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Clathrate formation and the fate of noble and biologically useful gases in Lake Vostok, Antarctica

C. P. McKay,[1] K. P. Hand,[2] P. T. Doran,[3] D. T. Andersen,[4] and J. C. Priscu[5]

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[1] Lake Vostok is a large lake located 4 km beneath the East Antarctic Ice Sheet that should be supersaturated with dissolved gases in equilibrium with clathrate present in the water column. Here we show that if the age of the lake is such that the lake water mass has been cycled over 30 times then the total dissolved gas equilibrates at about 2.5 liters (STP) of gas per kg of water; high enough to have important implications for drilling into this deep subglacial lake. Different air gases are preferentially incorporated into the clathrate and thus the molar ratios in the water column will reflect the presence of clathrate and indicate a more precise age of the lake. Preferential incorporation of CO_2 into the clathrate would result in the clathrate sinking if the carbon input is 1% of the air input and the lake water is fresh water. The redox state of the lake is set by the high oxygen concentration which is 50 times more than air-equilibrated water and may be a severe biological stress. *INDEX TERMS:* 1806 Hydrology: Chemistry of fresh water; 1863 Hydrology: Snow and ice (1827); 1845 Hydrology: Limnology; 1827 Hydrology: Glaciology (1863); 4820 Oceanography: Biological and Chemical: Gases. **Citation:** McKay, C. P., K. P. Hand, P. T. Doran, D. T. Andersen, and J. C. Priscu, Clathrate formation and the fate of noble and biologically useful gases in Lake Vostok, Antarctica, *Geophys. Res. Lett.*, *30*(13), 1702, doi:10.1029/2003GL017490, 2003.

1. Introduction

[2] Lake Vostok [*Kapitsa et al.*, 1996; *Siegert et al.*, 2000], and over 70 other lakes [*Siegert et al.*, 1996; *Price et al.*, 2002] deep beneath the polar plateau, appear to be part of a cycle of ice melt and freezing. Estimates of the mass residence time for Lake Vostok range from 5,000 years [*Phillipe et al.*, 2001] to 125,000 years [*Kapitsa et al.*, 1996]. *Bell et al.* [2002] calculated the amount of refrozen ice leaving the lake to compute a value of 13,300 years. Estimates for the age of the lake water range from one million years [*Kapitsa et al.*, 1996] to 15 million years [*Siegert et al.*, 2003].

[3] As the ice melts into the lake it brings with it trapped air at a concentration of about 90 cm^3 at STP per kg of ice [*Lipenkov and Istomin*, 2001; *Jouzel et al.*, 1999]. This gas is trapped as bubbles in the firn at the surface of the ice and is closed off and pressurized with depth. At depths of about 1 km the pressure is high enough that the ice and gas combine to form a solid solution known as clathrate [*Miller*, 1969]. Measurements [*Ikeda et al.*, 1999] in the ice show that at depths below the transition zone (>1000 m), the clathrate has the N_2/O_2 composition for air (3.71).

[4] Originally it was suggested that the gases in Lake Vostok would build up to supersaturation [*Ellis-Evans and Wynn-Williams*, 1996] as a result of this accumulation. However, *Lipenkov and Istomin* [2001] have shown that due to the temperature and pressure environment of Vostok, air clathrates are stable and should determine the level of dissolved gases. The analysis of *Lipenkov and Istomin* [2001] assumed that the lake water is always in equilibrium with the atmosphere although at high hydrostatic pressure. Thus the N_2 to O_2 ratio in the gas in the lake is 1.8, the value typical for air-equilibrated water (see Table 1) and the total dissolved gas was predicted to be 2.8 liters (STP) per kg of water.

[5] However, Lake Vostok is under many kilometers of ice and it is unlikely that the lake water is in equilibrium contact with air. We model the gas and clathrate balance in the lake with an alternative approach. We assume that the lake is a closed system at a constant pressure of 35 MPa and physiographically stable over time. Water and gas enter the lake where melting occurs and water without gas leaves the lake as ice accreted to the bottom of the ice sheet [*Bell et al.*, 2002; *Jouzel et al.*, 1999]. Gases are assumed to be completely excluded from the ice formed by refrozen lake water. The reformed ice contains only trace amounts of clathrates [*Siegert et al.*, 2001] compared with the glacial ice, and virtually no gas [*Jouzel et al.*, 1999]. The immediate implication of this is that the N_2 to O_2 ratio of the total gas (dissolved plus clathrate) in the lake is 3.71.

[6] We express the age of the lake in terms of the residence time, defined to be the time for the mass flow through the lake to equal the mass of the lake. Each residence time 90 cm^3 (STP) of air is added per kg of lake water and the total air contained in the lake increases linearly with the age of the lake.

2. Clathrate Formation

[7] We use the method of *Miller* [1974] to determine the stability relations between dissolved gas and clathrate. The dissociation pressure for the mixed air gases is determined [*Lipenkov and Istomin*, 2001]

$$P\text{diss}^{-1} = \sum_i \left[\frac{y_i}{P\text{diss}_i}\right] \qquad (1)$$

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[1] Space Science Division, NASA Ames, Moffett Field, California, USA.

[2] Department of Geological and Environmental Sciences, Stanford University, Stanford, California, USA.

[3] Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, Illinois, USA.

[4] Center for the Study of Life in the Universe, SETI Institute, Mountain View, California, USA.

[5] Department of Land Resources and Environmental Sciences, Montana State University, Bozeman, Montana, USA.

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Table 1. Dissociation Pressures and Gas Properties

Gas	*P*diss, atm (at 0°C)	*f*air	f_{H_2O} (at −3°C)	fugacity ratio (at 14.1 MPa)
N_2	160	0.7808	0.63	0.94
O_2	120	0.2095	0.35	0.87
Ar	95.5	0.00934	0.017	0.88
Ne	–	18.18 ppm	7.5 ppm	1.06
Kr	14.5	1.14 ppm	4.4 ppm	0.66
Xe	1.5	0.87 ppm	7.0 ppm	0.27
CO_2	12.5	–	–	0.25

where *P*diss is the dissociation pressure of the mixture, $P\text{diss}_i$ is the dissociation pressure of each gas, and y_i is the mole fraction of each gas with respect to the total dissolved gas. The dissociation pressure increases with the high hydrostatic pressure due to the volume difference between the clathrate and the water and gas [*Miller*, 1974]. For N_2 and O_2 at 35 MPa the dissociation pressure increases by a factor of 1.2. To determine the partial pressure of each dissolved gas we use the Redlich-Kwong equation of state [*Reid et al.*, 1987]. We compute the compressibility and fugacity ratio for each gas separately using the pressure of dissolved gas [*Reid et al.*, 1987]. The fugacity ratios at the dissociation pressure of Lake Vostok are shown for each gas in Table 1. When the gas pressure equals the dissociation pressure clathrate forms and the total fugacity of gas is equal to the fugacity of the clathrate. The relative partitioning of any two gas species within the clathrate is determined by the dissociation pressures of the clathrate and the fugacity of the dissolved gases [*Barrer and Stuart*, 1957; *Lunine and Stevenson*, 1985].

$$\frac{X_i P\text{diss}_i}{X_j P\text{diss}_j} = \frac{f_i}{f_j} \tag{2}$$

Where X_i is the mole fraction of gas *i* in the clathrate, f_i is the fugacity of the dissolved gas and the subscript *j* refers to another gas, usually N_2, the dominant gas in the clathrate. Once clathrate forms the amount of each gas in solution is determined by its fugacity equilibrium with the clathrate and the pressure correction [*Miller*, 1974] on the Henry's law coefficient [*Benson and Krause*, 1976].

[8] The results for the main air gases, N_2 and O_2 are shown in Figure 1. Figure 2 shows the molar ratios of the gases dissolved in the water and the molar ratio of N_2 to O_2 for the clathrate. When the lake has experienced less than 30 residence times, N_2 and O_2 remain completely in solution (Figure 1) with a ratio of 3.71 (Figure 2). Clathrate formation begins at 30 residence times and the dissociation fugacity of the clathrate is 14.1 MPa. Thereafter, the total dissolved gas remains approximately constant at 2.5 liters (STP) per kg of water. However, as more clathrate forms the N_2/O_2 ratio changes. It is straightforward to understand the limiting cases. When the clathrate just begins to form the ratio of N_2/O_2 in solution is 3.71 but the ratio of N_2/O_2 in the clathrate is larger by a factor of about 2 due to the higher fugacity of the less soluble N_2 compared to O_2 and reduced by a factor of 1.3 due to the lower dissociation pressure of O_2. Thus, the initial clathrate has a N_2/O_2 value of about 6. In the other limit, as the residence time goes to infinity all the gas is effectively in the clathrate and its ratio must go to the value of the incoming air, 3.71. The N_2/O_2 in the dissolved gas is then 2.3, in equilibrium with this value. At 100 residence times the N_2 to O_2 ratio is 4.5 and about 70% of the gas that has entered the lake has been incorporated into clathrate with the remaining 30% in solution in the water column. Although the fraction of gas tied up as clathrate is large, the fraction of total lake water as ice in the clathrate is small, 3%. If, however, the lake has experienced 1000 residence times as a closed system with respect to gas, 30% of the water in the water column would be converted to clathrate.

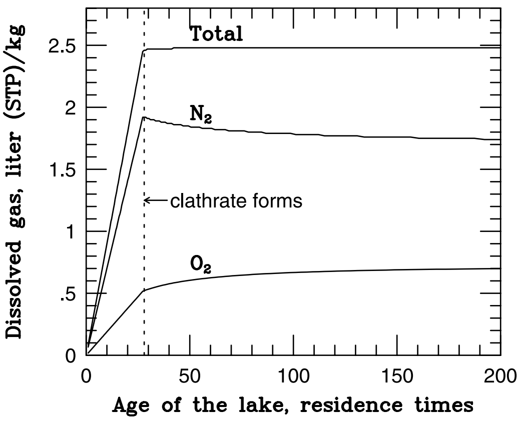

Figure 1. Dissolved N_2, O_2 and total gas amount in water of Lake Vostok as a function of the age of lake, with age expressed in units of residence time.

[9] Ar, Kr, Xe all readily form clathrates of the same type structure as N_2 and O_2. It has been long appreciated that clathrate formation will fractionate these gases [*Barrer and Stuart*, 1957] and, due to their low dissociation pressures relative to N_2 and O_2. For Argon this enrichment is offset by the change in solubility. Our theoretical analysis suggests that Ar will be depleted in the clathrate while Kr and Xe should be enriched, compared to the initial mixture. Our calculation predicts an enrichment by a factor of 2.9, 1.6, and 0.7 in the clathrate for Xe, Kr, and Ar, respectively. There is an inverse effect in the dissolved gas with depletion

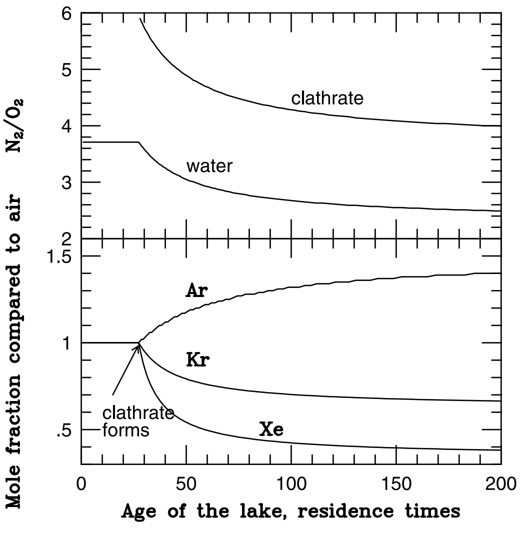

Figure 2. Molar ratios for the gases dissolved in the water of Lake Vostok as a function of the age of lake, with age expressed in units of residence time.

by the factors 0.4, 0.7, and 1.4, respectively (See Figure 2). This fractionation of the noble gases should occur in all natural clathrates. This has been reported for CH_4 clathrate with the same enrichment of Xe > Kr > Ar. The ratios are in the range expected given the relative dissociation pressures of CH_4 to Xe, Kr, and Ar. [*Winckler et al.*, 2002].

[10] Neon is present in air and should presumably be present in the air bubbles in the firn ice. However its molecular diameter is small enough that is it soluble in ice [*Hood et al.*, 1998; *Top et al.*, 1988] and as a result it may be squeezed out through the ice as the firn seals off and the gas is pressurized. This is reported for He [*Craig and Chou*, 1982] although to our knowledge no measurements have been made for Ne. Thus the amount of Ne entering the lake may be significantly less than the other air group gases. Once in the lake Ne may not accumulate; since it is soluble in ice it should be included in the refrozen lake water. Incorporation of Ne in ice during freezing has been directly observed in the laboratory [*Top et al.*, 1988] and in the lake covers of the Antarctic dry valley lakes [*Hood et al.*, 1998]. Neon in the water column would not enter the clathrate, since the equivalent dissociation pressure for Ne is above 1500 MPa [*Dyadin et al.*, 1999]. We predict Ne is present at levels within the refrozen ice above the lake at levels comparable to the glacier ice entering the lake and is not enhanced in the water column.

3. Clathrate Density and Carbon Dioxide

[11] CO_2 can be present in the water of Lake Vostok from three sources: from CO_2 in the air bubbles, from carbonate forming CO_2 in solution, and from dissolved and particulate organic carbon entering the lake that is then converted to CO_2 by reaction with O_2. Microorganisms could play a significant role in the later oxidation process [*Priscu et al.*, 1999]. It is interesting to consider the possibility of CO_2 incorporation into the clathrate that forms as a way to resolve an apparent mystery in Lake Vostok. If air clathrates are forming they should be lighter than the water and should therefore collect at the top of the lake. There they would be incorporated into the reforming ice and would be present in high concentrations in the accreted ice above the lake, but they are not observed [*Siegert et al.*, 2001]. We suggest that the clathrates in the lake sink due to CO_2 incorporation.

[12] To determine the density of clathrate containing CO_2, we use the CSMHYD software from [*Sloan*, 1998] developed by the Colorado School of Mines to compute the density of N_2 clathrate with increasing fractions of CO_2. The results are shown in Figure 3. At a mole fraction of 10% CO_2 there is a sharp increase in the density of the resulting clathrate due to the transition from type II (N_2 and O_2) to type I structure (CO_2). This transition results in a sharp increase in density because type I structures contain a larger fraction of medium sized cages capable of hosting gas molecules.

[13] The dissociation pressure of CO_2 (see Table 1) is about 10 times less than that for air while its solubility depends on pH. Considering only the effect of the dissociation pressure, an incorporation of 10% into the resulting clathrate would only require a mixing ratio of CO_2 to N_2 plus O_2 of 1%. This is much higher than the CO_2 in the air bubbles but sources of carbon into the lake could reach this level. Measurements of the organic carbon content of the overlying ice cover give values ranging from undetectable [*J.R. Petit* private communication] to less than 0.1 mg C per kg of ice [*Priscu et al.*, 1999]. This upper value corresponds to 0.2% mixing ratio of CO_2 to N_2 plus O_2, not adequate to sink the clathrate. However there is the possibility of other sources of carbon within the lake due to carbonate and organic carbon in the underlying rocks.

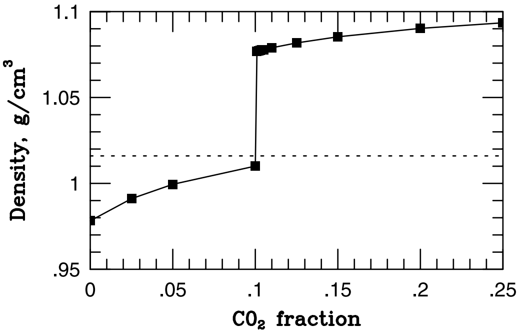

Figure 3. Density of air clathrate with CO_2 compared with the expected density of the water in Lake Vostok. If the clathrate contains over 10% CO_2 its density (1.08 g/cm^3) exceeds that for the range of possible densities of lake water in Vostok. The dotted line shows the expected density of the lake water [*Wuest and Carmack*, 2000].

4. Discussion and Conclusions

[14] The mechanism of gas concentration in the waters of Lake Vostok is similar in a general way to the gas enhancement mechanism reported for the lakes of the dry valleys of Antarctica. These lakes have a perennial ice cover of 4–5 meters, the thickness of which is determined by ablation and latent heat release [*McKay et al.*, 1985]. Mass flow as water into the lake and freezing at the bottom of the ice cover results in supersaturation of O_2 [*Wharton et al.*, 1986], N_2 [*Wharton et al.*, 1987], and Ar [*Andersen et al.*, 1998] in the water column and creates bubbles within the ice covers of these lakes [*Craig et al.*, 1992].

[15] It is interesting to consider glacial lakes that are under a thinner layer of ice than Lake Vostok. Clathrate forms in the ice cover at ~1000 m but is stable in a lake only if the depth is ~1500 m due to the differences between the stability of clathrate with respect to ice and bubbles and with respect to water and dissolved gas [*Lipenkov and Istomin*, 2001]. Thus, as more gas is forced into such a shallow lake the gas pressure will increase above the hydrostatic pressure and bubbles will form that will then be incorporated into the newly formed ice at the top of the lake. Once the bubbles are isolated into the ice they should reform the clathrate if the ice is thicker than 1000 meters. Thus the accretion ice in these relatively shallow lakes will have clathrate present, albeit in different morphology than the glacial ice.

[16] These considerations have important implications for plans to access the water in Lake Vostok. Firstly, the high gas concentrations may result in a vigorous gas-driven flow if lake water is brought to the surface. The concentration of N_2 plus O_2 in the lake water, 2.5 liters/kg, is about that in an unopened can of Coca Cola (where the gas is CO_2). The effects of rapid degassing of a Coca Cola are well known.

Secondly, the in-situ measurement of dissolved gases could provide important clues as to the physical and biological processes in the lake. Of particular interest as measurement targets are the relative concentrations of N_2 to O_2, and ratios of the noble gases Ar, Kr and Xe. Neon is predicted to be virtually absent from the lake water. High O_2 concentrations will have significant implications for some lake biota and we might expect that organisms adapted to living in the lake would have high concentrations of enzymes that deal with oxygen radicals; e.g., peroxidase, catalase, and superoxide dismutase. These substances or their genetic indicators might be detected in the accretion ice.

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C. P. McKay, Space Science Division, NASA Ames Research Center, Moffett Field, CA 94035, USA. (cmckay@mail.arc.nasa.gov)

K. P. Hand, Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305, USA. (khand@pangea.stanford.edu)

P. T. Doran, Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, IL 60607, USA. (pdoran@uic.edu)

D. T. Andersen, Center for the Study of Life in the Universe, SETI Institute, Mountain View, CA 94043, USA. (dandersen@seti.org)

J. C. Priscu, Department of Land Resources and Environmental Sciences, Montana State University, Bozeman, MT 59717, USA. (jpriscu@montana.edu)