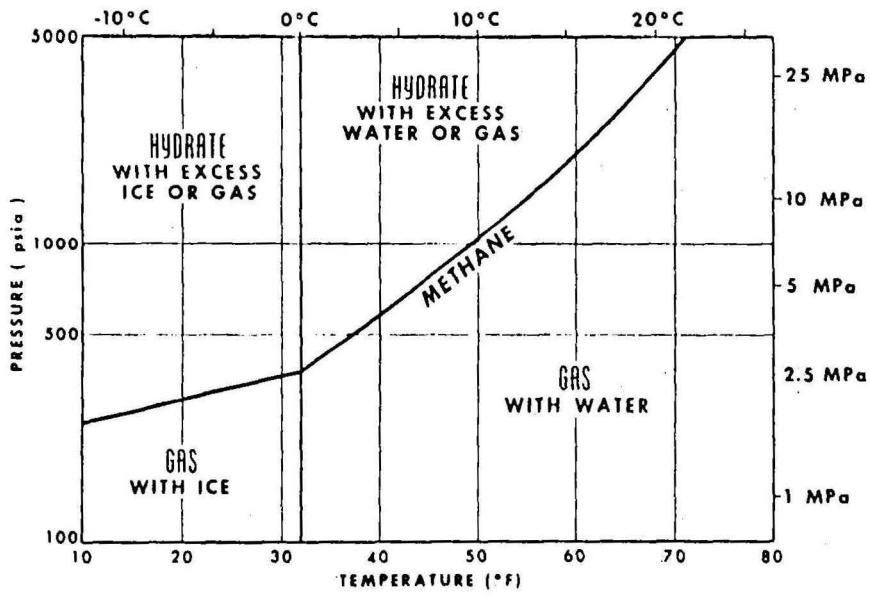


Figure 2. Conditions for methane-hydrate formation (from Bily & Dick, 1974).

At a given pressure, an increase in gas gravity increases the temperature at which hydrates will form. The pressures at which hydrates form are lower for natural gases than for methane, and heavy natural gases form hydrates at much lower pressures than lighter gases (Fig. 4).

In regions with normal and high temperatures, hydrates cannot form because the temperature increases with depth. However, if the ground were permanently frozen (Permafrost), where the temperature is just under 32°F (0°C), then conditions favourable to the formation of hydrate may exist. If temperatures were further lowered, then any hydrates formed would remain as hydrates.

Bily & Dick (1974) show the temperature and depth at which hydrates will form (Fig. 5). The hydrate zone is defined by the upper and lower intersection of the methane curve with the geothermal gradient. Heavier gas hydrates are stable over a greater depth range.

Bily & Dick (1974) also give two gas hydrate curves plotted with depth against depth of the permafrost (Fig.6). Here conditions include low salinity water, a sweet gas, a pressure gradient of 0.435 psi/ft (9.84 kPa/m), a temperature gradient below the Permafrost 1.5°F/100ft (0.027°C/m) and a temperature gradient within the permafrost zone 1.0°F/100ft (0.018°C/m). In areas where the geothermal gradient below permafrost is less than 1.5°F/100ft (0.027°C/m) or where hydrogen sulphide is present in the gas, there is an increase in the depth to which hydrates occur. For slightly higher salinity than fresh water there will be a decrease in the depth to which hydrates will occur.

Inhibiting factors

Many compounds have specific effects on gas hydrates. Salt reduces the activity (ability to crystallise, form bonds etc) of water; therefore, the higher the salt content in water the more unlikely it is to form hydrates. The presence of oil with glycol, and the gas to oil ratio inhibit hydrate formation, although the mechanisms are not fully understood.

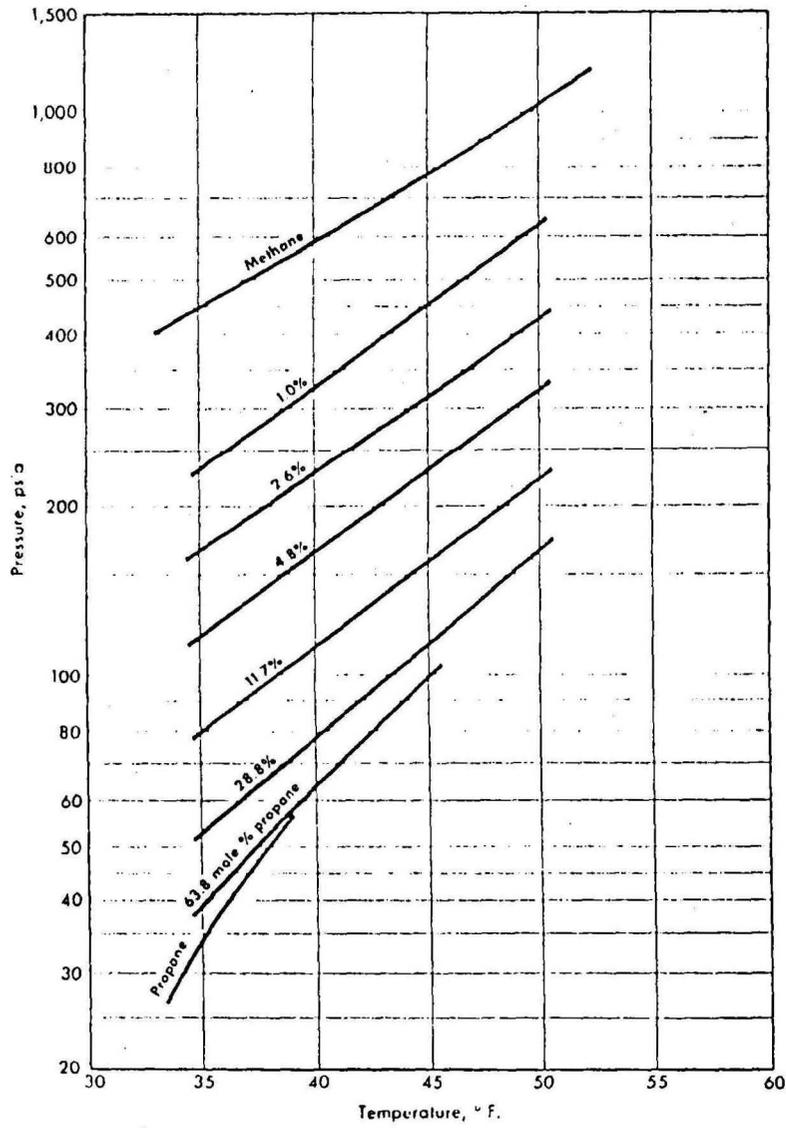


Figure 3. Hydrate-formation conditions of methane-propane mixtures (from Deaton & Frost, 1946).

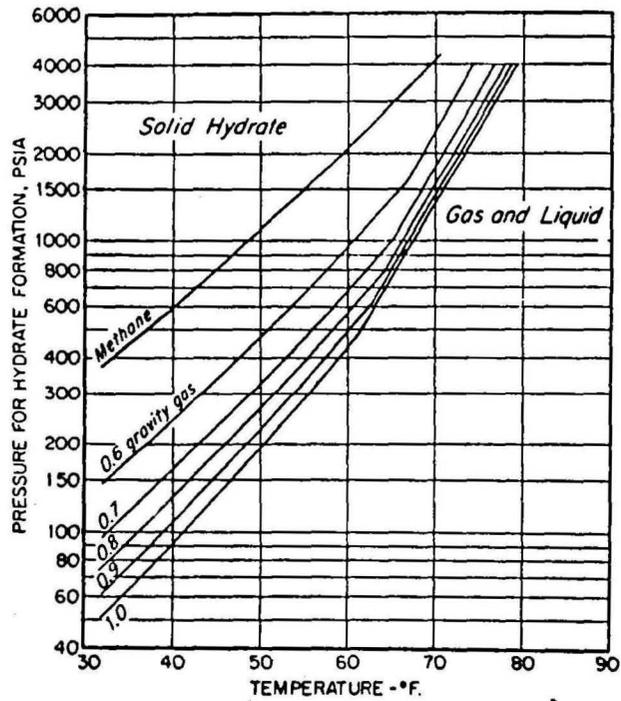


Figure 4. Hydrate-forming conditions for natural gases with various gravities (from Katz, 1971).

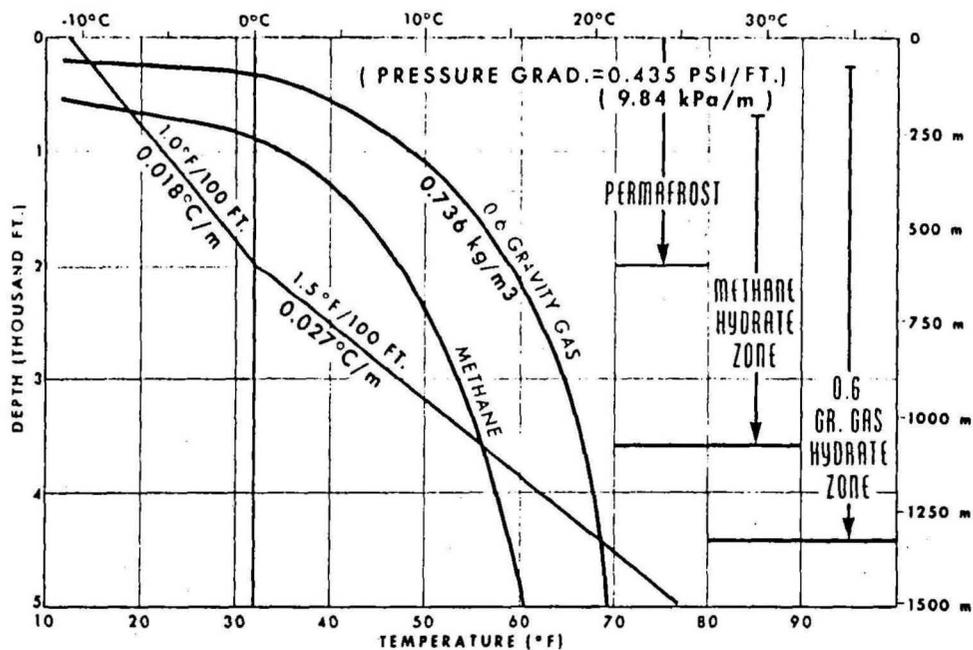


Figure 5. Determination of Gas Hydrate zone (from Bily & Dick, 1974).

As the various components of natural gas form hydrates under different conditions, selective formation may lead to the separation of the components. Hydrates may prevent migration of gas by sealing pore spaces in the strata.

Production and drilling

Drilling through hydrates pose problems. When the hydrate zone is penetrated at a normal rate the mud becomes gasified, resulting in a potential blow-out situation. Even when the hydrate zone has been penetrated the hydrates continue to decompose and gasify the drilling mud unless cooled to the hydrate equilibrium temperature. Increasing the mud weight is not effective in controlling gasification, but does maintain the circulation of the mud. The extremely high pressures that are generated by decomposition make attempts to core with conventional equipment dangerous. Therefore a pressure core-barrel is used with cooled drilling mud and temperature controls.

Production of gas from hydrates lowers the pressure causing hydrate decomposition. However permeability difficulties arise because the residual ice crystals block the flow towards the well bore.

OVERSEAS OCCURRENCE

Canada

In Canada onshore deposits of gas hydrates are found beneath permafrost at a depth of 1500 m (Judge). Permafrost covers most of the Mackenzie Delta and Arctic Islands. Surface temperatures in the eastern Mackenzie Delta range from -5° to -10°C (Judge) where the permafrost thickness ranges from 350-700 m (Judge). The Western region has a mean terrestrial surface temperature in the range of -0.4 to -2.3°C (Judge) where permafrost is discontinuous.

Offshore occurrence of hydrate in Canadian waters can be postulated by the area covered by permafrost. Permafrost is widespread across the Beaufort Sea where sea-bottom temperatures range from 0° to -1.8°C with thickness of 25 to 75 m depending on lithology of the bottom sediments.

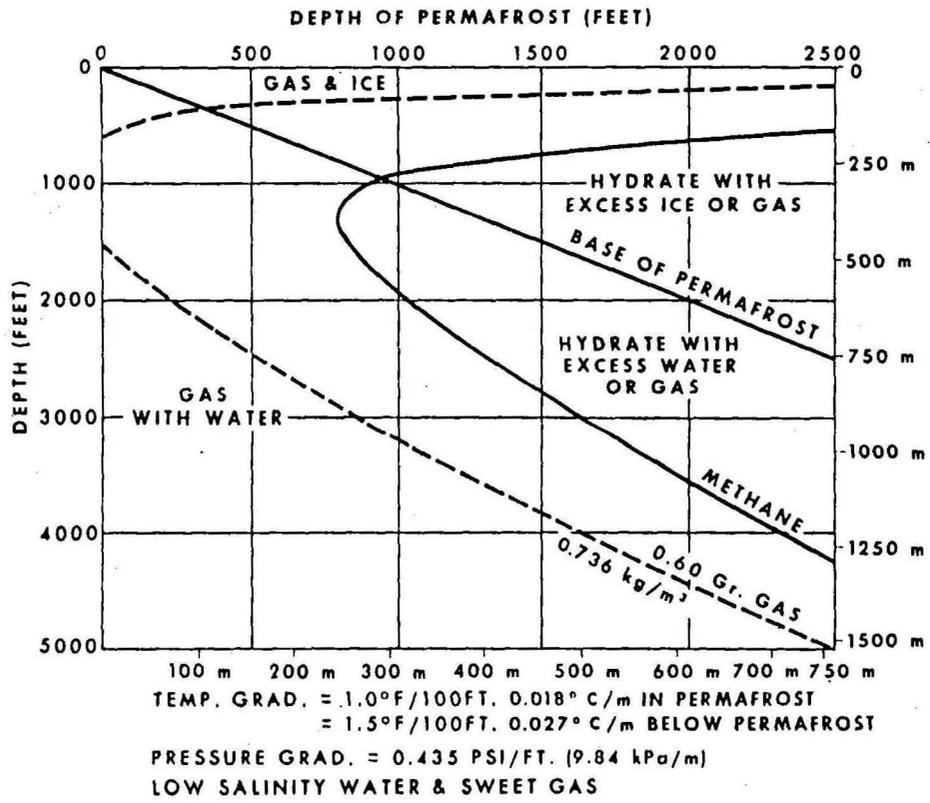


Figure 6. Reservoir Hydrate Zone (from Bily & Dick, 1974).

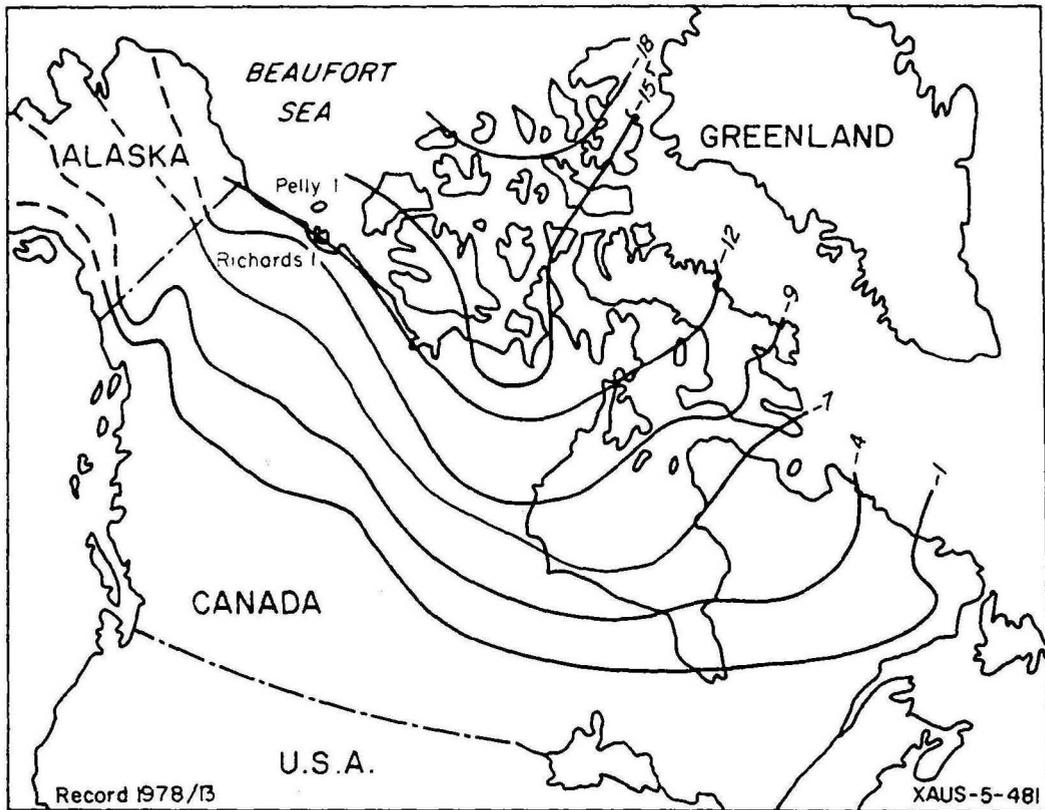


Fig.7 Mean atmospheric temperature in Arctic Regions of North America (after Katz, D.L. Depths to which Frozen Gas Fields (Gas Hydrates) may be expected, Journal of Petroleum Technology April 1971)

— -15 Isotherm (°C) Based on the Decade -1951/1960

Relict permafrost sediments are found north of Richards Island and west of Pelly Island in water depths of 60 to 80 m thinning out into deep water.

USSR

In Siberia the upper geological section to a depth of several hundred metres is below 0°C. Below this depth temperatures are above 0°C and formation pressures are high enough for hydrates to form.

Porous strata saturated by free gas show up on standard logs (figure 8(a)) but pore spaces filled with solid hydrates have a higher resistivity (figure 8(b)). However if the section contains hydrates, gas and water then it is not difficult to determine this using the logs (figure 8(c)).

AUSTRALIA & ANTARCTICA

Australia's position on the Earth's surface is influenced by tropic, and temperate climate. This is far from the Arctic region where gas hydrates occur. The average minimum temperature map for the coldest month in Australia (Fig. 9) clearly illustrates the remote possibility of temperature conditions approaching the limits for gas hydrate formation. Therefore it is highly unlikely that gas hydrates occur in Australia.

Although Antarctic onshore temperatures can accommodate conditions for hydrate formation, sediment for deposition of hydrocarbons is sparse. Permafrost has been reported by Calkin and Nichols (1970) but little is known about its temperature conditions, thickness and distribution.

Sedimentary sequences occur in two areas within the Australian Territory of Antarctica; the Beacon Group - along the Queen Maud Mountains adjacent to the Ross Ice Shelf - and the Amery Formation lying adjacent to the Amery Ice Shelf. Both units are composed of coal measures, sandstone and shales. The possibility of liquid water being present in these formations is minimal.

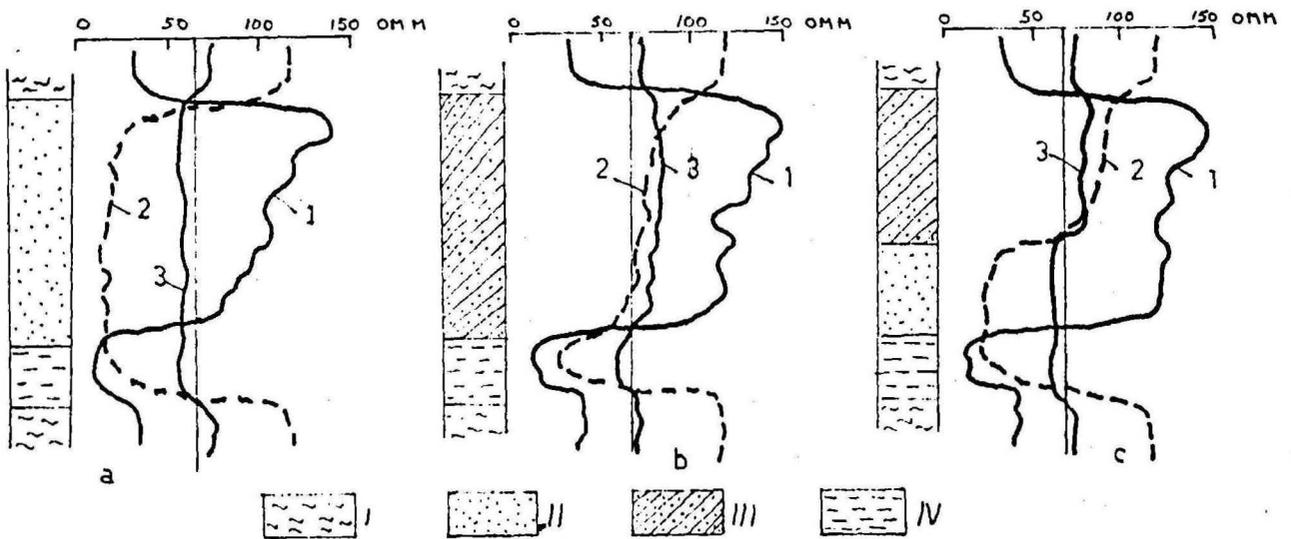


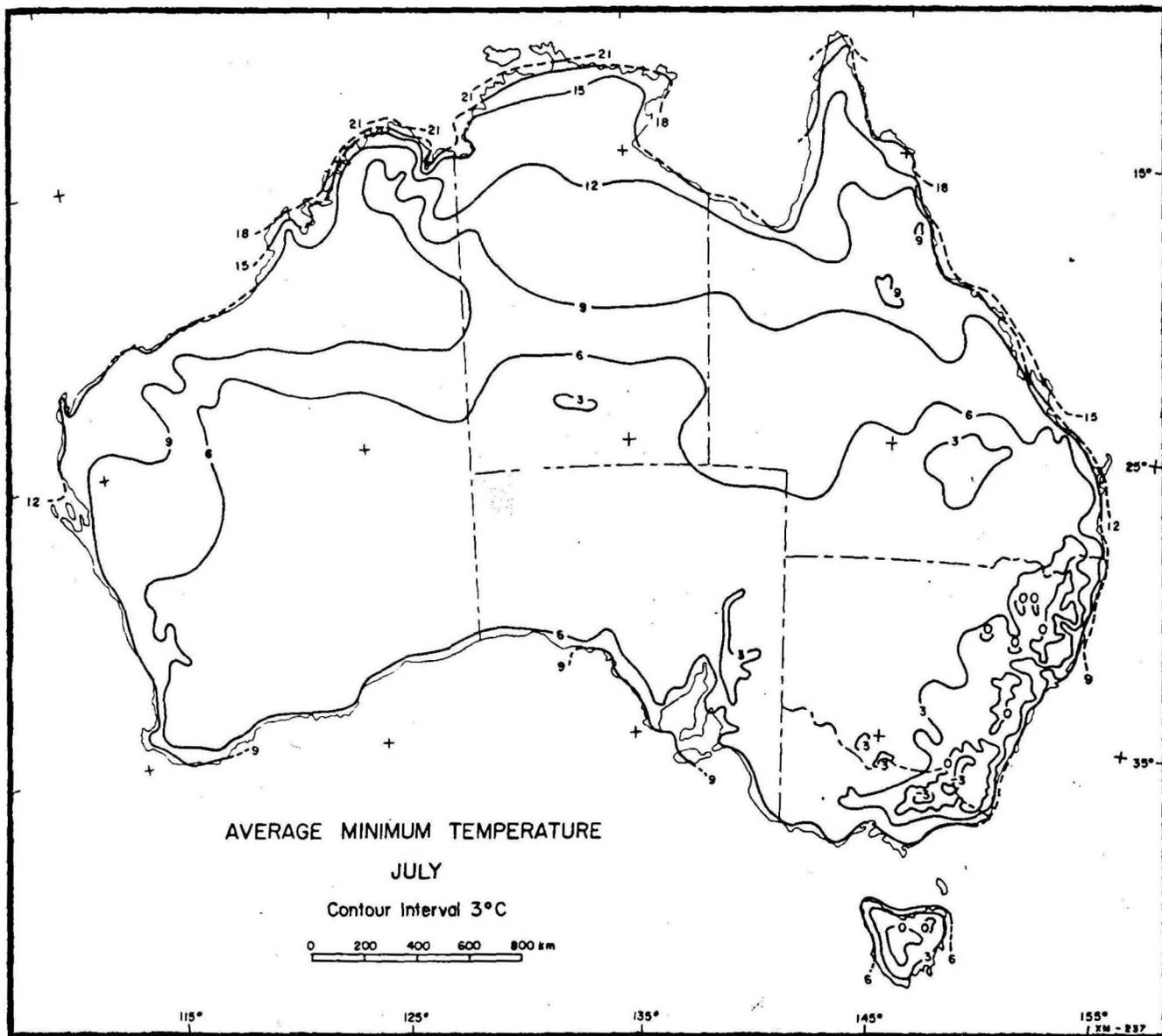
Figure 8. Geophysical-logging characteristics of strata containing free gas, hydrate, and formation water (after Sheshukov, 1973b).

- a) strata saturated by free gas with underlying water
- b) strata containing hydrates and underlying water
- c) intervals containing hydrates, free gas, and underlying water

- 1) resistivity log
- 2) SP log
- 3) caliper log

- I) claystone
- II) gas saturated sandstone
- III) sandstone containing hydrates
- IV) water saturated sandstones.

Figure 9.



Bureau of Meteorology Melbourne, June 1974.

The Dry Valleys of Victoria land are ruled out of speculation by the high content of salts although the temperature is at an ideal condition for gas hydrate formation. As mentioned earlier the presence of salt inhibits the formation of hydrate. The sediment is 10 m thick in Lake Vanda with a temperature range of 0° to 25°C (Fig. 10).

The most encouraging reports of hydrocarbon accumulation have come from the three holes drilled in the Ross Sea by the Deep Sea Drilling Project in December 1972 and February 1973 (Fig. 11) (Kaneps, 1975). Methane and ethane were recovered from the three holes (271, 272 and 273). These holes were abandoned when methane was first encountered, owing to the lack of facilities to prevent blowouts.

It has been reported that the methane was encountered at a depth of 265 m below the sea floor in No. 271, 245 m in No. 272, and 276 m in No. 273. Lithology has been described as diatomaceous silty claystone with sand content increasing at the bottom. The holes were drilled in 629 m of water for No. 272, 495 m for No. 273 and 562 m for No. 271. Unfortunately the temperature of the holes and sea floor were not recorded and the holes were not logged.

Other potential hydrocarbon areas do exist offshore from Antarctica. Off Wilkes land (and also outside the French Sector) a sequence of sediment at least 2.5 km thick exists. Outside Australian Territory the Bellingshausen Sea and Waddell Sea contain sediment up to 3-4 km thick. No one has reported permafrost existing in these sediments and other information relevant to the conditions of gas hydrate formation is not known.

CONCLUSIONS

Australia is unlikely to contain hydrates because formation conditions do not prevail. If hydrocarbons occur in the Antarctic region then conditions may persist for the formation of gas hydrates. The results of deep sea drilling in the Ross Sea did not produce conclusive evidence of hydrate accumulation because of the non-petroleum aims of the drilling project. The methane finds and the decrease in salinity are pointers to hydrate formation but more evidence as to the temperature - pressure conditions is needed.

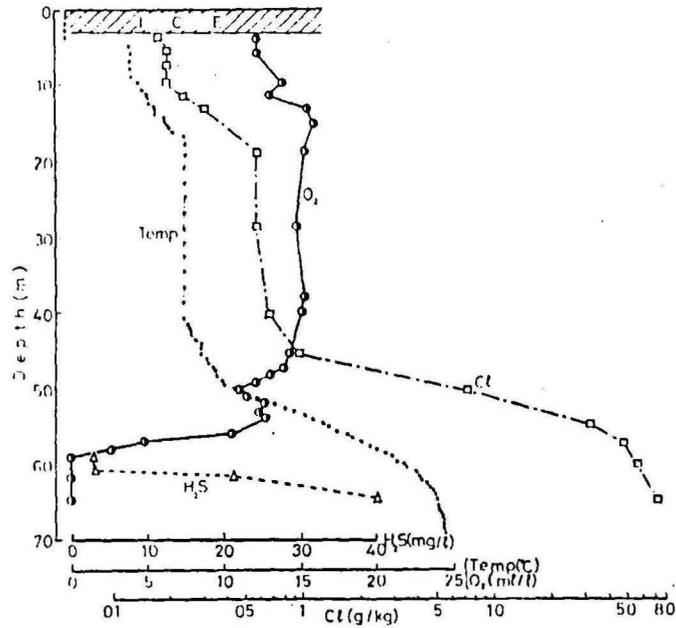


Figure 10. Vertical distribution of temperature, O₂, Cl and H₂S in lake Vanda Antarctic (after Torii, 1975).

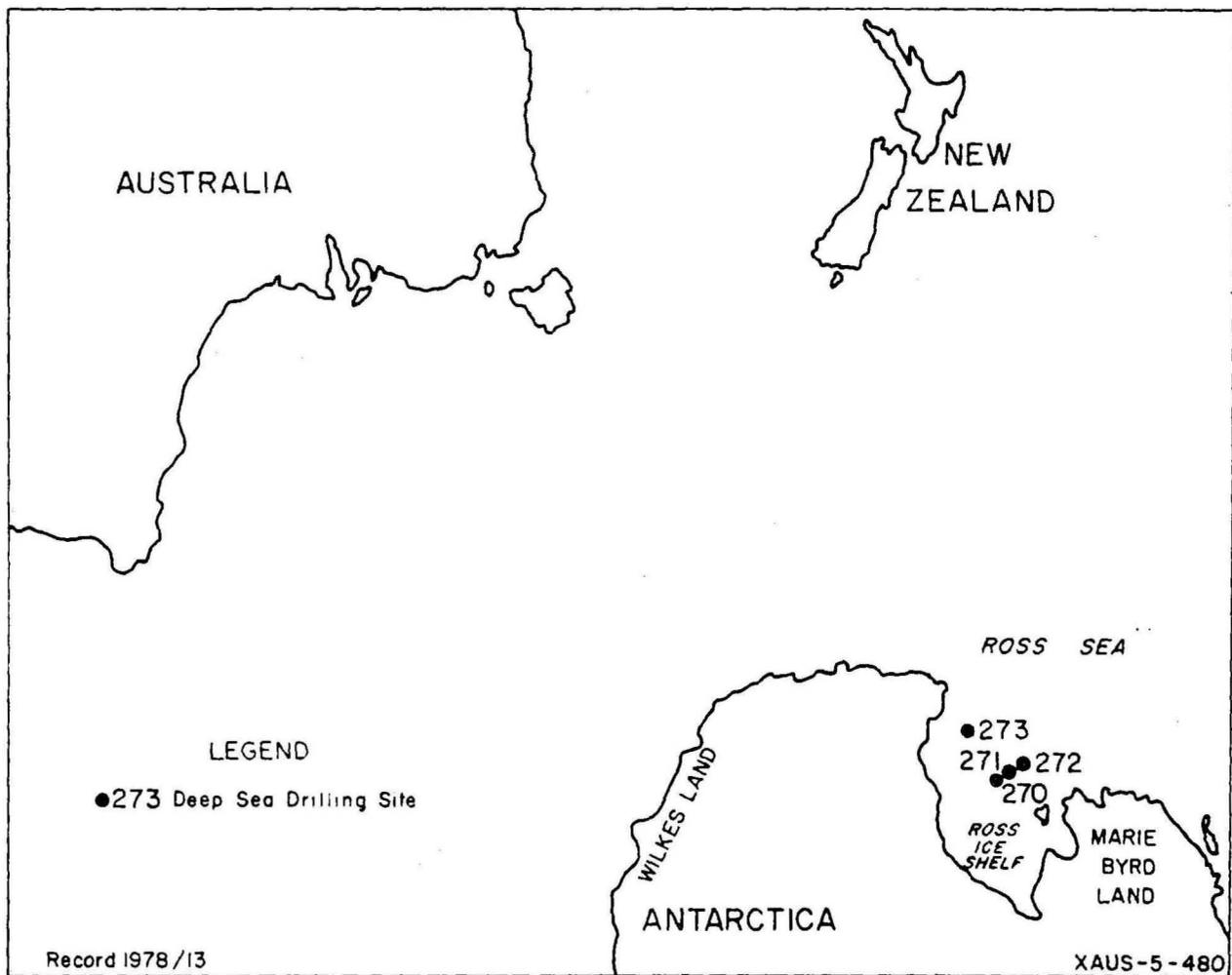


Fig.11 Location of sites drilled in Antarctic waters south of Australia and in the Ross Sea (after Initial Reports of the Deep Sea Drilling Project Volume XXVIII December 1972 - February 1973 prepared for the National Science Foundation by the University of California.)

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