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A theoretical investigation into the trapping of volatiles by clathrates in Lake Vostok, Antartica

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Abstract

Motivated by the possibility of comparing theoretical predictions of Lake Vostok's composition with in situ measurements, we accurately determine the composition of clathrates that should form in this environment. We establish a correlation between the lake's composition with that of air clathrates formed in situ, with the use of a statistical thermodynamic model based on experimental data.

1 Introduction

Over 100 liquid water lakes have been identified beneath the ice sheets of Antarctica. Lake Vostok, which lies buried beneath ∼4 kilometers of ice, is the largest of these freshwater reservoirs. Estimates for the age of this lake range from one million years to 15 million years. Because Lake Vostok is under many kilometers of ice, it is unlikely that the lake water is in equilibrium contact with air. From an exobiological point of view, the study of Lake Vostok is interesting because it could contain life forms in an environment that has been sealed off from light and atmosphere for possibly several millions of years. As such, the Lake Vostok environment could be analogous to that of the Jovian icy moon Europa, which is envisaged to harbor a subsurface ocean with conditions compatible with habitability.

Here, motivated by the possibility of comparing theoretical predictions of Lake Vostok's composition with in situ measurements, we reinvestigate the work of [1] by determining more accurately the composition of clathrates that should form in this environment. In order to establish a better correlation between the lake's composition with that of air clathrates formed in situ, we use a statistical thermodynamic model based on experimental data and derived from the original work of [2]. The major ingredient of our model is the description of the guest-clathrate interaction by a spherically averaged Kihara potential with a nominal set of potential parameters.

2 Modeling the lake composition

Our basic assumptions are similar to those formulated by [1]. We assume that Lake Vostok is a closed system at constant pressure of 35 MPa and physiographically stable over time. In our system, water and air are delivered to the lake when melting occurs and gas-free water leaves the lake as ice accretes to the bottom of the ice sheet [1, 3]. Air is assumed to be supplied to the lake at a concentration of about 90 cm^3 at STP ($T = 273.15$ K and $P = 0.1013$ MPa) per kg of melted ice [3, 4]. We express the age of the lake in terms of the residence time, which corresponds to the time needed for the mass flow through the lake to equal the mass of the lake. At ∼28 residence times, the concentration of air dissolved in Lake Vostok reaches the solubility limit, which is ∼2500 cm^3 (STP) per kg of water [1], and clathrate formation begins. Thereafter, the total dissolved gas in Lake Vostok remains approximately constant at this value and the gas in excess continuously forms clathrate. Because the composition of clathrate strongly departs from that of the coexisting gas phase, its progressive formation induces a feedback on the composition of the gas dissolved in Lake Vostok. Based on this approach, we have elaborated a computational procedure aiming at calculating the volume of each gas dissolved in Lake Vostok (per unit of kg of lake water) and trapped in the forming air clathrates, as a function of the temporal evolution of the lake (in units of residence times).

To calculate the relative abundances of guest species incorporated in a clathrate from a coexisting gas of specified composition at given temperature and pressure, our subroutine follows the method described by [5, 6, 7], which uses classical statistical mechanics to relate the macroscopic thermodynamic properties of clathrates to the molecular structure and interaction energies. It is based on the original ideas of [2] for clathrate formation, which assume that trapping of guest molecules into cages corresponds to the three-dimensional generalization of ideal localized adsorption.

3 Results

Figure 1 represents the volumes of gases dissolved in the water of Lake Vostok (per unit of kg of water) as a function of the age of the lake. Our calculations show that the N_2 volume in Lake Vostok is larger than the one predicted by [1] ($\sim$ 2300 cm^3 vs. 1750 cm^3) at infinite residence time. In contrast, we predict a lower O_2 volume in the lake compared to the one predicted by [1] ($\sim$ 200 cm^3 vs. 700 cm^3). We also predict a lower mole fraction of Ar in the lake compared to its atmospheric value. Our computations show that Kr and Xe are both efficiently trapped in clathrates formed in Lake Vostok, implying their strong depletion in the gas phase dissolved in the lake water.

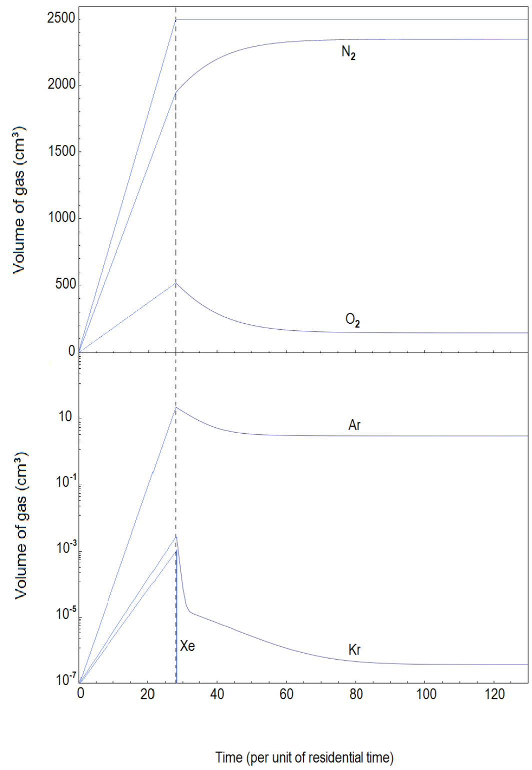

Figure 1: Volumes of gases dissolved in the water of Lake Vostok calculated in the case of structure II clathrate formation (structure of N_2-dominated clatharte) and expressed as a function of the age of lake, with age expressed in units of residence time.

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