What is an evaporite? Solar versus cryogenic (freeze-dried) salts

Introduction to cryogenic salts

The term evaporite is usually used to describe sediment precipitated during the solar-driven desiccation of a standing water body in a saltern or salina, or a near-surface pore brine in an evaporitic mudflat or sabkha. Almost all the modern and ancient examples of bedded salts that we work with in the rock record are thought to have crystallised via this process of solar evaporation. The chemical dynamics of solar evaporation are simple; on average, water molecules within a standing at-surface brine lake or in near-surface pore spaces, near a water-table and its associated capillary zone, do not have enough kinetic energy to escape the liquid phase and so cross the surface tension barrier (Figure 1). Otherwise, liquid water would turn to vapour spontaneously and any at-surface liquid phase would spontaneously disappear, while recharge to an underlying water-table would be an impossibility.

Every so often in this situation, the level of solar energy transfer (heat absorption) at the molecular collision site is sufficient to give a water molecule (near the water-air interface) the heat energy necessary to pass into the vapour phase and so exit the liquid water mass (Figure 1). That is, for a water molecule to escape into the vapour phase it must absorb heat energy, be located near the liquid surface, be moving in the proper direction and have sufficient energy to overcome liquid-phase intermolecular forces and then pass through the surface tension interface. As the concentration of the residual brine increases, the specific heat capacity decreases, and the density increases (the effects of specific heat and density increases on evaporite mineralogy and distribution in the depositional setting will be the topic of a future blog).

But salts, some with the same mineralogy as solar evaporation salts, can also form as a water or brine body freezes to leave behind cryogenic salt layers (aka the “freeze-dried” salts). This is the process that forms significant volumes of the sodium sulphate salts in various cold-zone brine lakes and saline ice-sheets around the world. Unlike solar evaporites, cryogenic brines and associat-
ed salts require temperatures at or below the freezing point of the liquid phase. Cryogenic salts, such as mirabilite (Na₂SO₄·10H₂O), hydrohalite (NaCl·2H₂O), antarcticite (CaCl₂·6H₂O) and epsomite (MgSO₄·7H₂O), can then accumulate. These cryogenic salts crystallise in cold, near-freezing, residual brines as they concentrate via the loss of the liquid water phase as it converts/solidifies to ice. As the volume of ice grows, the various anions and cations are excluded from the expanding ice lattice. Hence, concentration of the residual brine increases until it reaches saturation with a salt phase that then precipitates (Figure 2). There are a number of well-documented cryogenic salt beds in various Quaternary-age cold-continental lacustrine settings. Probably the best known are the sodium sulphate salts in Karabogazgol, Turkmenistan, where strand-zone stacks of cryogenic mirabilite form each winter. Beneath the lake centre there are subsurface beds (meters thick) of Quaternary-age cryogenic glauberite-halite.

In the Turkmen language, Karabogazgol means “lake of the black throat,” so named because the gulf is continually gulping down the waters of the Caspian Sea, via a narrow connecting natural channel (Figure 3). Ongoing evaporation in Karabogazgol keeps the water surface in the perennial brine lake depression around a metre below that of the Caspian. It is one of our few natural examples of evaporative drawdown occurring via a hydrographic (surface) connection to the mother water body. Groundwater seepage connections with the mother water mass are more typical, especially in hot arid basins.

Only since the end of the Soviet era and the re-opening of the lake’s natural connection to the Caspian Sea in 1992, by a newly independent Turkmen government, did Karabogazgol re-fill with perennial brines. Since then, a natural cryogenic mirabilite winter cycle has returned the Karabogaz hydrology to its longterm natural state. Today, the main open water body in the centre of Karabogaz is a Na-Mg-Cl brine, sourced via gravitationally-driven inflow of Caspian Sea waters. Perennial Karabogaz brines today have a density of 1.2 g/cm3, and pH values that range between 7.2 and 9. Surface water temperatures in the lake centre range from around 4°C in December (winter) to 25°C in July (summer). Temperature fluctuations and the cool arid steppe climate (Koeppen BSk) of Karabogazgol combine to drive the precipitation of different mineral phases during the year. Calcite, aragonite and perhaps hydromagnesite usually precipitate from saturated lake surface waters in spring, gypsum and glauberite in summer (via solar evaporation), while rafts of cryogenic mirabilite form at the air brine interface in the winter. These winter rafts are then blown shoreward, to form stacked strand-zone-parallel accumulations of cryogenic mirabilite and halite. By the following summer much of the strandzone mirabilite has deliquesced or converted to glauberite. In the 1920s and 30’s, prior to the

Cryogenic brines & salts are made up of residual ions that were excluded as ice formed

Cryogenic salts are not “true” evaporites as formation does not require evaporation of water mass
Cryogenic salts typify glacial deserts on Earth and occur on Mars & more distal planets & moons

Cryogenic salts indicate periodic freezing of saline waters

said to indicate halite cryogenesis (Figure 6). Hydrohalite crystals have distinctive pseudo-hexagonal cross sections (c.f. typical cucurbit form). Hydrohalite is another common cryogenic salt, it quickly redissolves as brine temperatures rise above 0 degrees centigrade and so is not a persistent bedform. There is little evidence of hydrohalite in modern saline lakes.

NaSO₄ lakes of Mexico and Turkey. Only one (Big Quill Lake) of the Canadian sites remains operational. Subaqueous salt beds in the Canadian lakes were sources of commercial NaSO₄ salts (Figure 5). However, extraction of brine and solid salts and an increasingly expensive product meant this area no longer competes with cheaper product from the solar evaporite process. There are similar cryogenic salt beds preserved in perennial saline lakes across the cold arid portions of the Great Plains of Canada and there is also a mirabilite bed preserved beneath Holocene sediments in Great Salt Lake, Utah. Last century, some of the richer subaqueous salt beds in the Canadian lakes were sources of commercial NaSO₄ salts (Figure 5). However, extraction of brine and solid salts and an increasingly expensive product meant this area no longer competes with cheaper product from the solar evaporite process.

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bic forms of halite) and crystals or NaCl-filled pseudomorphs have been recognised in a number of modern cold saline lake settings. For example, hydrohalite has been extracted from the lake bottom sediments in saline Lake Bonney in Antarctica, where the bottom water temperatures vary between +2.0 and -2.0°C. It also can precipitate in winter in the Baskunchak salt lake, located some 300 km northwest of the Caspian Sea (48°N latitude). There hydrohalite was directly observed on two occasions when formative brine temperatures were between -3° and -23°C. In summer, halite precipitates via solar evaporation in the same saline lake. Hydrohalite also occurs in bottom sediments in salt-saturated cryogenic lakes in Saskatchewan, at about 51°N latitude, and has been observed in nearby saline springs sediments of the Northern Great Plains. Hydrohalite pseudomorphs occur as halite crystals with hexagonal cross sections in cores some 100-140m deep, in Death Valley, California, indicating NaCl cryogenesis occurred in the Pleistocene Death Valley Lake at a time when brine temperatures were less than 0°C.

When polar seawaters freeze on Earth, hydrohalite and mirabilite precipitate from the residual marine brines and accumulate in ice sheet fissures, or in load-induced fractures in the ice understory wherever an increasingly saline brine sinks into rock fractures beneath the growing ice sheets. For example, there are mirabilite layers on the ice floes of the Ross Ice Shelf near Black Island. Likewise, there are dense residual saline brines in interstitial waters extracted from deep cores in sediments of McMurdo Sound. It seems that when ice sheets retreat, the at-surface cryogenic salts dissolve in the freshened at-surface hydrology, but dense hypersaline brines can remain behind in deep fissures, held and preserved in the rock fractures. In the extreme setting of at-surface brine freezing in some of the small saline depressions in the Dry Valleys of Antarctica, a solid form of calcium chloride, antarcticite, grows cryogenically. Antarcticite precipitates today in Don Juan Pond, Antarctica, in what is probably the most saline perennial natural water

![Figure 5. Canadian cryogenic Lakes. A) Ingebright Lake, B) Freefight Lake, Saskatchewan, Canada, showing perennial lake areas and surrounding saline pan - mudflat. These are two of numerous such NaSO4 lakes scattered across the Canadian Great Plain.](image)

Historically, cryogenic NaSO₄ was mined or extracted via brine processing in the cold arid regions of the former Soviet Union and Canada.
mass on Earth (47% salinity). Although the Don Juan pond is often cited in the saline literature as a most impressive example of an extremely-hyper-saline modern closed-basin cryogenic hydrology, it should be pointed out that this cryogenic salt pond measures some 100 by 300 metres across and is tens of centimetres deep (Figure 7).

On Earth, the volume of salt beds formed by cryogenesis is much less than the volumes that result from solar evaporation. Extraterrestrially, in planets and moons of our solar system with liquid water and located further out than the earth’s orbit, there are likely, at least locally, volumes of cryogenic salts that are significant. Cryogenesis explains sulphate salt (epsomite-dominant) phases that typify ice crack fissures crisscrossing the surface of Europa (a moon of Jupiter). Sulphate salts also grow seasonally in soils of Mars where, for example, widespread gypsum forms via ice ablation in the circumpolar Martian dune-field. But, for now, I will leave the discussion of the significance of these extraterrestrial cryogenic salts, it will be the topic of a future blog dealing with liquid water indications in and on a variety of planets and moons located beyond the earth’s orbit.

On Earth, as ground temperatures increase, cryogenic salts tend to deliquesce or convert to their higher temperature daughter salts (thenardite, glauberite and halite). But worldwide, in appropriate cold climatic settings, there are numerous examples of cryogenic salt beds; the volumes grow even larger if we include sediments containing cryogenic hydrated calcite (ikaite-glendonite; Ca\(\text{CO}_3\cdot6\text{H}_2\text{O}\)). Across deep time, the volume of cryogenic salts increases during glacial episodes, their susceptibility to deliquescence and conversion as temperatures increase means a low propensity for significant preservation other than as pseudomorphs. If such pseudomorphs are to be found across the rock record, then there will be a greater likelihood of their retention and recognition in sediments of the late Tertiary, the Permo-Carboniferous, the Ordovician and the late Neoproterozoic, which are all times of an icehouse climate.

Figure 7. Dry Valleys, Antarctica showing relative positions and sizes of Don Juan pond and Lake Vanda, sites of cryogenic CaCl\(_2\) and CaCO\(_3\), respectively. The base geotiff is from <http://eoimages.gsfc.nasa.gov>.

Antacticite, a CaCl\(_2\) mineral, salts out cryogenically as the pond almost freezes
This pond, Don Juan Pond, contains some of the Earth’s saltiest waters and never completely freezes