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NOBLE GASES AND THE CRYOSPHERE

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Introduction

Ice formation and melting strongly influence a wide range of water properties and processes, such as dissolved gas concentrations, exchange of gases between the atmosphere and the ocean, and dense water formation. As water freezes, salt and gases dissolved in the water are expelled from the growing ice lattice and become concentrated in the residual water. As a result of the increased salt content, this residual water becomes more dense than underlying waters and sinks to a level of neutral buoyancy, carrying with it the dissolved gas load. Dense water formation is one of the primary mechanisms by which atmospheric and surface water properties are transported into the interior and deep ocean, and observation of the effects of this process can answer fundamental questions about ocean circulation and the ocean–atmosphere cycling of biogeochemically important gases such as oxygen and carbon dioxide. Because it is not possible to determine exactly when and where dense water formation will occur, it is not an easy process to observe directly, and thus information about the rates of dense water formation and circulation is obtained largely through the observation of tracers. However, when dense water formation is triggered by ice formation, interaction of surface water properties with the ice and the lack of full equilibration between the atmosphere and the water beneath the growing ice can significantly modify the concentrations of the tracers in ways that are not yet fully understood. Consequently, the information provided by tracers in these ice formation areas is often ambiguous.

A suite of three noble gases, helium, neon, and argon, have the potential to be excellent tracers in the marine cryosphere, providing new information about the interactions of dissolved gases and ice, the cycling of gases between the atmosphere and ocean, and mixing and circulation pathways in high latitude regions of the world's oceans and marginal seas. The physical chemistry properties of these three gases span a wide range of values, and these differences cause them to respond to varying degrees to physical processes such as ice formation and melting or the transfer of gas between the water and air. By observing the changes of the three tracers as they respond to these processes, it is possible to quantify the effect the process has on the gases as a function of the physical chemistry of the gases. Subsequently, this 'template' of behavior can be used to determine the physical response of any gas to the process, using known information about the physical chemistry of the gas. Although this tracer technique is still being developed, results from laboratory experiments and field programs have demonstrated the exciting potential of the nobel gases to provide unique, quantitative information on a range of processes that it is not possible to obtain using conventional tracers.

Noble Gases in the Marine Environment

The noble gases are naturally occurring gases found in the atmosphere. **Table 1** shows the abundance of the noble gases in the atmosphere as a percentage of the total air composition, and the concentrations

Table 1 Noble gases in the atmosphere and sea water

Gas	*Abundance in the atmosphere (%)*	*Concentration in seawater ($cm^3\ g^{-1}$)*
Helium	0.0005	3.75×10^{-8}
Neon	0.002	1.53×10^{-7}
Argon	0.9	2.49×10^{-4}

of the gases in surface sea water when in equilibrium with the atmosphere.

Other sources of these gases in sea water include the radioactive decay of uranium and thorium to helium-4 (^{4}He), and the radioactive decay of potassium (^{40}K) to argon (^{40}Ar). For most areas of the surface ocean, these radiogenic sources of the noble gases are negligible, and thus the only significant source for these gases is the atmosphere.

The noble gases are biogeochemically inert and are not altered through chemical or biological reactions, making them considerably easier to trace and quantify as they move through a system than other gases whose concentrations are modified through reactions. The behavior of the noble gases is largely determined by the size of the molecule of each gas and the natural affinity of each gas to reside in a gaseous or liquid state. The main physical chemistry parameters of interest are the solubility of the gas in liquid, the temperature dependence of this solubility, and the molecular diffusivity of the gas. The suite of noble gases have a broad range of these properties, and the behavior of the noble gases determined by these properties, can serve as a model for the behavior of most other gases.

One unique characteristic of the noble gases that makes them ideally suited as tracers of the interactions between gases and ice is that helium and neon are soluble in ice as well as in liquids. It has been recognized since the mid-1960s that helium and neon, and possibly hydrogen, should be soluble in ice because of the small size of the molecules, whereas gases having larger atomic radii are unable to reside in the ice lattice. These findings, however, were based on theoretical treatises and carefully controlled laboratory studies in idealized conditions. It was not until the mid-1980s that this process was shown to occur on observable scales in nature, when anomalies in the concentrations of helium and neon were observed in the Arctic.

The solubility of gases in ice can be described by the same principles governing solubility of gases in liquids. Solubility of gases in liquids or ice occurs to establish equilibrium, where the affinities of the gas to reside in the gaseous, liquid, and solid state are balanced. The solubility process can be described by two principle mechanisms:

1. creation of a cavity in the solvent large enough to accommodate a solute molecule;
2. introduction of the solute molecule into the liquid or solid surface through the cavity.

In applying this approach to the solubility of gases in ice, it follows that if the atomic radius of the solute gas molecule is smaller than the cavities naturally present in the lattice structure of ice, then the energy required to make a cavity in the solvent is zero, and the energy required for the solubility process is then only a function of the energy required to introduce the solute molecule into the cavity. For this reason, the solubility of a gas molecule capable of fitting in the ice lattice is greater than its solubility in a liquid. The solubilities of helium and neon in ice have been determined in two separate laboratory studies, and although the values agree for the solubility of helium in ice, the values for neon disagree. The size of neon is very similar to the size of a cavity in the ice lattice, and the discrepancies between the two reported values for the solubility of neon in ice may result from small differences in the experimental procedure.

During ice formation, most gases partition between the water and air phases to try to establish equilibrium under the changing conditions, whereas helium and neon additionally partition into the ice phase. As water freezes, salt and gases are rejected from the growing ice lattice, increasing the concentrations of salt and gas in the residual water. Helium and neon partition between the water and ice reservoirs according to their solubility in water and ice. The concentrations of the gases in the residual water that have been expelled from the ice lattice, predominantly oxygen and nitrogen, can become so elevated through this process that the pressure of the dissolved gases in the water exceeds the *in situ* hydrostatic pressure and gas bubbles form. The gases then partition between the water, the gas bubble, and the ice according to the solubilities of the gases in each phase. This three-phase partitioning process can occur either at the edge of the growing ice sheet at the ice–water interface, or in small liquid water pockets, called 'brine pockets' in salt water systems, entrained in the ice during rapid ice formation.

Table 2 quantitatively describes how the noble gases partition between the three phases when a system containing these three phases is in equilibrium in fresh water at 0°C. The numbers represent the amount of the gas found in one phase relative to the

Table 2 Noble gas partitioning in three phases

Partition phases	*Helium*	*Neon*	*Argon*
Bubble to water	106.8	81.0	18.7
Bubble to ice	56.9	90.0, 56.3	∞
Ice to water	1.9	0.9, 1.4	0

other. For example, the first row describes the amount of each gas that would reside in the gaseous bubble phase relative to the liquid phase; thus for helium, there would be 106.8 times more helium present in the bubble than in the water. This illustrates the small solubility of helium in water and its strong affinity for the gas phase. Because helium is 1.9 times more soluble in ice than in water, helium partitions less strongly between the bubble and ice phases compared to the partition between the bubble and water phases. The two numbers shown for neon represent the two different estimates for the solubility of neon in the ice phase. One estimate suggests that neon is less soluble in ice than in water, whereas the other suggests that it is more soluble in ice.

Application of the Noble Gases as Tracers

The noble gases have been used as tracers of air–sea gas exchange processes for more than 20 years. Typically, the noble gases are observed over time at a single location in the ocean along with other meteorological and hydrodynamic parameters to characterize and quantify the behavior of each of the gases in response to the driving forces of gas exchange such as water temperature, wind speed, wave characteristics, and bubbles injected from breaking waves. Because both the amount and rate of a gas transferred between the atmosphere and ocean depend on the solubility and diffusivities of the gas, the noble gases have long been recognized as ideal tracers for these processes. In addition, argon and oxygen have very similar molecular diffusivities and solubilities, making argon an excellent tracer of the physical behavior of oxygen. By comparing the relative concentration changes of argon and oxygen over time, it is possible to account for the relative contributions of physical and biological processes (such as photosynthesis by phytoplankton in the surface ocean) to the overall concentrations, thus constraining the biological signal and allowing for estimates of the biological productivity of the surface ocean.

The observations of anomalous helium and neon concentrations in ice formation areas and the suggestion that these anomalies could be the result of solubility of these gases in the ice were made in 1983, and since that time, a number of laboratory and field studies have been conducted to characterize and quantify these interactions. The partitioning of the noble gases among the three phases of gas, water, and ice creates a very distinctive 'signature' of the noble gas concentrations left behind in the residual water. Noble gas concentrations are typically expressed in terms of 'saturation', which is the concentration of a gas dissolved in the water relative to its equilibrium with the atmosphere at a given temperature. For example, a parcel of water at standard temperature and pressure containing the concentrations of noble gases shown in column 2 of **Table 1** would be said to have a saturation of 100%. Saturations that deviate from this 100% can arise when equilibration with the atmosphere is incomplete, either because the equilibration process is slow relative to some other dynamic process acting on the system (for example, rapid heating or cooling, or injection of bubbles from breaking waves), or because full equilibration between the water and atmosphere is prevented, as in the case of ice formation.

Typical saturations for the noble gases in the surface ocean range from 100 to 110% of atmospheric equilibrium, due mostly to the influx of gas from bubbles. Ice formation, however, can lead to quite striking saturations of -70 to -60% for helium and neon and $+230\%$ for argon in the relatively undiluted residual water. Ice melting can also lead to large anomalous saturations of the noble gases, showing the reverse of the freezing pattern for the gas saturations, where helium and neon are supersaturated while argon is undersaturated with respect to the atmosphere.

The interactions of noble gases and ice have been well-documented and quantified in relatively simple freshwater systems. Observations of large noble gas anomalies in a permanently ice-covered antarctic lake were quantitatively explained using the current understanding of the solubility of helium and neon in ice and the partitioning of the gases in a three-phase system. Characteristics of ice formed from salt water are more complex than ice formed from fresh water, and the modeling of the system more complex. Using a set of equations developed in 1983 and measurements of the ice temperature, salinity, and density, it is possible to calculate the volume of the brine pockets in the ice and the volume of bubbles in the ice. With this type of information, a model of the ice and the dissolved gas balance in the various phases in the ice and residual water can be constructed. Such an ice

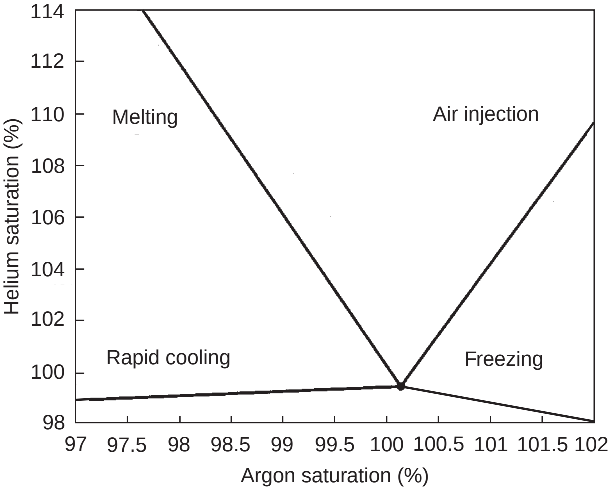

Figure 1 Vector diagram of helium and argon saturation changes in response to upper ocean processes.

model was developed during a field study of gas–ice interactions in a seasonally ice-covered lagoon, and the model predicted the amount of argon, nitrogen, and oxygen measured in bubbles in similar types of sea ice. No measurements are available for the amount of helium and neon in the bubbles of sea ice to verify the results for these gases. It is also possible to predict the relative saturations of the noble gases in the undiluted residual water at the ice–water interface, and this unique fingerprint of the noble gases can then serve as a tracer of the mixing and circulation of this water parcel as it leaves the surface and enters the interior and deep ocean. In this manner, the supersaturations of helium from meltwater have been successfully used as a tracer of water mass mixing and circulation in the Antarctic, and the estimated sensitivity of helium as a tracer for these processes is similar to the use of the conventional tracer, salinity, for these processes.

As an illustration of the ways in which the noble gases can be used to distinguish between the effects of ice formation, melting, injection of air bubbles from breaking waves, or temperature changes on dissolved gases, **Figure 1** shows a vector diagram of the characteristic changes of helium compared to argon resulting from each of these processes.

From a starting point of equilibrium with the atmosphere (100% saturation), both helium and argon saturations increase as a result of bubbles injected from breaking waves. Ice formation increases the saturation of argon and decreases the saturation of helium, whereas ice melting has the opposite effect. Changes in temperature with no gas exchange with the atmosphere to balance this change can lead to modest changes in the saturations of the gases, where the gas saturations decrease with decreasing temperature and increase with increasing temperature. The trends presented here are largely qualitative indicators, since quantitative assessment of the changes depend on the exact nature of the system being studied. However, this diagram does illustrate the general magnitude of the changes that these processes have on the noble gases and conversely, the ability of the noble gases to differentiate between these effects.

Conclusions

The use of the noble gases as tracers in the marine cryosphere is in its infancy. Our understanding of the interactions of the noble gases and ice have progressed from controlled, idealized laboratory conditions to natural freshwater systems and simple salt water systems, and the initial results from these studies are extremely encouraging. This technique is currently being developed more fully to provide quantitative information about the interactions of dissolved gases and ice, and to utilize the resulting effects of these interactions to trace water mass mixing and circulation in the range of dynamic ice formation environments. Water masses in the interior and deep ocean originating in ice formation and melting areas have been shown to have distinct noble gas ratios, which are largely imparted to the water mass at the time of its formation in the surface ocean. By understanding and quantifying the processes responsible for these distinct ratios, we will be able to learn much about where and how the water mass was formed and the transformations it has experience since leaving the surface ocean. These issues are important for our understanding of the global cycling of gases between the atmosphere and the ocean and for revealing the circulation pathways of water in the Arctic, Antartic, and high latitude marginal seas. The noble gases could represent a significant addition to the set of tracers typically used to study these processes.

See also

Arctic Basin Circulation. Air–Sea Gas Exchange. Bottom Water Formation. Bubbles. CFCs in the Ocean. Freshwater Transport and Climate. Ice–Ocean Interaction. Long-term Tracer Changes. Oxygen Isotopes in the Ocean. Polynyas. Sea Ice: Overview. Stable Carbon Isotope Variations in the Ocean. Sub Ice-shelf Circulation and Processes. Thermohaline Circulation. Tritium–Helium Dating. Water Types and Water Masses.

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NON-ROTATING GRAVITY CURRENTS

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Gravity currents (also known as 'density currents') in the ocean are flows of water that are principally due to differences in density (due to differing temperature and/or salinity) between neighboring water bodies. These density differences cause lateral pressure gradients that produce the horizontal motion. They may occur on length scales ranging from centimeters to hundreds of kilometers, and they have a characteristic structure that is described below. In the oceanic environment there are three main types, as follows. Firstly, gravity currents may move along the ocean bottom, with denser (colder or saltier) water moving under a lighter water mass. Secondly, a body of lighter water may move along the ocean surface, above denser water, and thirdly, a homogeneous body of water of intermediate density may penetrate a larger stratified water body of varying density, with lighter fluid above and denser fluid below. The latter process is termed an intrusion. If these flows last for more than a significant fraction of the inertial period, the Earth's rotation (via the Coriolis force) has an important effect on the flow, and these rotational effects are discussed elsewhere (*see* **Rotating Gravity Currents**). This article gives some examples of these flows, and then describes their basic dynamical properties for flows that move horizontally in one direction, and that move radially outward in two dimensions. It then proceeds to discuss gravity currents that flow down slopes, taking into account the effects of environmental stratification.

Examples

Gravity currents exist in the ocean in a wide variety of forms. On the smallest scale of interest here, they are man-made. Prominent examples are sewage outfalls, in which effluent is piped to some distance offshore and is then released into the ocean. If the effluent is denser than the environment it may spread laterally over the local bottom, but if lighter, it may rise in a plume to the surface and spread there. Another example is effluent from power stations; this may be released on the surface, but it then behaves in a similar fashion to the sewage outfall. Oil released on the surface (as from a shipwrecked tanker) will initially spread as a buoyant gravity current, although being immiscible with water, its mixing properties will be quite different from the previous examples.

Moving to larger scale, gravity currents may be found in rivers, lakes, and estuaries. A sudden surge of water down a river into a lake or estuary can form a gravity current on the bottom or at the surface. If the lake is deep and density-stratified, and the flow into the lake is denser (e.g., colder) than the surface water, most of this inflow may begin as a downslope current, but end up as an intrusion.