

GES 206 Paper, Prof. R. Dunbar & A. Cooper
dunbar@stanford.edu, acooper@usgs.gov
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Kevin Hand, khand@stanford.edu

Air clathrate hydrate formation in Antarctic sub-glacial lakes

1. Introduction

The sub-glacial lakes of Antarctica are one of the last unexplored liquid water environments known to exist on our planet. It is estimated that some of these lakes have been isolated from the atmosphere for more than one million years (Kapista et al.), (Priscu et al.). As such, they harbor many interesting questions regarding life in extreme environments and the chemical pathways that may, or may not make life possible deep below the ice sheet. Answers to such questions could serve to guide us in the coming decades of solar system exploration and the search for life beyond planet Earth.

In particular, the formation of oxygen, carbon dioxide, or hydrogen sulfide hydrate reservoirs within the lakes could serve as the source of a significant redox gradient capable of driving biochemical cycles in sub-glacial lake ecosystems. In the following paper I provide a survey of known and calculated conditions for Antarctic sub-glacial lakes and analyze the extent to which various hydrates may occupy such environments. Values are calculated for hydrate densities and from this, estimates are made about behavior of hydrates in sub-glacial lakes.

Finally, using the terrestrial case, extrapolations are made to other planetary environments in our solar system. Specifically, the case for hydrates with the putative subsurface ocean of Europa is analyzed and the case for sub-glacial lakes at the Martian polar caps is examined.

2. Distribution of sub-glacial lakes in Antarctica

As of 1996, seventy-seven sub-glacial lakes had been identified below the Antarctic ice sheet (Siegert et al. 1996). Discovery of such lakes relies on satellite altimetry and airborne radio echo sounding (RES). The altimetry data is used to locate anomalous near-flat regions while the RES data is used to identify anomalies below the ice sheet. Using a 60MHz RES signal, sub-glacial lakes appear as strong, flat reflections amidst more dynamic sub-glacial terrain.

Given the 50-100km flight line separation for the RES data, and the vast unexplored regions of the ice sheet subsurface, it is expected that many more lakes will be discovered (Siegert, 2000). In addition, lakes covered in regions where the ice sheet is experiencing significant basal sliding will likely go undetected in RES data. The ice sheet base retains some of the surface morphology and thus the RES reflections lack the characteristic strong, mirror reflection. Furthermore, lakes less than 4 km cannot be identified via radar altimetry because there will be no observable flat surface topography on the ice surface 3 km above the lake.

The largest of the known sub-glacial lakes is Lake Vostok, measuring roughly 230 km in length and 50 km in maximum width. With an estimated average depth of 510 m and a total surface area of approximately 14,000 km², this corresponds to ~7000

km³ of water isolated from the surface environment (note: more conservative estimates of average depth bring this number down to ~2800 km³).

Excluding Vostok, the combined estimated surface area of known lakes is ~15,000 km². The average length of these much smaller lakes is 10.8 km; only 5% have been measure to be longer than 30 km. These values are of course minimum values since the RES data was not necessarily collected along the longest axis of the lakes.

Other than Vostok, there are only six known examples of radio-echo reflections from lake-floors. These lakes are estimated to be 10-20 m in depth and the depths of the remaining lakes are estimated to be 10-100's of meters. Using these numbers, the total water volume contained in these lakes is expected to be between 4,000-12,000 km³.

Based on the attenuation of the RES signal, an interpretation of the lake salinity can be made. The radiation attenuation is a function of the lake water conductivity that in turn is a function of salinity. The conductivity of the lake water is measured to be between 3.08×10^{-4} mhos m⁻¹ and 5.36×10^{-4} mhos m⁻¹. The conductivity of fresh water is 10^{-4} mhos m⁻¹. From this data it has been estimated that the sub-glacial lakes are very pure and fresh and contain only small amounts of dissolved salts.

2.1. Formation of sub-glacial lakes

Roughly 70% of the known sub-glacial lakes are clustered in the two regions of Dome C and the Ridge B region of East Antarctica. No lakes of comparable magnitude to that of Vostok have been reported from the altimetry data below the ERS-1 latitudinal limit of 82 degrees South (Siegert, 2000).

Based largely on the region of formation, three types of lakes have been characterized. The first group includes lakes formed in basins within the ice-sheet interior. This includes Vostok and the majority of other lakes. The second group includes lakes perched on the flanks of mountains. The third group consists of lakes formed at the onset of enhanced ice flow.

With regard to the formation of sub-glacial lakes, two proposals dominate. One hypothesis is that the lakes have formed as part of a relatively stable ice sheet configuration. In this case, the source of the sub-glacial water is geothermal heating. The run-off water then travels into a bedrock trough and the lake is formed. Since the water originated with the glacier, this model predicts that the lake salinity would be roughly equal to the salinity of the basal ice.

In the second proposal, the lakes pre-date the formation of the glacial ice sheet. As the ice sheet grew the lakes were covered and isolated from the surface. In this model the salinity of the sub-glacial lakes could be much higher than in the first proposal. Not enough is yet known about the sub-glacial lake environments to draw a conclusive picture regarding their formation.

2.2. Lake Vostok

Vostok is by far the largest of the known sub-glacial lakes. Due to the relatively obvious flat topographic signature from satellite altimetry data, it is unlikely that a comparable lake has been overlooked.

Satellite radar altimetry of the ice sheet above Vostok indicates a North-South slope of 0.004 degrees (0.25 m/km) (Siegert, 2000). The ice sheet thus drops ~40m over its 230 km length and the surface of the lake is then tilted with a ~440 m drop in the opposite direction. As a result, ice is melting from the bottom surface at the shallow northern end and re-freezing to the ice sheet base at the southern end. A 200-250 m thick layer of accreted ice exists at the southern end of the ice sheet (Lipenkov & Istomin, 2001). While the average age for the water in the lake is estimated to be about one-million years since deposition at the surface, estimates for the residence time of the water in the lake are in the range of 10,000 years (Kapista et al., 1996), (Priscu et al., 1999).

This cycle establishes flow patterns within the lake that are largely dependent on the density, and thus salinity, of the lake water. If the lake water is nearly pure, then the melting basal ice will be of comparable density and significant mixing of the melt water will occur throughout the lake. If, however, the lake water salinity is such that the melt water is considerably less dense than the lake water, then the melt water will flow up-slope to the southern end without much mixing in the lake. Once it reaches the southern end of the lake, the melt water will refreeze to the bottom of the glacier. The difference between these two scenarios has significant consequences for the interpretation of life discovered in the deepest sections of Vostok ice cores. More will be said about this in later sections.

Vostok is the only sub-glacial lake for which we have seismic data. The thickness of the ice sheet over the northern end of the lake is just over 4 km, while that just below Vostok station is roughly 3.5 km. To date, an ice core has been drilled to a depth of 3623 m, approximately 120 m above the lake surface. The lowest 85 m of this ice core is from ice accreted to the bottom of the ice sheet. Density of the ice at the base of the ice sheet is estimated to be 0.913 g/cm³. The salinity is estimated to be between 0.00 to 0.05 parts per thousand (seawater: 35 ppt).

3. Sub-glacial lake environments

3.1. Thermal properties of the Antarctic ice sheet above sub-glacial lakes

3.1.1. The pressure melting temperature of ice

The presence of a sub-glacial lake indicates that in the region of the ice sheet surrounding the lake, the temperature of the ice sheet base is at the pressure melting point. In the simple case of pure water ice, the Clapeyron equation (Sloan, 1998),

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H}$$

yields a slope of $-0.075 \text{ K MPa}^{-1}$. This can then be applied to an equation for approximating the freezing/melting of ice under pressure (Lipenkov & Istomin, 2001),

$$T_f(S, P) = T_f(S, 0) - 7.53 \times 10^{-2} P(\text{MPa})$$

Here S represent salinity and $T(S, 0)$ is 273.1 K for pure water. For the case of Antarctic glacial ice with, the slope of the Clapeyron equation needs to be modified to correspond to the equilibrium between water-air hydrate-ice (Lipenkov & Istomin, 2001). Fitting experimental data to a line, Lipenkov and Istomin approximate the Clapeyron temperature-pressure slope for this mixture to be $-0.079 \text{ K MPa}^{-1}$. Assuming the water temperature in is 270.15 K , the above equation yields a pressure of 37.34 MPa . Given uncertainties in the slope calculation and other variables, Vostok is generally considered to have pressures in the range of $35\text{-}40 \text{ MPa}$.

3.1.2. Geothermal contribution to heat flux

Factors affecting the basal ice sheet temperature include thickness, surface temperature, accumulation rate, heat transported through horizontal advection of ice, heat from internal deformation, geothermal flux and heat from sliding.

The basal heat gradient is a function of the ice flow at the base and the geothermal heating. The flow at the base of the sheet is in turn a function of the distance from the ice sheet divide since velocity increase as we move away from the divide. Therefore, we make the approximation that at the ice divide all heating is geothermal. From Siegert, (Siegert, 2000) we have the following expression for the temperature at the base of the ice sheet:

$$T_B = T_S - \frac{\sqrt{\pi}}{2} l \frac{dT}{dz} \Big|_B \operatorname{erf} \left(\frac{h}{l} \right) \quad l = \sqrt{\frac{2kh}{b}} \quad , \quad \frac{dT}{dz} \Big|_B = -\frac{\Lambda_{geo}}{K}$$

The key parameters here are T_S and T_B , surface and basal ice sheet temperatures; h , the ice sheet thickness above the lake; b , the surface accumulation of ice per year; k , thermal diffusivity per year ($36.3 \text{ m}^2/\text{year}$); K , thermal conductivity (2.10 W/m

degree C); and Λ_{geo} , the geothermal heat flux in mW/m^2 . Using data from the Antarctic ice sheet and RES from sub-glacial lakes near ice divides, the above equation can be solved for the geothermal heat flux. Siegert finds that minimal heating for the lakes in the Dome C, Talos Dome, and Titan Dome regions is between $41\text{-}58 \text{ mW/m}^2$; heating for lakes in the Ridge B region is between $37\text{-}42 \text{ mW/m}^2$; heating for lakes around Hercules Dome is $\sim 60 \text{ mW/m}^2$; and the heating for the Vostok region is at or below 43 mW/m^2 (Siegert, 2000). By comparison, the mean continental heat flux for Earth is 65 mW/m^2 and the mean oceanic flux is 101 mW/m^2 . The combination leads to a mean surface heat flux of 87 mW/m^2 for Earth (Schubert et al., 2001).

4. Conditions for clathrate hydrate formation

Owing largely to its potential as a fuel and its propensity to be a nuisance in natural gas pipelines, much is known about methane hydrates and the hydrates of short hydrocarbon chains (primarily ethane and propane). While these hydrates could serve as interesting 'food' for sub-glacial microbes, the origin of the host molecule is itself dependent on a pre-existing ecosystem. For this reason, we will not examine such hydrates in detail. Instead, we are interested in the formation of air hydrates (oxygen, nitrogen, and carbon dioxide) and hydrogen sulfide hydrates. Such gases are known to exist on other planets in the solar system and thus their hydrated form may carry implications for extraterrestrial ecosystems.

The formation of the hydrogen-bonded ice-cages that constitute hydrates depends strongly on the temperature and pressure environment and the properties of the host molecule. Here we examine the key parameters for air hydrates and the implications sub-glacial lake environments.

4.1. Hydrate Lattices

Formation of hydrate ice cages occurs primarily in three different, cubically symmetric structures. Other structures may be possible under conditions yet to be explored. All known forms involve combinations of two or more types of polyhedral cages. Here we discuss Structures I and Structure II as they are relevant to air and hydrogen sulfide hydrates. Structure H hydrates are typically less stable but can house some alkanes, alkenes, and aromatics.

The unit cell of Structure I hydrates is 12 cubic angstroms in volume and consists of two small cages and six large cages for a total of 46 water molecules. The Structure I small cages are 3.95 Å in radius and can house molecules less than 5.1 Å in diameter. The large cages have a radius of 4.3 Å and can hold molecules as large as 5.8 Å in diameter. Typical Structure I hydrates include methane, carbon dioxide, and hydrogen sulfide. While each unit cell could potentially hold eight host molecules, in reality not all cages are filled. For instance, in the case of methane hydrates a typical unit cell

will only be occupied by 6-7 methane molecules (6.667 methane molecules is the calculated value, the fractional occupancy ratio is therefore approximately 0.833).

Structure II hydrates house oxygen and nitrogen gases as well as a host of larger molecules. The unit cell consists of 136 hydrogen bonded water molecules arranged in 16 dodecahedral cages and 8 hexadecahedral cages. The 16 small cages have a radius of 3.91 Å and can hold molecules with diameter less than 5 Å. The 8 large cages are 4.73 Å in radius and can hold molecules with diameters of 6.7 Å or less. The Structure II cubic unit is 17 Å on a side.

It should be noted that if a gas mixture is present, then the resulting hydrate will also be mixed. The binding of a given gases molecule into a hydrate cage is only dependent on the relative size and the magnitude of the van der Waals interaction between the host and the surrounding water molecules. Determining the relationship between a gas phase mixture and its corresponding hydrate mixture depends on the inverse ratio of the dissociation pressures of the pure hydrates (Miller, 1959).

4.2. Hydrate Stability

4.2.1. Hydrate Dissociation Pressures

The key parameter to consider when attempting to determine hydrate stability at a given temperature is the dissociation pressure. At the dissociation pressure, ice, gas, and hydrate are in equilibrium. Above this pressure, the hydrate phase is stable and the ice and gas phases will combine to form the hydrate. Below the dissociation pressure, the hydrate becomes unstable and only the ice and gas phases are present.

For temperatures above 273 K, liquid water is stable and a solution is formed with the gas such that the solution is in equilibrium with the gas. If pressure is increased, a point is reached at which water, gas, and hydrate phases are in equilibrium. Note that ice is not a stable phase at this point. For a given gas hydrate, there exists a quadruple point (the Q-point) at which all four phases of water-ice-gas-hydrate are in equilibrium. The Q-point can be found by plotting dissociation pressure versus temperature for a given phase boundary. The intersection of the lines for gas-water-hydrate and gas-ice-hydrate represents the Q-point for the system.

For a given gas hydrate, the dissociation pressure scales with temperature as follows:

$$\log P_d = A + B/T$$

The dissociation pressure, P , is given in MPa and the temperature in Kelvins. The parameters A and B are experimentally determined for a specific system in a given temperature range.

For the case of methane, the quadruple point is at 2.6 MPa and -0.12 C (slightly below 0 C because dissolved methane lowers the freezing point of water) (Miller, 1959). For the case of oxygen, the Q-point is at a pressure of approximately 11.1 MPa and -1 C. Molecular nitrogen has a Q-point at 14.35 MPa and -1.25 C (Lipenkov &

Istomin, 2001). Note that the critical point for each gas should not be ignored. Methane, for instance, reaches its gas-liquid critical point at -82 C and depending on the pressure below that point the hydrate will be stable with either the liquid or gas phase of methane.

Having calculated individual dissociation pressures, values for various hydrate gas mixtures can be approximated by assuming that the hydrate behaves as an ideally dilute solution and that the fractional occupancy ratio is constant and the same for all gases (Lipenkov & Istomin, 2001). With these assumptions, the mixed gas dissociation pressure can be expressed as:

$$P_{d(mix)} = \left[\sum \frac{y_i}{P_{di}} \right]^{-1}$$

Here y is the mole fraction of the component in the gas phase. Using this equation for a mixture of oxygen and nitrogen, we get:

$$P_{d(air)} = \frac{P_{dN_2} P_{dO_2}}{y_{N_2} P_{dO_2} + y_{O_2} P_{dN_2}}$$

This expression for the dissociation pressure for air can now be used in conjunction with the initial equation and a phase diagram for the nitrogen-oxygen gas mixture can be created. Lipenkov and Istomin use values of $A=13.186$ and $B=-3279$ for pure nitrogen and oxygen hydrates at the air-water-air hydrate equilibrium and values of $A=3.875$ and $B=-745.8$ for pure nitrogen and oxygen hydrates at the air-ice-air hydrate equilibrium. The two lines intersect at the air hydrate Q-point of $T = 271.8\text{ K}$ and $P = 13.3\text{ MPa}$. The Lipenkov and Istomin phase diagram of air hydrates is provided at the end of this paper (Lipenkov & Istomin, 2001). The area of critical interest is the upper right quadrant, where water and air hydrates are in equilibrium. In order to understand whether or not hydrates will be stable in this region we need to examine the solubility of air in water for the hydrate-gas-water mixture. As a crystal of hydrate becomes exposed to the liquid water of the lake, will it dissolve or will it remain as a hydrate crystal?

4.2.2. Air solubility

As the system moves further out into the water-hydrate region of the phases diagram (i.e. increase P and T), the solubility of air in water is affected. Determining the solubility of air in water for a given system will let us predict what the maximum air concentration is in the lake. In addition, it will allow us to predict the behavior of incoming hydrates - will they dissolve or will they remain as crystals?

Lipenkov and Istomin use the following equation to determine solubility as a function of temperature and pressure (Lipenkov & Istomin, 2001):

$$X_i(P, T) \approx X_i(P_{d(air)}) \exp\left[-\frac{\alpha(P - P_{d(air)})}{RT}\right]$$

With a lake-water temperature of 270.15 K, the dissociation pressure of air is 11.17 MPa, far below pressures expected in Vostok. Thus we expect the solubility of air to be considerably lower in the Vostok system. Lipenkov and Istomin calculated solubilities for the conditions in Vostok (35-40 MPa) and find that at a concentration of 2.2×10^{-3} mole fraction, air hydrate is in equilibrium with both nitrogen and oxygen dissolved in the lake water. A table summarizing the results of Lipenkov and Istomin is given below:

Quantity	Gas content of lake water	
	Min	Max
Mole fraction of air in aqueous solution.	7e-5	2.2e-3
Mole fraction of N2 in aqueous solution.	5.5e-5	1.45e-3
Mole fraction of O2 in aqueous solution.	1.5e-5	7.5e-4
Freezing T at P=37.8 Mpa, melting site M	-2.86	-3.15
Freezing T at P=33.9 Mpa, freezing site F	-2.62	-2.85

4.3. Hydrate Densities

If conditions for hydrate formation and stability are such that hydrates form in equilibrium with liquid water, then the issue of hydrate density plays an interesting role in where such hydrates will be found. For a given aqueous solution and hydrate host, one would expect the hydrate crystals to either float on the surface or sink to the ocean/lake floor.

Density calculations are obviously dependent on the cage structure and host molecule, but in addition the fractional occupancy of the host at a given temperature and pressure must be known. The equation for calculating hydrate density is:

$$\rho = \frac{\frac{N_w}{N_{Ave}} MW_{H_2O} + \sum_{j=1}^c \sum_{i=1}^n y_{ij} v_i MW_j}{V_{cell}}$$

where:

Variable	Description
Nw	# of H2O molecules/cell
Nave	Avagadro's #
MWj	Molecular Weight of j
y	fractional occupation of cavity i by component j
v	# of cavities of type i
Vcell	Volume of a unit cell
n	number of cavity types in unit cell
c	# components in hydrate phase

Results for density calculations for oxygen, nitrogen, carbon dioxide, and hydrogen sulphide are given in Chart 1 at the end of this paper. Fractional occupancies at a variety of temperatures were determined using the CSMHYD software (Sloan, 1998). For instance, in the case of nitrogen at 270 K the three-phase (Ice-Hydrate-Vapor) equilibrium conditions are 12.15 Mpa and cage occupation values of: small cage = 0.8831, large cage = 0.9097.

The CSMHYD software does not allow for calculating fractional occupancies of oxygen hydrates. As a result, I used nitrogen as a proxy for oxygen in determining these values. Both molecules are enclathrated by Structure II hydrates and the diameter of molecular oxygen is only slightly greater than that of molecular nitrogen (4.1 Å vs. 4.2 Å) (Sloan, 1998). I am unsure how van der Waals forces might alter fractional occupancy in this case. Assuming van der Waals differences are negligible, using the fractional occupancy of nitrogen as a proxy for oxygen would yield higher density values since the occupancy of a smaller molecule would presumably be higher than a larger molecule.

The resulting density calculations indicate that oxygen hydrates sink in pure water and float in salt water. Nitrogen hydrates float in cold pure water and under most conditions will float in salt water. Carbon dioxide hydrates sink in both pure water and salt water. Hydrogen sulphide hydrates also sink in pure water and salt water.

Note, adding salts to the solution affects hydrate formation by increasing the fractional occupancy values. The above density calculations were rerun with fractional occupancies determined using a 3.5% by weight value for NaCl in solution. As can be seen from the results (Chart 2), the densities of the hydrates increases but the float/sink stability remains the same.

Additionally, for real systems one would want to consider the hydrate density of hydrates formed in gas mixtures. Air hydrates are mostly a mixture of nitrogen and oxygen and thus the density of such hydrate could be poised right on the line between floating and sinking. Lipenkov and Istomin find that the equilibrium density of air hydrates varies between 0.98 g/cc and 1.025 g/cc (Lipenkov & Istomin, 2001). Factoring in sub-glacial lake temperature and pressure conditions they expect that air hydrates will always float on the 1.016 g/cc sub-glacial water.

4.4. Implications for sub-glacial lakes

4.4.1. Lake Vostok

Lipenkov and Istomin have examined hydrate stability in Vostok and calculated upper and lower limits for dissolved oxygen concentrations in the lake (Lipenkov and Istomin, 2001). Once gases trapped at the surface are transported down to the 1300 m depth line, the ice-gas mixture changes phase and turns into an air hydrate. From

there it is transported downward until it reaches the ice-water interface at the lake surface boundary. The air hydrates then either dissolved into the water or remain as hydrate crystals floating/sinking in the lake; the difference between the dissolved gas phase and hydrate phase depends on the air solubility of the lake water. As previously described, the pressure and temperature conditions in Vostok set the maximum solubility of air at 2.2×10^{-3} mole fraction. If the lake is saturated with oxygen and nitrogen then the air hydrate will remain in its crystal form. Here we examine factors affecting air concentration in lake Vostok.

Lipenkov and Istomin conclude that ice accretion results in an increase in the gas content of the lake water beyond the baseline level of 7×10^{-5} mole fraction that would be expected from glacial melt water concentrations. Using an accretion rate of 4 mm per year over half the lake area, they calculate that the bulk air content of the lake would increase by $\sim 1 \times 10^{-10}$ mole fraction per year (using a lake volume of 2100 cubic km) (Lipenkov & Istomin, 2001). The bulk concentration of air in the lake can be expressed as the baseline concentration (7×10^{-5} mole fraction) multiplied by the ratio of the lake's steady state duration and the residence time of the water. Estimates for residence time range from 5000 to 50,000 years (Jean-Baptista et al., 2001), (Kapista et al., 1996). From this, Lipenkov and Istomin calculate that the air concentration in the lake could reach maximum solubility in 0.16-1.6 million years if no biological or chemical systems are influencing the concentrations. This calculation assumes that the water exchange between the base of the ice sheet and the lake water has been cycling at the same efficiency for the duration.

Interestingly, Lipenkov and Istomin make no estimate of hydrate accumulation over this time period. If the mole fraction of air delivered to the lake exceeds the air solubility, then air hydrate crystals will grow. If we assume that Vostok has been isolated for one million years and that the hydrate stability equilibrium concentration of 2.2×10^{-3} was reached after 0.2 million years, then there would have been 0.8 million years of accumulation of oxygen. Using Lipenkov and Istomin's figure of 1×10^{-10} mole fraction increase in air per year, I calculate a delivery of 1.185×10^7 moles of air per year. Approaching the same calculation by using ice volume melted per year and air concentration of the ice, I get 9.7×10^5 moles of air delivered per year. Assuming a nitrogen to oxygen ratio of 3.7, I find that oxygen delivery rates per year could be in the range of 2.06×10^5 to 2.52×10^6 moles per year. Over the course of 0.8 million years, this translates into 5.286×10^{12} to 6.46×10^{13} g of oxygen hydrate accumulation. By comparison, photosynthesis on Earth produces $\sim 1 \times 10^{16}$ moles per year of oxygen (Walker, 1977).

The above calculation is an upper limit for hydrate delivery and accumulation. If we assume the other extreme of 1.6 million years for reaching a 2.2×10^{-3} air concentration, then lake Vostok has not yet reached the dissolved gas solubility max and the incoming hydrates will be metastable and likely dissolve into the water. However, the accretion rate used above may be a lower limit; Siegert et al. suggest that rates as high as 11mm per year could be possible (Siegert et al., 2001). Thus the incoming flux could be substantially higher. Given that hydrates are observed in the core from the

accreted ice we can reach two possible conclusion: 1) The observed hydrates indicate a high level ($\sim 2.2 \times 10^{-3}$ mf) of dissolved gas in the lake water, or 2) The observed hydrates represent gases trapped in the accreted ice that later became enclathrated. One might expect to be able to distinguish these two cases by measuring the oxygen content of the ice core clathrates. If the nitrogen-oxygen ratio matches the atmospheric ratio (3.7) then it may be likely that the crystal has been intact since introduction at the north end of the lake. If the ratio is larger, then one could suspect biological or chemical depletion of the oxygen. Additionally, one might be able to measure an oxygen isotope fractionation. Presumably the O-18 would sink and thus newly formed hydrates in the accreted ice would be O-18 depleted. Given the many factors affecting the O-18 in the original glacial ice (e.g. T, large/small scale climate variations), it might be difficult to separate out any effect occurring in the lake water. Perhaps simply comparing the O-18 of the molecular oxygen to that of the oxygen in the water would suffice. In this case, the critical relationship would be the atmospheric O-18 to precipitation O-18 ratio.

If the above concentration (or any significant concentration) of hydrates were to exist, then they should float to the southern end of the lake (according to Lipenkov and Istomin's mixed hydrate density value). If such a concentration were to exist at the southern end, then we would expect to see a significant fraction of hydrates in the accreted portion of the Vostok ice core. While hydrates do exist in this part of the ice core, I have not been able to find any data or estimates of the density of such crystals in the water ice. Siegert et al. mention that fifteen hydrate structures between 3-5 mm in diameter were observed in a 32-cm-long vertical section of ice (note: these values are for the expanded ice) (Siegert et al., 2001). While I am presently unsure of the ice core diameter and thus volume of this section, this appears to be a lower concentration than I might expect if the hydrates were accumulating in the region of ice accretion.

Several scenarios can be envisioned to solve this potential paradox. First, the hydrates may in fact sink or if they are of roughly equal density then we would expect the crystals to mix throughout the lake. However, when addressing density Lipenkov and Istomin argue that due to convective turbulence, hydrate crystals that are slightly more dense than water will remain in suspension as long as they are not larger than 200 microns in diameter (Lipenkov & Istomin, 2001).

A second scenario could be that the hydrates are indeed significantly lighter than the surrounding water and they accumulate in high concentrations at higher points in the lake. We only have one deep core that penetrates into the accreted ice and thus the observed hydrate density may not be a good metric for the rest of the accreted ice. Not enough is known about the basal ice sheet topography to understand how, and where, low-density hydrates would accumulate.

Another possible explanation is that a significant microbial community exists in Vostok and thus consumes the incoming hydrates. In this case, the microbes would convert oxygen to carbon dioxide. Once the carbon dioxide maximum solubility point

is reached, then the carbon dioxide hydrate, being heavier than water, would precipitate and accumulate as sediment on the lake floor. Indeed, it could be the case that this carbon dioxide is then utilized by autotrophs combing the lake floor for resources. The limiting factor for these communities could very well be available carbon. In the following section, we look at known values for dissolved organic carbon and use the above numbers to estimate the size of this potential microbial community.

4.4.2. *Potential Elsewhere: Dome C & Ridge B Lakes*

One of the key parameters for hydrate formation and concentration in sub-glacial lakes is the accretion time of the over-lying ice sheet. A shorter accretion time will result in the transport of more gases to the lake and to regions where hydrates could potentially form. In the case of Vostok, this time is on the order of ~400,000 years. The limited data on other lakes indicates that accretion times for lakes formed on the flanks of sub-glacial mountains may be shorter than that for other types of lakes (Siegert, pers. comm.). If this is so, then we may expect these lakes to have reached maximum solubility for dissolved gases faster and consequently the time for hydrate formation and accumulation would be longer. Needless to say, the temperature and pressure conditions in these lakes is likely to vary significantly and until more data is collected it will be difficult to make any predictions about the subsurface environments.

One interesting parameter to consider is the surface to volume ratio of the lakes if we assume that the transport rate through the ice is constant. If we approximate the lakes as half-spheres, then the ratio is $3/(2R)$ where R is the lake radius and depth. From this we can see that it will be considerably easier for smaller lakes to reach higher concentrations if all other parameters are set equal (e.g. residence time of water in the lake, transport rates, etc.). The effect is enhanced if we make the fair assumption that the lake surface radius is much greater than the lake depth. This has important implications for choosing lakes for further exploration.

5. Hydrates as an energy source for biological systems

Having established that air hydrates are likely in sub-glacial environments, what does this imply for life and potential ecosystems? The key factor here is the need to understand the nature and distribution of biologically useful chemicals. If oxygen is available in a sub-glacial lake, what form will it take? Once we understand the answer to this question, then we can speculate about the ways in which life might harness such a resource.

Life has been found in the deepest sections of the Vostok ice core (Priscu et al., 1999), (Karl et al., 1999). Coccoid bacteria were discovered in core samples from 3589 m depth and 3603 m depth and it is suspected that the remaining ~20 m of core (3623 m total) will contain similar organisms (Priscu et al.). The ice from these

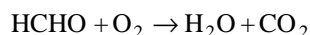
samples is from the accreted zone and thus it is highly possible that these organisms at one time resided in the lake itself.

Concentrations of the organisms in the 3589 m sample were measured to be 2.8×10^3 to 3.6×10^4 cells per milliliter (Priscu et al., 1999). An analysis of the 16S ribosomal DNA indicates a low genetic diversity in the population and suggests that the organisms are closely related to the extent *alpha*- and *beta*-*Proteobacteria* and the *Actinomycetes* (Priscu et al., 1999). Using samples from a core at 3603 m, Karl et al. found lower concentrations (2×10^2 - 3×10^2 cells/mL) but they were able to revive the bacteria in the lab (Karl et al., 1999). It is interesting to note that this concentration is about ten times less than any other extreme environment on Earth (Mackenzie, 1999). According to Karl, the bacteria were not growing in the ice due to a lack of water. In addition, they were observed to be unusually small; a likely result of starvation (Mackenzie, 1999).

Priscu notes that the dissolved organic carbon concentration in their core was measured to be 0.51 milligrams of carbon per liter, indicating that heterotrophic organisms might be able to survive in the lake. By comparison, the dissolved organic carbon concentration of Greenland snow is measured to be 0.11 mg C per liter. This may even be an order of magnitude too high if corrected for human generated pollution (Priscu et al., 1999).

On the issue of oxygen concentration and viable microbes in lake Vostok, terrestrial macrofauna need oxygen concentrations in the range of at least ~ 20 - $40 \mu\text{M}$ [3.6×10^{-4} mf] (Chyba & Phillips, 2001), (Fenchal & Finlay). Given Lipenkov and Istomin's calculated range of dissolved oxygen in lake Vostok (1.5×10^{-5} to 7.5×10^{-4} mole fraction oxygen), the molality of oxygen is in the range of 0.83 mM to 41.67 mM. This is plenty of oxygen for supporting life in Vostok.

As mentioned in the previous section, oxygen from the incoming melt water could potentially feed a much larger microbial population. If we use the same volume of melt water per year as was used for estimating oxygen delivery (2.8×10^{10} kg H₂O / year) and the figure of 0.51 g carbon/liter from Priscu et al. (Priscu et al., 1999), I find carbon delivery to be $\sim 1.2 \times 10^9$ moles of carbon per year. Thus, from a biochemical standpoint, it would appear that oxygen is the limiting factor for productivity. *Hyphomicrobium* bacteria harness 4.7 eV through the following reaction (Chyba & Phillips, 2001):



Chyba and Phillips use a microbial biomass efficiency of ~ 1 g/kcal. Using this number combined with the 2.05×10^5 to 2.52×10^6 moles of oxygen delivered per year, I find that Vostok could support 4.34×10^{21} to 4.34×10^{22} *Hyphomicrobium* cells per year. Using a biological turnover time of ~ 1000 years (Chyba & Phillips, 2001), this yields a steady state biomass of $\sim 1 \times 10^{25}$ cells of *Hyphomicrobium*.

While the above is an interesting exercise, it must be kept in mind that at present we have no knowledge of any organism capable of consuming air hydrates. The closest analog organisms we have are methane hydrate harvesters that exist in the methane

hydrate deposits of regions such as the Gulf of Mexico (A. Cooper, pers. comm.). Syntrophic microbial communities of methanotrophs and hydrogen-oxidizing sulphate-reducers are known to exist in these regions and apparently have little difficulty utilizing the hydrate phase for food (DeLong, 2000), (Boetius et al., 2000). Methane hydrates may be easier in this regard given the lower pressures needed for hydrate formation. Oxygen or carbon dioxide hydrates could be considerably more difficult to metabolize.

5.1. Ice Accretion, Hydrates & Organisms

In the context of microbial life, a potentially interesting cycle to consider is the flow of melt water from the northern end of the lake to the southern end. The lower elevation basal ice at the northern end will melt and deliver hydrates and dissolved organic carbon to the water. Thus, this is likely to be a biologically productive region.

If we now assume (as seems to be the case) that the Vostok water is very pure and thus not much of a density gradient exists, then the mixing that occurs will be hard to predict. However, if the density of the mixed gas hydrate is such that nitrogen dominates and thus causes the hydrate to be buoyant, then the hydrates will travel south along the lake surface and accrete at the southern end of the lake. Indeed, hydrates have been found in the accreted ice (Siegert et al., 2001). One could then envision microbes latching onto the incoming hydrates and traveling, via hydrate conveyor belt, to the southern end. If the microbes were able to selectively consume the oxygen hydrates, then the buoyancy of the hydrate would increase, thus amplifying the conveyor belt effect.

Alternatively, if the Vostok water does contain dissolved salt, then the effect will be further amplified. In this case, the pure melt water and the hydrates would travel south along the lake surface, creating a direct flow line from north to south.

When considering the effects of such a flow from north to south it is important to keep in mind that the organisms observed in the accreted ice core may very well have originated from surface deposition and delivery to the deep glacial ice in the north. Given the 16S rDNA results showing a close relationship with modern day biota, it is likely that the microbes discovered in the ice core followed this cycle.

5.2. Hydrogen Sulfide and Geothermal Vents

While we would not necessarily expect hydrogen sulfide to be delivered from the surface through the ice sheet, it is possible that geothermal vent systems in sub-glacial lakes serve as a source of this gas. Measurements of the geothermal heat flux across the Antarctic plate vary from 37 to 65 mW m⁻² (Siegert, 2000). Using helium isotopes from the accreted water ice core of Vostok, Jean-Baptiste et al. have been able to place constraints on hydrothermal processes in the lake. The low ³He/⁴He ratio indicates that there is no significant hydrothermal energy input from mantle processes (Jean-Baptiste et al., 2001).

The question of whether or not vent systems do exist in any sub-glacial lake is beyond the scope of this paper. Ultimately, this question seems to be limited by the lack of available data for sub-glacial lakes. Nevertheless, one can speculate that if hydrogen sulfide is available it could be utilized by microbes in the lakes. Once dissolved hydrogen sulphide reached maximum solubility levels in the lake, hydrates would precipitate and accumulate on the lake floor. Such sediments would be a rich resource for life in the lakes.

6. Hydrates in the solar system

In attempting to characterize hydrate formation throughout the solar system, Miller experimentally determined parameters needed for calculating various hydrate dissociation pressures at extremely low temperatures. The table below is reconstructed from his analysis (Miller, 1959):

Hydrate	Dissociation pressure (atm)	Temp. range measured (K)
Methane	$\log P = -9474.4/T + 4.8711$	175-207 K
Ethane	$\log P = -1381.1/T + 5.7262$	161-243 K
Ethylene	$\log P = -1278.3/T + 5.4103$	163-240 K
Acetylene	$\log P = -1163.9/T + 4.9959$	158-231 K
Carbon Dioxide	$\log P = -1121.0/T + 5.1521$	175-232 K

Miller examined the case of carbon dioxide hydrates in greater detail (Miller, 1970) and used the data below to define the following relationship:

$$\log P(mb) = 10.5591 - 1338.4/T - 6.585 \times 10^{-3} T$$

Temp. (K)	Pressure (mb) [=10 ⁻⁴ MPa]
192.54	218.78
186.75	144.92
182.15	102.66
176.86	67.73
171.54	42.01
167.07	28.08
162.37	17.65
151.52	5.35

Using Miller's results, we can examine a few interesting possibilities in the solar system.

6.1. Hydrates in a European ocean

Two particularly interesting hydrate scenarios are considered for Europa. First, one could envision carbon dioxide hydrate formation in the ocean as a result of dissolved CO_2 being exposed to the right temperature and pressure conditions. Second, one could consider the fate of oxygen and other potential hydrate gases in the $\sim 10\text{km}$ ice shell. Are the conditions suitable for hydrate formation in the shell? Are the conditions suitable for hydrate stability at the ice-water interface?

In the first case, Crawford and Stevenson have used a total CO_2 mass on Europa of 10^{21} - 10^{24} g to yield mole fraction concentration levels between 2.6×10^{-4} to 0.21 (Crawford & Stevenson, 1988). Using a solubility analysis similar to that of Lipenkov and Istomin as described above, Crawford and Stevenson find that the carbon dioxide equilibrium concentration for a 272 K ocean, where $P_{\text{top}} = 100$ bar [10 MPa] and $P_{\text{bottom}} = 1000$ bar [100 MPa], is 3×10^{-3} mole fraction. According to (Kargel et al, 2000) and (Milton, 1974), carbon dioxide hydrates are stable at 272 K if the pressures are greater than 9.6 bars. Thus, if the available carbon in Europa's ocean is significantly larger than the solubility max concentration (as indicated by their 0.21 mf carbonaceous chondrite formation estimate) the excess carbon will go into hydrate crystals. Whether these crystals will float or sink depends on the salinity of the European ocean.

Considering the second scenario, we know that the surface radiation environment produces formaldehyde, O_2 , and H_2S (Carlson et al., 1999). Thus, hydrates of these species could form in the ice shell or in the ocean if conditions were suitable. According to Lipenkov & Istomin, if pressures in the ice shell exceeded ~ 9.7 MPa for temperatures > 267 K then oxygen hydrates would form in the ice. Such conditions might be expected at the base of the ice shell or in regions of high tidal stress/strain. The surface temperature on Europa is ~ 100 K. Unfortunately, no experimental data (analogous to Miller's CO_2 data) was found to be available for oxygen hydrate formation at these low temperatures (100 K – 260 K).

If we make the generalization that the solubility of oxygen in Europa is equal to that calculated for the Vostok temperatures and pressures, then we can estimate the extent to which the European ocean might contain dissolved oxygen and hydrates. Taking an estimate based on radiolytic surface production of hydrogen peroxide (which decays to oxygen) and subsequent delivery to the ocean, it has been argued that Europa could have an annual oxygen flux of 1×10^{12} moles. Over the course of the ~ 50 million year resurfacing timescale, this would produce a ~ 0.020 mole fraction of oxygen in the ocean (Chyba & Hand, 2001). By comparison with Lipenkov and Istomin, this exceeds the 2.2×10^{-3} maximum solubility for air and thus we would expect to see oxygen hydrate formation in the European ocean. Several caveats apply: 1) I have used the solubility for air, not pure oxygen; 2) The gases delivered to the ocean would be at ~ 10 MPa and 272 K, this is not a high enough pressure for hydrate stability, however if the pressure were to reach levels of 11-12 MPa then hydrates would be

stable; 3) If Europa is sufficiently 'salty' then the hydrates would float and remain on the hydrate/gas stability curve of temperature and pressure.

One curious aspect of hydrate formation is the influence of an electromagnetic field. Growth rates and densities are apparently highly effected. Hydrate crystals grown in a static electromagnetic field were much more dense than those grown without the presence of a field (Makogon, 1974). In addition, the dielectric constant of structure I and II hydrates is nearly half that of pure ice (Sloan, 1998). Furthermore, hydrates have different mechanical properties than regular ice and thus could play a significant role in some of the tidal fracturing and resurfacing processes observed on Europa .

6.2. Martian polar cap

The poles of Mars are covered with ice caps of both water ice and carbon dioxide ice. In addition, the thin atmosphere of Mars is dominated by carbon dioxide. Thus, any hydrate formation on Mars would likely be carbon dioxide hydrates. Indeed, carbon dioxide hydrates are known to be seasonally stable within the polar ice caps (Miller, 1970). Miller notes that one would not find ice and solid carbon dioxide together in the polar caps. Instead, the phase diagram for hydrate dissociation pressure and CO₂ vapor pressure indicates that one would find CO₂ hydrates mixed with CO₂ ice and CO₂ gas, and CO₂ hydrates mixed with CO₂ gas and water ice.

It has been speculated that the dissociation of hydrates on Mars could play a significant role in the observed geomorphology of the planet's surface (Kargel et al., 2000), (Milton, 1974). While many mechanisms of hydrate formation are proposed a few of the more interesting concepts are: (1) A freezing ocean reaches maximum solubility of dissolved gases and hydrates then precipitate (interesting for snowball Earth too!) (2) Atmospheric carbon dioxide pressure reaches >9.6 bars and temperatures < 272 K cause carbon dioxide hydrates to form directly in reaction with surface water and ice (3) Melting of basal carbon dioxide ice in polar caps reacts with ground ice or water and forms hydrates (Kargel, 2000).

If all of the carbon dioxide on Mars was in gas phase in the atmosphere, Kargel et al. calculate a global carbon dioxide inventory of 2.6-16 bars. This, they estimate, would correspond to a global carbon dioxide hydrate layer of >200 m (assuming a 40km thick crust with 0.06 wt % CO₂ outgassed). A higher estimate of >1300 m comes from scaling the Martian inventory based on the atmosphere of Venus (high levels of CO₂ outgassing from the crust). The stability of carbon dioxide hydrates within the Martian upper crust extends all the way to the equator. Gas rising from the mantle would first become liquid CO₂ and then as it moved higher in the crust it would reach a point of clathrate stability in a region where liquid water is also stable (~10km depth). Groundwater in equilibrium with the hydrate would be saturated to 7 wt % CO₂ (Kargel et al., 2000). Consideration of carbon dioxide hydrates and outgassing could be an important factor in the formation of the recently observed cliff and crater wall gulleys on Mars.

6.3. Elsewhere in the solar system

Given that Saturn's moon Titan has an atmosphere heavy with methane (2.2×10^{-3} atm), Miller speculates that any water on Titan will be found in the form of methane hydrates and not ice (Miller, 1959). Currently, the Cassini spacecraft is en route to Saturn and in 2006 it is scheduled to deploy the Huygen's probe into Titan. The probe will analyze the atmosphere and hopefully survive the landing long enough to send back some data on the nature of Titan's surface and atmospheric chemistry. Perhaps it will land on an icy lake of methane hydrates.

Comets might also be an interesting system to analyze, especially in the context of organic chemistry and delivery of such organics to Earth and other planets. Curiously, Miller touches on the issue of comets but neglects to connect this to his classic 'prebiotic soup' work for life on Earth. One side note on comets: how do hydrates affect the dynamics of an impact? Is there a rapid expansion as the object comes through the atmosphere and heats up? Upon impact is there a tremendous release of pressurized gases?

Miller also speculates about carbon dioxide hydrate crystals in the atmosphere of Venus. Interestingly, he notes that this might be a possible explanation for the anomalous polarization of reflected sunlight from Venus (Miller, 1959). Given the date of the paper, it would be interesting to return to this problem and see if any progress has been made.

Along with the atmosphere of Venus, Miller also notes the potential for hydrate precipitation out of the atmospheres of Earth and Mars. In the case of Earth, he suggests that this could be a possible source of elevated CO₂ concentrations in ice cores. If this were indeed the case, what would this imply for our paleoclimate record? Obviously there is much room for interesting research in this area, and in the field

7. Conclusion

Much work remains to be done on sub-glacial lakes and on the role of the hydrate phases that may exist in extreme environments on Earth and throughout the solar system. Given that water has played such a crucial role in life on Earth, we would be well served to explore and understand all possible forms it may take. Hydrates will limit the available concentrations of biologically useful gases in aqueous solutions, however they may also provide a useful niche for enterprising organisms.

The sub-glacial lakes of Antarctica offer a unique opportunity for exploring these systems. Obviously, as we explore these pristine environments we must keep issues of contamination in mind (Rummel, 2001), (Wynn-Williams et al., 2000). For this reason it seems backwards that we are exploring Vostok, the jewel of the sub-glacial

lakes, first. Instead, my recommendation would be to test our capabilities on small, relatively isolated sub-glacial lakes. Based on the inventory by Siegert et al., I would select lakes 44, 19, and 61 for initial exploration (Siegert, 1996). These lakes are near the Transantarctic mountains and well isolated from other known lakes. As a result, there would not be tremendous concern over contaminating several lakes or a whole region by exploring these lakes. In addition, the ice sheet above these lakes is on the order of 2000 to ~2500 meters thick and thus the task of melting through the ice would be considerably easier.

Through careful and meticulous exploration of the Antarctic sub-glacial lakes we can learn much about our planet and its past, while simultaneously preparing ourselves for the future of exploration and the search for life beyond Earth.

Hydrate Densities: O₂, N₂, CO₂, H₂S

$$\rho = \frac{\frac{N_w}{N_{ave}} \left[MW_{H_2O} + \sum_{j=1}^C \sum_{i=1}^N y_{ij} V_i MW_j \right]}{V_{cell}}$$

Density Calculation Variables

Temp. (K)	O ₂ (g/cc)	N ₂ (g/cc)	CO ₂ (g/cc)	H ₂ S (g/cc)
270	1.0046	0.9953	1.104347	1.045112
273	1.0039	0.9945	1.103535	1.044629
277	1.0142	1.0045	1.110477	1.046759
298	1.03	1.0198	1.132418	1.053155

Density of Water at 3.98 C (277 K), g/cc	Density Ratio: Water/Salt Water
0.999	0.97045
rho salt h2o	1.0294

# of water molecules per unit cell	Avagadro's Number	Molecular Weight of water	Molecular Weight of component	# of cavity types per unit cell	# of components in hydrate phase
Nw-II	Nave	MW-water	MW-O2	Structure I	c
136	6.02E+23	18	32	n-small	1
Nw-I			MW-N2		
46			28	n-large	2
			MW-CO2	Structure II	
			44		6
Structure I Length of unit cell (A)	Structure II Length of unit cell (A)		MW-H2S	n-small	
12	17.3		34	16	
				n-large	
				8	

Fractional Occupancy and Pressure values for N₂ (and O₂) at varying Temperature

Conclusions:

- O₂ Hydrates sink in pure water and float in salt water.
- N₂ Hydrates float in cold pure water and always float in salt water.
- CO₂ Hydrates sink in pure water and salt water.
- H₂S Hydrates sink in pure water and salt water.

Note: Salt has not been included in the fractional occupancy calculation

T (K)	P (MPa)	Small cage	Large cage
270	12.15	0.8831	0.9097
273	12.77	0.8789	0.9085
277	23.38	0.9239	0.945
298	168.25	0.9942	0.9965

Fractional Occupancy and Pressure values for CO ₂ at varying T			
1.005	0.7123	0.9799	
1.113	0.7054	0.979	
1.948	0.7704	0.9847	
175.618	0.9864	0.9992	

Fractional Occupancy and Pressure values for H ₂ S at varying T			
0.093	0.9077	0.9706	
0.105	0.9039	0.9694	
0.158	0.9197	0.975	
1.311	0.9693	0.9911	

Chart 1. Hydrate density calculations for hydrate formation in pure water

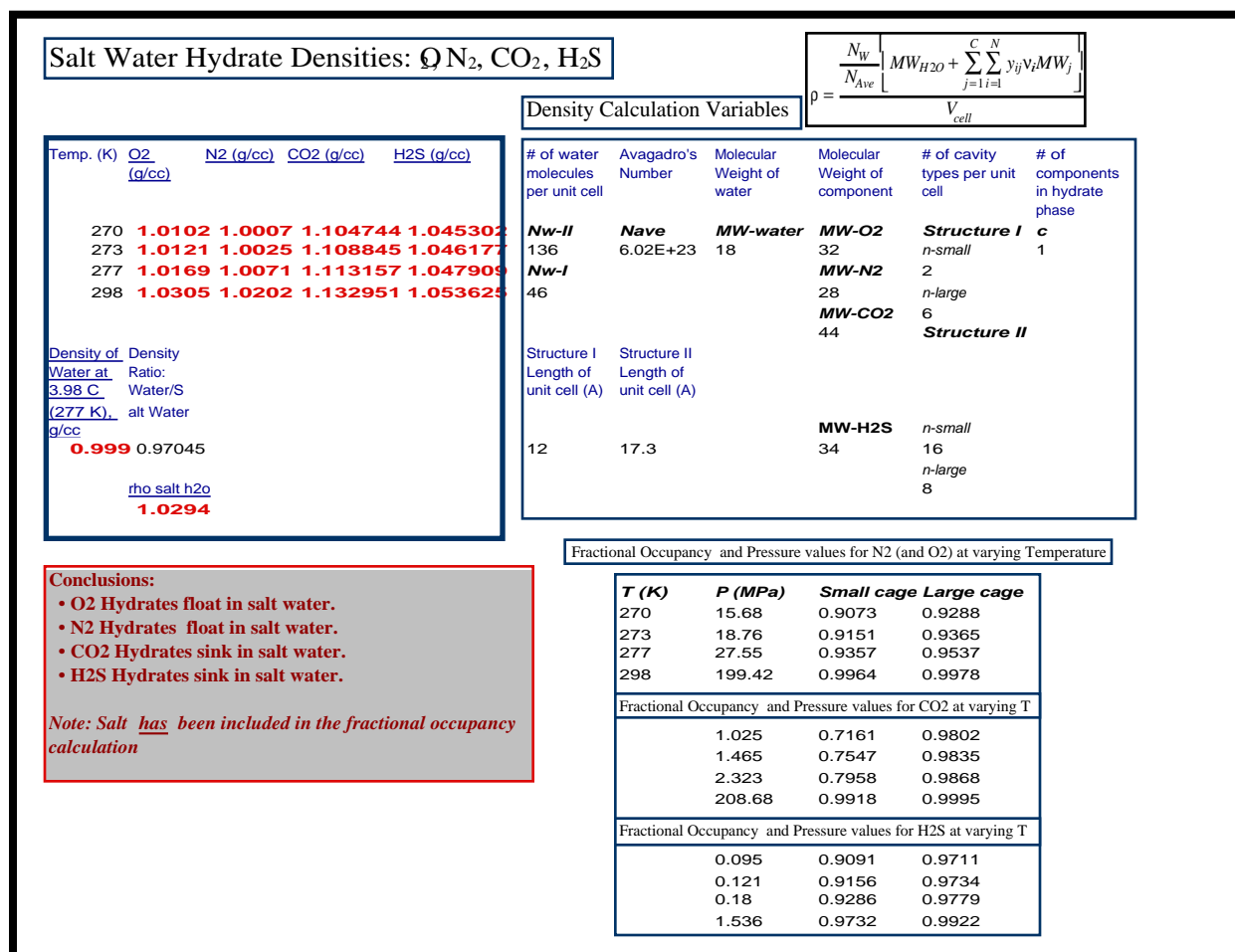
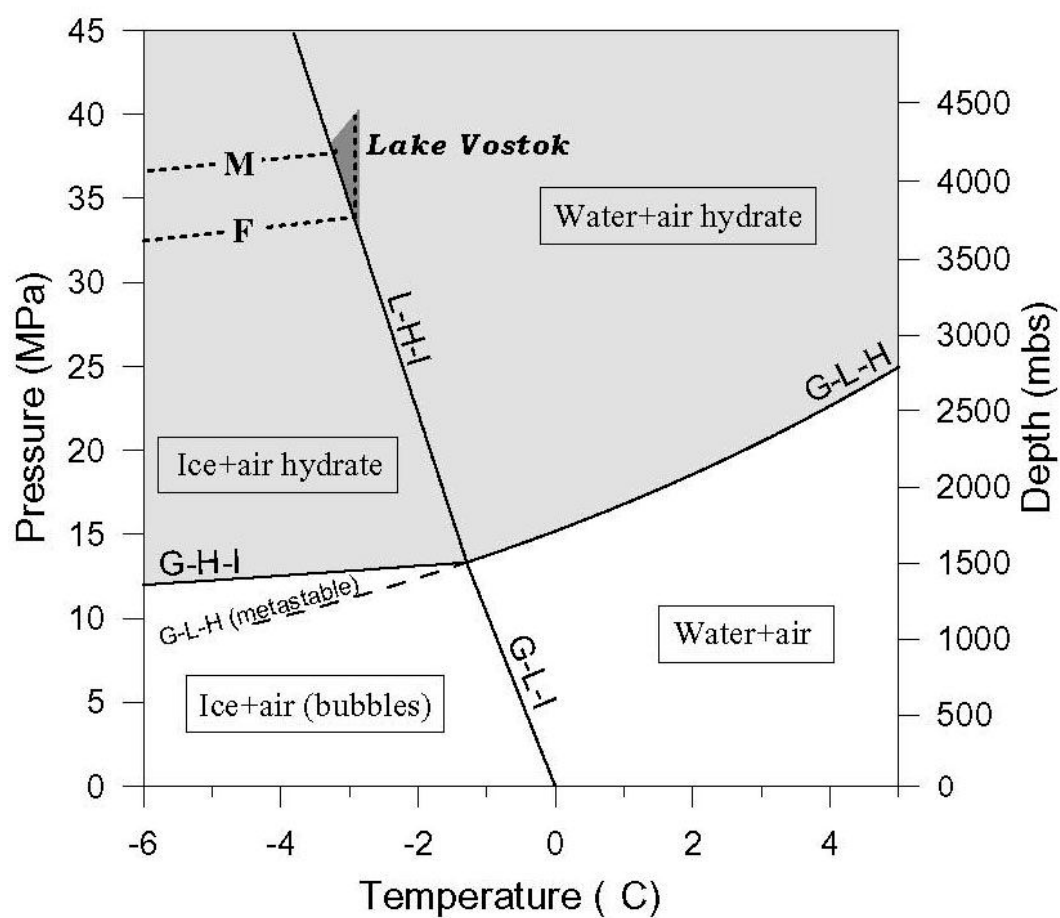


Chart 2. Hydrate density calculations for hydrate formation in sea water

Phase diagram for air hydrates. Figure 5 from (Lipenkov & Istomin, 2001).



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