

Salty Matters

John Warren - Tuesday March 31, 2020

Brine density & persistence: Part 1 Physical properties of a brine

Introduction

Evaporite sediments precipitate in a brine and can dissolve into a brine. The formative brine is always saline (more saline than freshwater) and the levels of salinity in the brine will increase or decrease depending on the relative rate of fluid input to output in the location where the evaporite mass is accumulating at the earth's surface or residing in the subsurface. That is, rates of fluid input to loss to and from an evaporite geobody change both in the at-surface depositional environment and in the subsurface environment. More saline brines have higher concentrations of ionic constituents in the aqueous host than less saline brines. Accordingly, more saline brines have somewhat higher densities and lower specific heat capacities than less saline brines.

The higher density of a free-standing brine or porosity-held brine compared to an overlying fresher, less-dense free-standing brine layer or surrounding fresher pore fluids in non-evaporite sediment can drive geochemical stability,

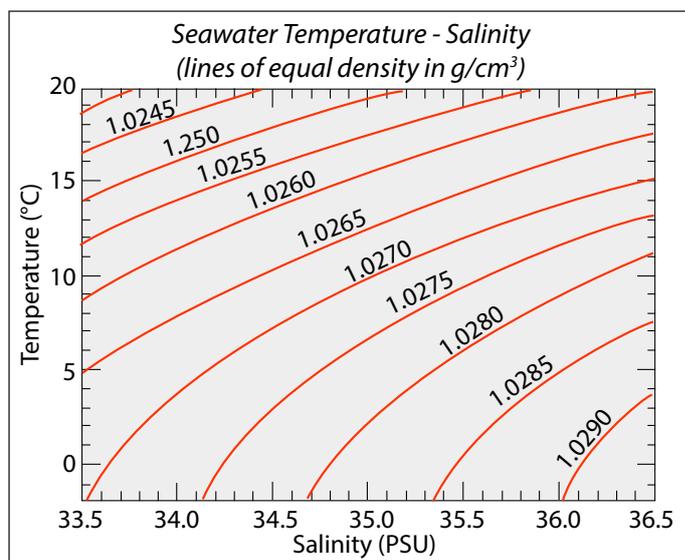


Figure 1. Relationships between seawater salinity (PSU = practical salinity units), temperature and density.

	Brine Stage	Mineral Precipitate	Salinity (‰)	Evap.	H ₂ O (%) loss	Density (gm/cc)
Sea	Marine or euhaline	Skeletal & inorganic carbonate	35-37‰	1x	0	1.040
Hypersaline	Mesohaline or vitahaline	Alkaline earth carbonates	37 to 140‰	1-4x	0-75	1.040-1.100
	Penesaline	CaSO ₄ (gypsum/anhydrite)	140 to 250‰	4-7	75-85	1.10-1.214
		CaSO ₄ ± Halite	250 to 350‰	7-11x	85-90	1.214-1.126
	Supersaline	Halite (NaCl) Bittern salts (K-Mg salts)	>350‰ Extreme (‰ vary)	>11x >60x	>90 ≈99	>1.126 >1.290

Table 1. Salinity-classification tying together mineral paragenesis and brine properties, including density range, based precipitation series with concentration of modern seawater (after Usiglio, 1949). Hypersaline is defined as >35‰. Compared to this mineral-based classification, biologists working in saline waters use a somewhat different hierarchy; fresh water (less than 1‰), subsaline (1-3‰), hyposaline (3-20‰), mesosaline (20-50‰), and hypersaline (greater than 50‰). Geohydrologists tend to refer to fresh water as less than 1‰, brackish water as 1-10‰, saline water as 10-100‰, and brine as greater than 100‰.

interaction and alteration across time frames measured in months to hundreds of millions of years, from the time of deposition through diagenesis and uplift. The distinct properties of evaporite-associated brine also influence the generation of viable oil and gas accumulations and ore deposits. Over the next four articles, we consider brine in this context of short-term and long-term pore fluid stability and alteration, starting with this article discussing various physical properties of evaporite and cryogenic brines.

Marine brine chemistry and density

Today the chemical make-up and the proportions of the major ions in seawater are near-constant in all the world's oceans. Ions dissolved in seawater are dominated by Na and Cl, with lesser amounts of SO₄, Mg, Ca, K, CO₃ and HCO₃. Using the brine classification of Eugster and Hardie (1978), modern seawater is a Na-(Mg)-Cl-(SO₄) water, with an average density of 1.03 gm/cc and a salinity of 35 ± 2‰ (Table 1). Oceanwide, the density of seawater is not a constant but varies slightly according to interactions with salinity and temperature. Density of surface seawater ranges from about 1020 to 1029 kg/m³, depending on temperature and salinity. At a temperature of 25 °C, a sa-

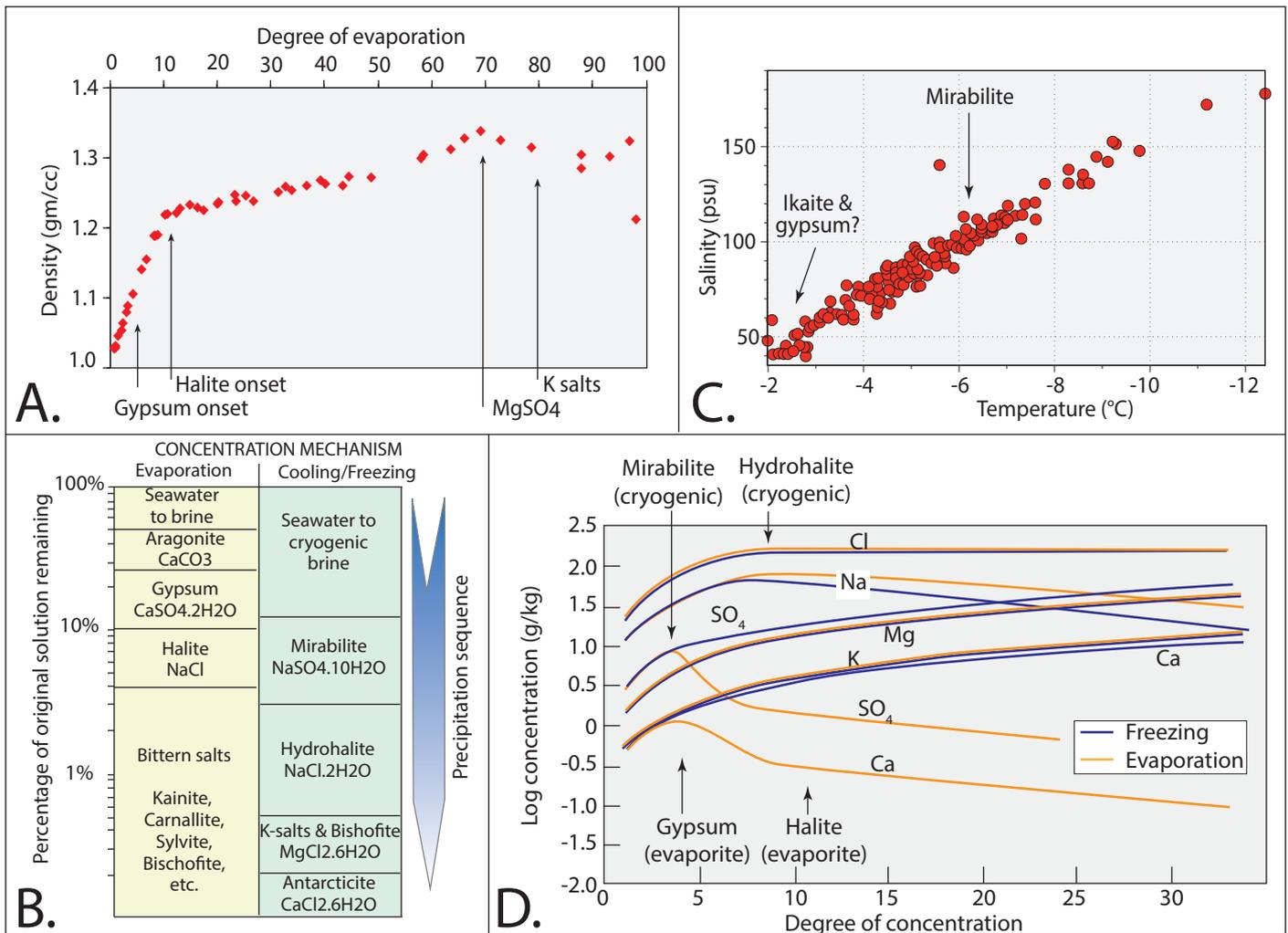


Figure 2. Marine brine evolution. A) Evaporation pathway of modern seawater, showing how density increases. B) Evaporation series where seawater is concentrated by solar heating (evaporation) versus brine freezing (cryogenesis). C) Cryogenic brine salinity increases with decreasing temperature. D) Ionic evolution and proportions as well as main salts precipitated in a concentrating seawater brine upon its freezing or evaporation (see *Salty Matters* May 18, 2019, for details on reference sources).

linity of 35‰ and 1 atm pressure, the density of seawater is 1023.6 kg/m³. Deep in the ocean, under high pressure, seawater can attain a density of 1050 kg/m³ or higher. As temperature increases the density of seawater decreases. Similarly, colder seawater tends to be denser than warmer seawater and so warmer seawater masses tends to float atop colder masses. This sets up pycnoclines or density interfaces in the open ocean (see Warren et al., in press, for a paper dealing with the implications of marine pycnoclines and the associated passage of internal waves in creating of some types of hydrocarbon reservoir sands in SE Asia).

For this series of articles, we are more interested in the geochemical and geophysical effects related to increases in brine density, tied to evaporative concentration, freezing, or dilution of a brine, both at the depositional surface and in the diagenetic realm.

When seawater evaporates, a predictable suite of primary evaporite minerals crystallise from increasingly concentrated hypersaline waters (Figure 2a; Table 1). The

sequence of marine precipitates was first documented by Usiglio (1849) and is still used to classify marine water salinities based on the associated mineral suits (Table 1). As seawater concentrates, the first mineral to precipitate is CaCO₃, usually as aragonite. This begins in mesohaline waters where the brine reaches twice the concentration of seawater (40 to 60‰) and achieves a density ≈1.10 gm/cc. As the brine continues to concentrate and approaches four to five times the concentration of seawater, that is 130 to 160‰, gypsum precipitates from penesaline waters with densities around 1.13 gm/cc (Figures 2a, b, 3a). At 10 to 12 times the original seawater concentration (340 to 360‰) and densities around 1.22 gm/cc, halite drops out of supersaline marine waters. If seawater desiccates completely, the greatest volume of salt extracted from seawater is halite (Figure 3a). After halite, the bittern salts (potassium or magnesium sulphates/chlorides) precipitate from hypersaline waters at concentrations that are more than 70-90 times that of the original seawater. Carnallite and epsomite are the dominant bittern precipitates from

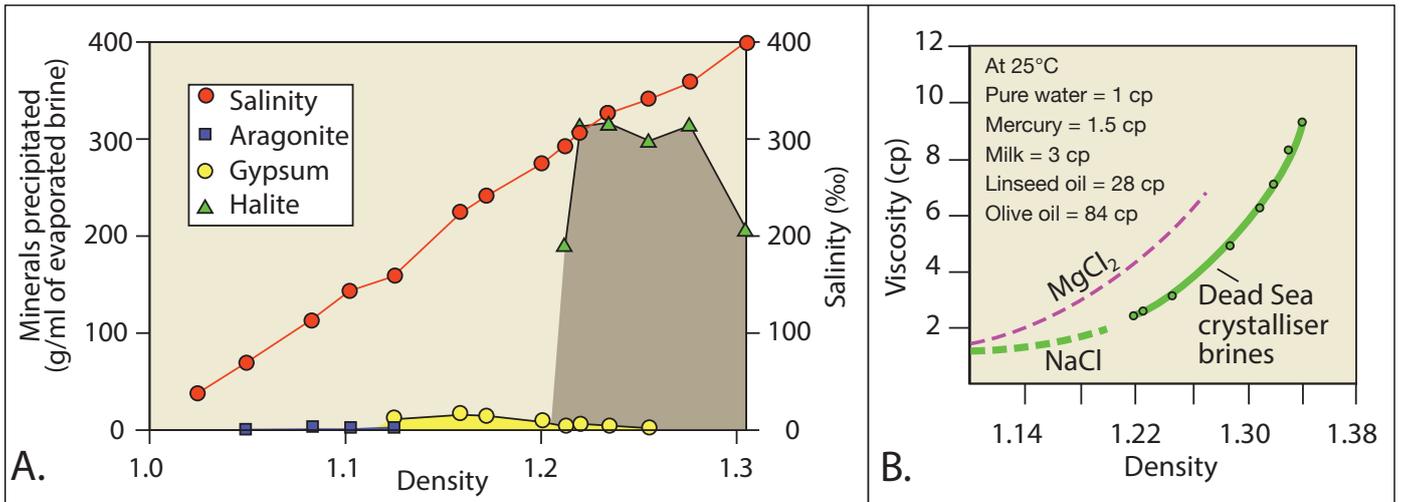


Figure 3. Brine evolution. A) Pre-bittern mineral precipitation sequence in a concentrating marine brine (replotted from Table 1 in Briggs, 1958). B) Viscosity increases with brine concentration (replotted from Karcz and Zak, 1987).

a modern marine brine source. Brine density by this stage of concentration is more than 1.30 gm/cc and brine viscosity and feel approach that of olive oil (Figure 3b).

As a brine freezes, cryogenic salts can form. Cryogenic brines and associated salts require temperatures at or below the freezing point of the liquid phase. These salts crystallise from a cold, near-freezing, residual brine as it concentrates via the loss of its liquid phase, which is converting/solidifying to ice (Figure 2c, d). As cryogenic brine concentration increases, the freezing temperature decreases and minerals such as ikaite, hydrohalite, mirabilite, epsomite, potash bitterns and antarcticite can crystallise from the freezing brine (Figure 2d; See Salty Matters May 18, 2019). Brine freezing ends when the phase chemistry attains the eutectic point. This is the point when all compounds (including H₂O) pass to the solid state. Depending on the initial mineralization and composition of the brine, the eutectic point is reached between -21 and -54 °C.

Specific heat and thermal conductivity

Specific heat of any evaporating brine decreases as the salinity increases (Kaufmann 1960). Specific heat is the amount of heat needed to raise one gram of a substance by 1°C (Figure 4a). Specific heat of any brine decreases as the salinity increases (Kaufmann 1960). For a given amount of heat input, a unit volume of hypersaline water will show a greater increase in temperature than a less saline water. For example, when the salinity of the surface waters of the Dead Sea increased from 210‰ in the 1940s to 275‰ in the early 1980s, the specific heat decreased from 3,085 J/kgK to 2,985 J/kgK (Niemi et al. 1997; p. 127).

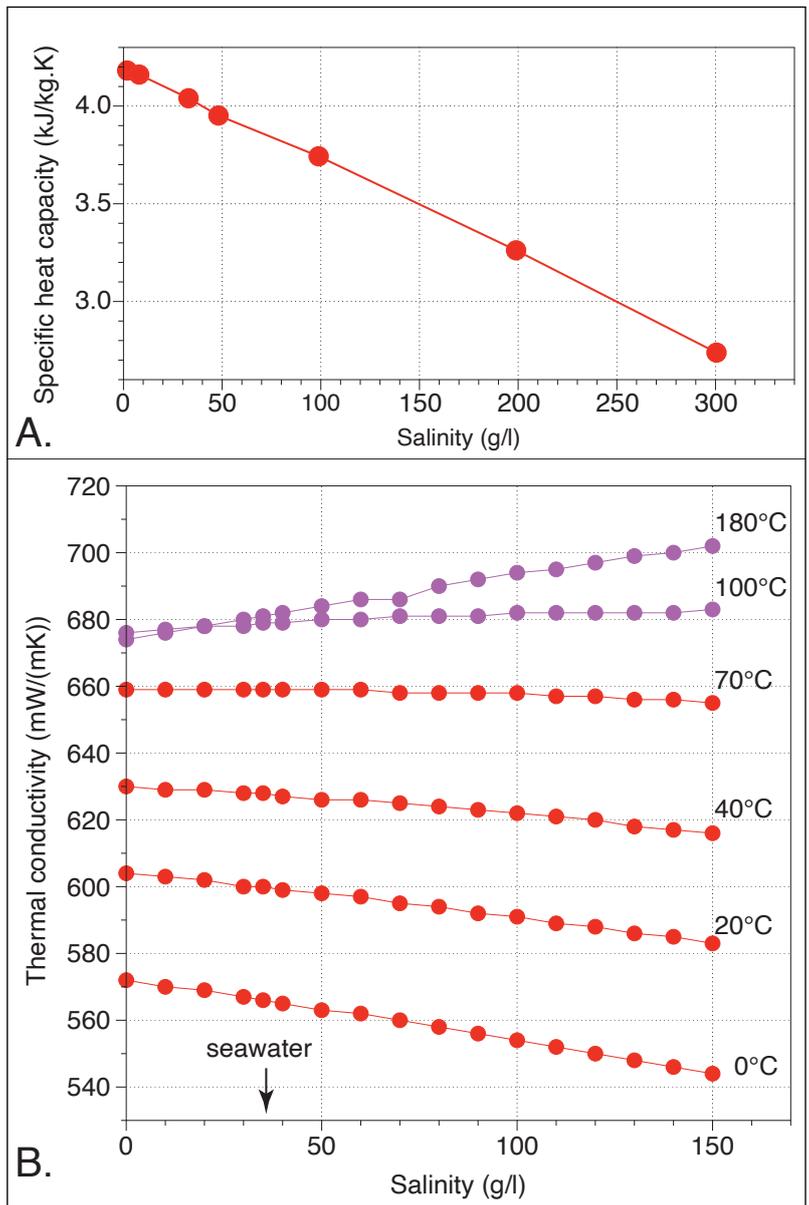


Figure 4. Salinity versus A) Specific heat and B) Thermal conductivity across a range of temperatures (replotted from Shadrin, 2017).

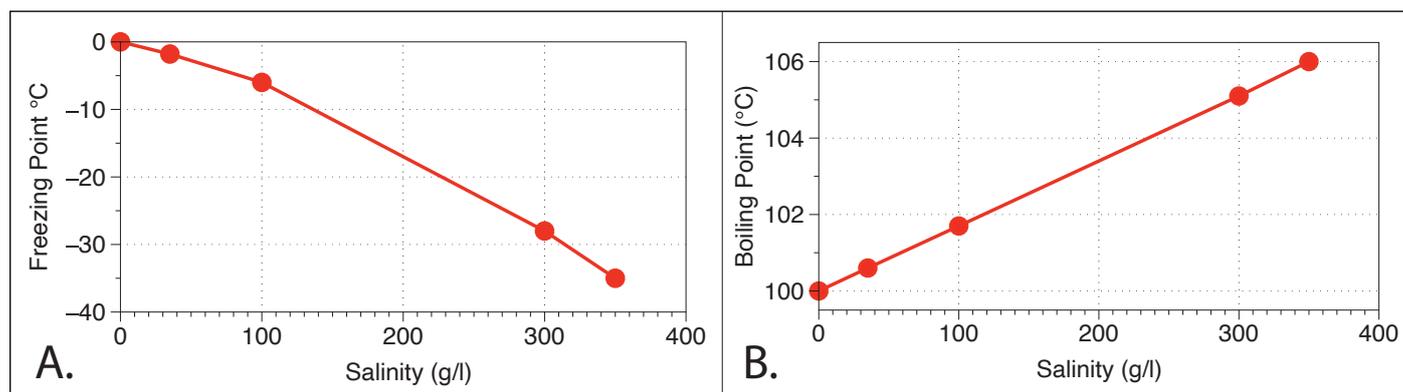


Figure 5. Salinity (g/l) versus A) Freezing point °C. B) Boiling point °C.

Thermal conductivity is the rate at which heat passes through a specified material, expressed as the amount of heat that flows per unit time through a unit area with a temperature gradient of one degree per unit distance. From 0 to 100°C, it too decreases with increasing brine salinity (Figure 4b); beyond 100°C, the thermal conductivity of a brine increases (Shadrim, 2017).

In a layered brine column, with less dense (fresher) water overlying denser (more saline) brine, the sharp contrast in physical properties across the brine contact or interface (aka halocline) leads to strong gradients of salinity and temperature, even in shallow saline lakes. In mid-winter, in Deep Lake, located in the Innes National Park on the southern end of York Peninsula, Australia, there is a contrast of more than 10°C across the halocline, in a water column some 80-100cm tall.

Given the same degree of insolation in any density-stratified brine (evaporative or cryogenic), it takes less heat to raise brine temperature by one degree in the lower more dense more saline brine. Hence, stratified brine masses generally become heliothermic, with bottom brines tending to be warmer than fresher surface waters (Part 2 in this series of articles). The temperature differences can be substantial, with surface waters at ambient atmospheric ($\approx 30^\circ\text{C}$), while bottom waters can approach temperatures of 60°C in some density-stratified perennial desert lakes, such as in the 5m-deep Solar Lake on the Sinai coast (et al., 2000). The resulting greater increase in temperature in the hypersaline bottom water, compared to a less saline upper water layer in a heliothermal brine mass, can detrimentally effect thermally-intolerant benthic species (see Part 2).

Freezing and boiling of brine

Salinity also influences the freezing and boiling points of a brine. The freezing point decreases to -35°C in a cryogenic brine salinity of 350 g/l, \approx halite saturation (Figures 3c, 5a) The boiling point of a brine is raised by 0.5°C for every 29.2 g of salt dissolved in each kg of the aqueous host (Figure 5b). When seawater or any hypersaline water is cooled to an appropriate temperature, freezing begins;

the first ice crystals have the shape of a very thin elongate hexagonal prisms, similar to needles (Figure 6). These ice crystals do not contain salts, which remain in the brine solution, increasing its salinity until a range of cryogenic ("freeze-dried") salts precipitate (Salty Matters, May 18, 2019, for details on the brine chemistry and mineralogy of the various cryogenic salts).

Life can metabolise only in liquid water. A decrease of the freezing point and an increase of the boiling point when salinity increases, increases the viable temperature range for life on the planet. The extension of the lower end of the liquid water temperature range with increasing salinity is why there is liquid water and life in some subglacial hypersaline Antarctic lakes. It may also have facilitated the growth of extraterrestrial life in some ice-covered planets and moons further out from the sun than the earth.

The temperature of maximum water density is 4°C for freshwater. Freshwater expands when it freezes at 0°C , making ice less dense than the water from which it freezes. For this reason, ice floats on a freshwater surface. This segregation of ice on top, liquid below, is crucial for organisms living in temperate freshwater lakes. For example, fish and bottom organisms in a freshwater lake can survive the winter because ice forms in the upper layer of water, adequately insulating the rest of the lake below the ice, preventing the water column from freezing from top to bottom.

A salinity increase in a freezing brine leads to a decrease in the temperature of maximum water density. This decrease is more rapid than the decline in the freezing point temperature. As a result, in a hypersaline lake ice forms slowly compared to freshwater ice. Dense brine, created by growth of the at-surface ice sheet, tends to sink away from the expanding ice undersurface. This occurs before the sinking brine cools enough to freeze. That's also why sub-ice in the polar regions and beneath perennial hypersaline lakes, we observe a combination of brinicles and bottom ice, still with liquid water above.

Locally, this combination of brinicles and bottom ice presents a big problem for benthic animal life in such saline

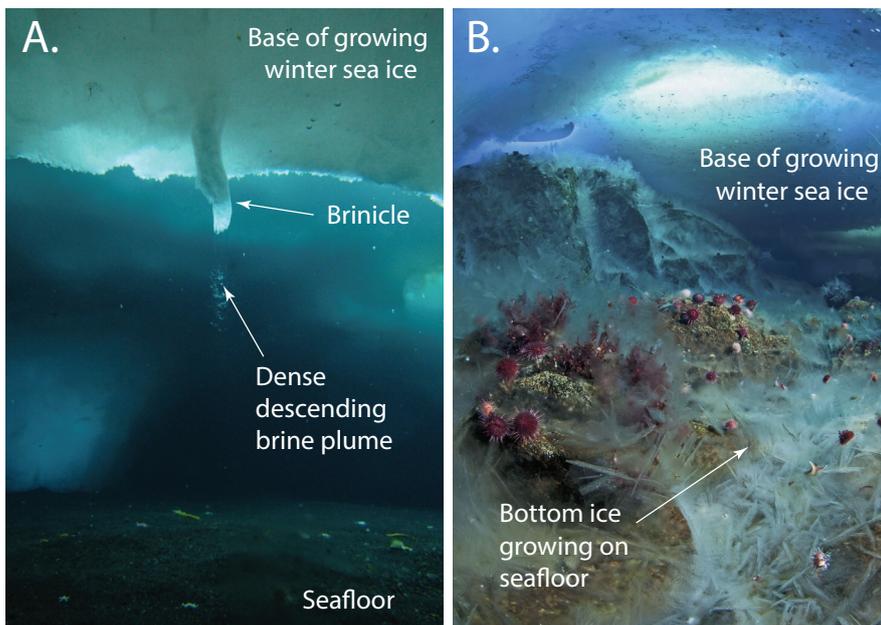


Figure 6. Brinicle growth and bottom ice. A) Downward growing brinicle tube created by the freezing of adjacent seawater around a dense descending plume of very cold hypersaline brine. The cryogenic brine was created during the growth of the sea ice cover. B) Region of Antarctic bottom ice and frozen life created by contact of cold, dense brine plume with the seafloor.

lakes. Such brinicles, instigating bottom ice growth, are also widespread phenomena in shallow marine waters below the coastal ice sheets of Antarctica (Figure 6; Vance et al., 2019).

Brine density layers and their persistence

The fundamental property of higher density tying to higher salinity across all hypersaline brine settings, be it evaporative or cryogenic, and the associated set up of density stratification, has wide-ranging implications across geological time. At the time of deposition, brine stratification in the precipitative water mass tends to isolate the denser interior of the brine mass from its less dense surrounds. This isolation tends to facilitate longer-term persistence of physical and chemical properties of the bottom brine and its underlying brine curtain (see Chapter 2 in Warren, 2016). Persistence helps explain why Permian halophiles are still viable, held in largely-unaltered brine inclusions within their chevron-textured halite host

The less-dense brine surrounding the denser brine mass may be a pore fluid in laterally adjacent on underlying sediment, or it can be a free-floating fresher water mass sitting atop the denser brine mass. The sharp interface between less-dense surrounds and a more-dense hypersaline fluid core, creates a region with chemical and physical contrast. Dense to less dense brine interactions can setup an across-interface contrast in ionic proportions, oxygen

levels, halobiotical constituents and temperatures. The various effects and processes tied to the creation of dense brine and associated interfaces with less dense brine surrounds include periodic heliothermy, brine reflux, leaching or cementation, evaporite mineral alteration or replacement. These interfaces can persist across the eogenetic to mesogenetic transition. In the mesogenetic realm, halokinesis and edge dissolution can set up similar interfaces. Uplift and reentry into the active phreatic realm will also set up density contrast interfaces in the pore fluid haloes surrounding a dissolving evaporite bed or mass. In some mesogenetic scenarios, evaporite dissolution and brine creation set up the prepared ground for base metal ore deposits, in others, it creates reservoirs for oil and gas fills.

The next three salty matters articles document a range of at-surface and subsurface settings and situations where brine density and persistence are critical factors.

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