



## Letter

**Cite this article:** Neuhaus SU, Tulaczyk SM (2022). Mechanism for the subglacial formation of cryogenic brines. *Annals of Glaciology* **63**(87–89), 121–124. <https://doi.org/10.1017/aog.2023.28>

Received: 30 September 2022

Revised: 27 February 2023

Accepted: 20 March 2023

First published online: 8 May 2023

**Keywords:**

Glacier hydrochemistry; ice/ocean interactions; meltwater chemistry

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# Mechanism for the subglacial formation of cryogenic brines

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**Abstract**

Cryogenic brines are under-studied, despite the fact that they may contain information about past ice-sheet behavior. Cryogenic brines form through cryoconcentration of seawater, although the specific setting and mechanism of formation have been debated. Previous conceptual models of brine formation require seawater isolation from the ocean in a closed basin experiencing freezing. We propose instead that they may form in pore spaces of marine sediments subjected to repeat cycles of ice-sheet advance and retreat. During periods of basal freezing, cryoconcentration produces hypersaline brines which experience downward flow driven by unstable density stratification. Our advection-diffusion model of porewater chemistry evolution successfully recreates the porewater chemistry of two deep Antarctic cores containing cryogenic brines (AND-1B and AND-2A), suggesting that cryogenic brines can be formed through the repeated isolation and cryoconcentration of marine waters within subglacial sediment pore spaces of modern and past ice sheets.

**1. Introduction**

Cryogenic brines are common in formerly glaciated regions in the Northern Hemisphere, having been found in deep boreholes across the Canadian Shield (Frape and Fritz, 1982; Bottomley and others, 1994) and Fennoscandia (Starinsky and Katz, 2003). Fewer cryogenic brines have been found in Antarctica, however this may simply be due to the difficulty of obtaining deep porewater samples from Antarctica. In fact, subsurface brines may be widespread around the edges of the Antarctic continent where basal freezing dominates (Foley and others, 2019; Frank and others, 2022; Piccione and others, 2022). We examined cryogenic brines collected from the pore spaces of two deep boreholes drilled into the seafloor in McMurdo Sound, Antarctica (Pompilio and others, 2007; Frank and others, 2010).

Chemical signatures in the cryogenic brines indicate that they are derived from the freezing (cryoconcentration) of seawater (Starinsky and Katz, 2003; Frank and others, 2010, 2022; Gardner and Lyons, 2019; Lyons and others, 2019), but their water isotopes are strongly depleted. The two prevailing conceptual models for the formation of cryogenic brines require the isolation of seawater in a basin which freezes over (Starinsky and Katz, 2003; Grasby and others, 2013; Frank and others, 2022). During freezing, seawater solutes are preferentially retained in the remaining liquid, resulting in the formation of a dense brine which seeps into the underlying sediments. Although the idea of an isolated marine basin could be used to explain the formation of cryogenic brines found in the Northern Hemisphere, it is difficult to transplant that idea to the Ross Sea Sector of Antarctica due to the lack of evidence for bathymetric highs large enough to have isolated marine waters from the ocean in the past (Tinto and others, 2019). Here, we propose a new model in which brines form in the sediment pore spaces below a marine-based ice sheet, without the need for an isolated marine basin.

**2. Summary of methods and results**

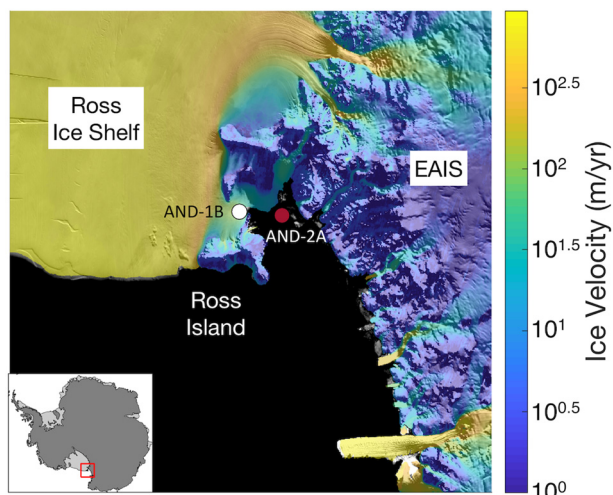
We modeled the concentration of  $\text{Cl}^-$  and  $\delta^{18}\text{O}$  in sediment porewaters that have experienced multiple cycles of glacial retreat and advance and compared our results to brines found in cores AND-1B and AND-2A (Pompilio and others, 2007; Frank and others, 2010), recovered from drill sites located beneath the McMurdo Ice Shelf (Fig. 1). We modeled the formation and vertical dispersal of cryogenic brines using a finite-difference code solving the 1-D vertical advection-diffusion equation:

$$\frac{\partial C}{\partial t} = D_{\text{sed}} \frac{\partial^2 C}{\partial z^2} + \frac{\partial D_{\text{sed}}}{\partial z} \frac{\partial C}{\partial z} + K \frac{\Delta \rho}{\rho} \frac{\partial C}{\partial z} \quad (1)$$

where  $C$  is chemical concentration,  $t$  is time,  $D_{\text{sed}}$  is the diffusion coefficient of the chemical parameter through sediments,  $z$  is depth below the seafloor,  $K$  is the hydraulic conductivity of the sediments and  $\rho$  is the density of the porewater. Derivation of this equation and the variables  $D_{\text{sed}}$ ,  $K$  and  $\rho$  is shown in the Supplemental materials.

We modeled porewater concentrations of  $\text{Cl}^-$  and  $\delta^{18}\text{O}$  for a 2 km sediment column (seafloor to 2000 mbsf) which has experienced 100 000-year cycles of ice-sheet retreat and re-advance. We chose to model the concentrations of  $\text{Cl}^-$  and  $\delta^{18}\text{O}$  because we expect that they did not interact chemically with the sediments at temperatures prevailing in the shallow





**Figure 1.** Location of AND-1B and AND-2A boreholes. Ross Sea is indicated in black. The MODIS Mosaic of Antarctica (Haran and others, 2021) and ice velocity data (Rignot and others, 2017) are plotted using Antarctic Mapping Tools (Greene and others, 2017).

subsurface (Morin and others, 2010), and thus are solely indicators of freezing- and transport-related processes in the sedimentary column. In our model runs, we exposed the simulated sedimentary column to three different upper boundary conditions (Fig. 2), representing the different parts of a simplified glacial cycle: (i) seawater exposure representing deglaciations during interglacials (e.g. modern conditions), (ii) basal melting when the ice sheet is overriding the study site and climatic (e.g. surface temperature) as well as glaciological conditions (e.g. large ice thickness) lead to a positive thermal energy balance at the ice base, and (iii) basal freezing when the ice sheet is overriding the study site and climatic and glaciological conditions lead to a negative thermal energy balance at the ice base. A description of how we altered the boundary conditions is shown in the Supplementary materials.

Because we were interested in determining whether cryogenic brines could form in sediment pore spaces, we altered the free parameters to allow the model outputs to fit the observations from AND-1B and AND-2A, respectively. In doing so, we were able to fit our model simulations to the observed concentrations of  $\text{Cl}^-$  and  $\delta^{18}\text{O}$  (Fig. 3) using reasonable model parameters and simplified glacial cycles, thus demonstrating the feasibility of our mechanism. The  $R^2$  values indicating model fit are shown in Figures 3c and f. A list of all free parameters and the corresponding range of values over which we examined the free parameters is outlined in Table S1. Our model of the AND-1B core produced  $\text{Cl}^-$  concentrations that were 1.8 times more concentrated than the local seawater, and our model of the AND-2A

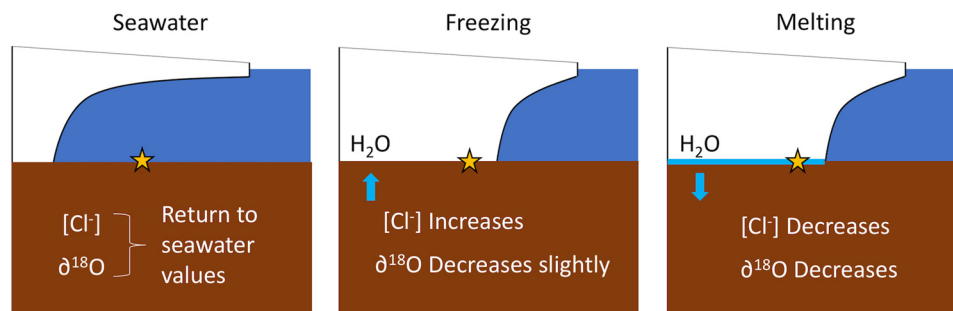
core produced  $\text{Cl}^-$  concentrations that were five times more concentrated than the local seawater.

### 3. Conclusions and future research directions

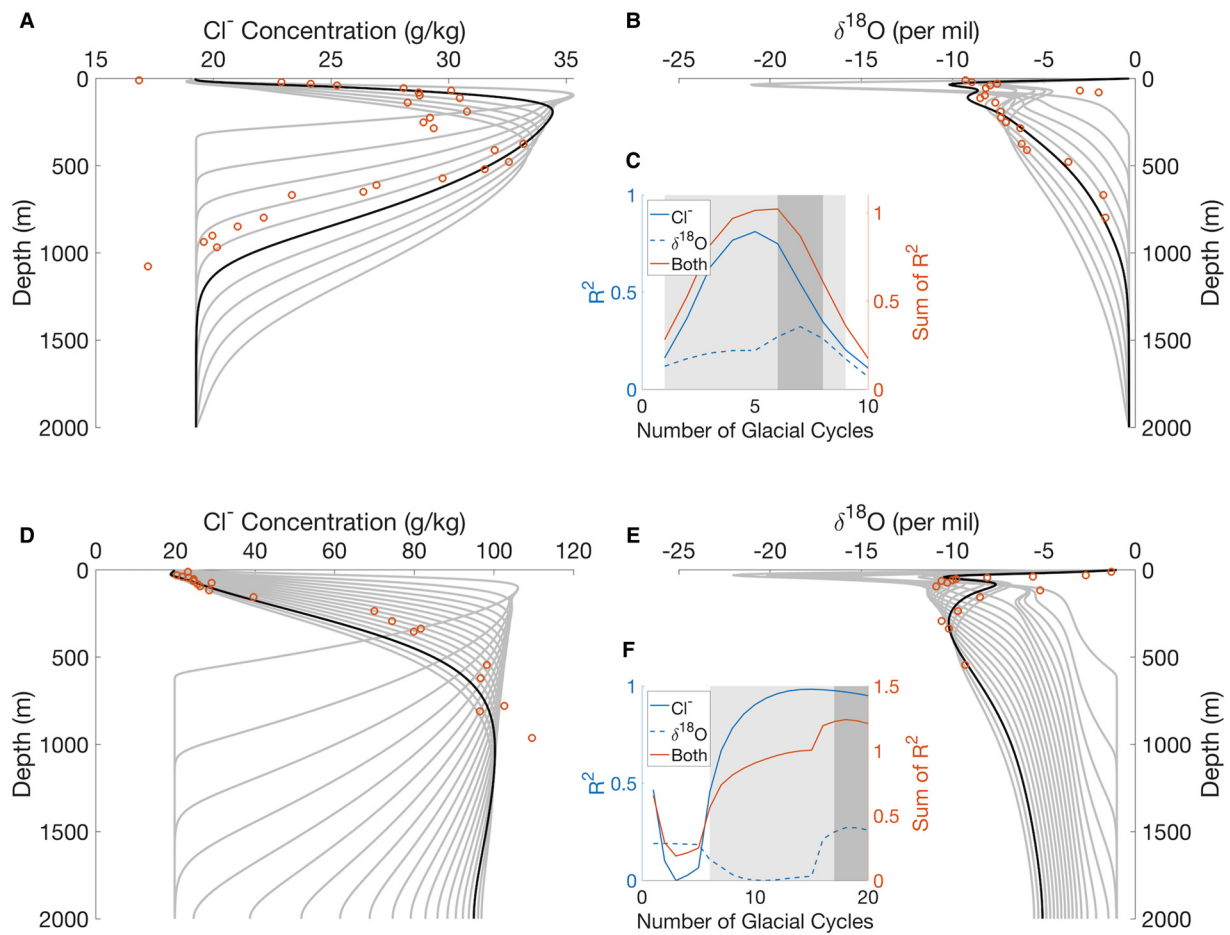
The model was able to create cryogenic brines of similar  $\text{Cl}^-$  and  $\delta^{18}\text{O}$  composition to the brines observed in the pore spaces of the AND-1B and AND-2A cores. We thus conclude that cryogenic brines may form in sediment pore spaces just as well as in an isolated marine basin. The mechanism proposed here is a more plausible explanation, at least in the Antarctic setting considered here (McMurdo Sound). Given the current lack of a forebulge in the presence of the Antarctic Ice Sheet or a moraine large enough to cut off access to the ocean, it is unlikely that these locations were isolated from the ocean except when overridden by ice. However, we do not rule out other methods of cryogenic brine formation in other Antarctic settings – namely in the McMurdo Dry Valleys where the topographic and glaciologic history may permit brine formation in an isolated marine basin (Frank and others, 2022).

This mechanism of cryogenic brine formation is exciting because it allows for the possibility of interpreting past ice-sheet behavior. Given the number of free parameters tuned in our study to allow the model outputs to fit the observations from the AND-1B and AND-2A cores, it is unlikely that our results are unique. However, future studies may be able to perform a more robust determination of the free parameters for a specific field site to produce unique model results. These results would allow for the determination of past ice-sheet dynamics, namely the timing of past grounding line advance and retreat as well as conditions at the base of the ice (i.e. freezing or melting). This could be a useful tool to help pinpoint the timing of grounding line retreat following the Last Glacial Maximum (LGM) (e.g. Neuhaus and others, 2021). Dating the timing of post-LGM grounding line retreat in the Ross Sea has been notoriously difficult (Anderson and others, 2014) due to the paucity of datable material in the Ross Sea sediments. Examining cryoconcentrated porewater samples could provide another avenue of investigation.

Additionally, cryogenic brines may be of interest to planetary scientists as they represent analogs of the types of fluids hypothesized to exist on other planetary bodies (namely Mars, Europa and Enceladus) and represent the most likely environment for finding extraterrestrial life in our own Solar System. For instance, there is evidence hinting at the presence of liquid water below the ice cap on Mars' south pole (Orosei and others, 2018; Lauro and others, 2021). Given the cold temperatures at the base of the Martian ice caps, the liquid water is assumed to contain high solute concentrations. These brines could have formed in the sediment pore spaces in a manner analogous to the mechanism proposed here.



**Figure 2.** Schematic of the three different periods examined during the 100 000-year model runs. During seawater periods, the porewater in the topmost element reflect seawater concentrations. During freezing periods,  $\text{Cl}^-$  concentration increases, and  $\delta^{18}\text{O}$  decreases slightly. During melting periods,  $\text{Cl}^-$  decreases, and  $\delta^{18}\text{O}$  decreases significantly.



**Figure 3.** Model results compared to observed brine concentrations in the AND-1B core (a–c) and in the AND-2A core (d–f). (a, d)  $\text{Cl}^-$  concentration. (b, e)  $\delta^{18}\text{O}$ . (c, f)  $R^2$  values indicating model fit after each glacial cycle. Light gray shading denotes cycles over which the  $R^2$  value is significant for  $\text{Cl}^-$  and the dark gray shading denotes the cycles over which  $R^2$  was significant for both  $\text{Cl}^-$  and  $\delta^{18}\text{O}$ . The dark lines in (a), (b), (d) and (e) denote the model results from the glacial cycles that best fit the observations for both  $\text{Cl}^-$  and  $\delta^{18}\text{O}$  based on  $R^2$  values shown in (c) and (f). The results from ten glacial cycles are shown in (a) and (b). The results from 20 glacial cycles are shown in (d) and (e).

Despite containing information about past ice-sheet dynamics, cryoconcentrated brines are under-sampled largely because sampling of subglacial waters has been biased toward fast-moving ice (Kamb, 2001; Tulaczyk and others, 2014), where the ice sheet is not frozen to the bed and basal melting is prevalent. Because cryoconcentration can occur in sediment pore spaces, it is likely that there are brines hidden in the sediments where the Antarctic Ice Sheet is frozen to the bed, namely along most of the ice-sheet margin in Antarctica (Foley and others, 2019). If we were to sample deep sediment cores at those locations we would find cryogenic brines, which could inform us of the past ice-sheet dynamics at that site.

**Supplementary material.** The supplementary material for this article can be found at <https://doi.org/10.1017/aog.2023.28>.

**Acknowledgements.** This material is based upon work supported by the National Science Foundation under grant No. 1644187 and 1745124.

**Author contributions.** S. U. N. and S. M. T. co-designed this research. S. U. N. performed the analysis and wrote the manuscript with input from S. M. T.

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