Calcium Chloride (CaCl$_2$) Article 2 of 2: CaCl$_2$ minerals across time and space

Introduction
Found in association with some highly-saline calcium chloride brines are four naturally occurring CaCl$_2$ minerals with evaporite associations, namely; 1) tachyhydrite CaMgCl$_2$.12H$_2$O, 2) antarcticite (CaCl$_2$.6H$_2$O), 3) sinjarite (CaCl$_2$.2H$_2$O) and 4) chlorocalcite (KCaCl$_2$). For any CaCl$_2$ salt to precipitate in a saline setting requires a Ca-enriched mother brine completely depleted in sulphate (Table 1). Otherwise, gypsum precipitates and in so doing removes all calcium from the concentrating brine, well before the bittern stage.

Of the four, tachyhydrite is perhaps the most common solid phase, sinjarite or chlorocalcite the least. Bischofite is sometimes a co-precipitate with tachyhydrite and indicative of a mother brine with an elevated MgCl$_2$ content (Figure 1). Even so, tachyhydrite is still a rare bittern mineral phase across the Phanerozoic of Earth, although as we shall see later, the situation may be a little different on the martian regolith. Along with carnallite and bischofite, tachyhydrite typifies highly saline marine bittern assemblages in only a few ancient potash-rich evaporite systems. These same systems are also MgSO$_4$ poor, and tend to de-mineralise the mother brine with an elevated MgCl$_2$ content completely depleted in Mg, otherwise tachyhydrite forms, along with carnallite and bischofite. Carnallite, bischofite and tachyhydrite are not part of the bittern suite precipitated from today’s MgSO$_4$-rich oceans, where sulphate and magnesium levels are too high relative to calcium. At times in the past, these three salts were more common precipitates in the bittern stages of ancient CaCl$_2$ or MgSO$_4$-depleted oceans. These tended to be at times when rates of seafloor spreading, and hence volumes of through-circulated seawater, were greater than today (Lowenstein et al., 2014). It seems that most the highly

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mineral Properties: Mohs hardness, S.G., lustre, colour, other</th>
<th>Occurrences (natural sedimentary occurrences only)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antarcticite</td>
<td>simple halide – hydrated) 2-3, 1.7, vitreous, deliquescent, colourless</td>
<td>Hydroscopic, cryogenic, precipitate in the hyperarid Don Juan pool, Wright Valley, Antarctica (type area) and in association with halite, gypsum and celestite in anthropogenic brine seepage pools excavated in Bristol Dry lake, California. Also occurs in minor amounts in the Kunetl Salt Lake on the Tibetan Plateau</td>
<td>Tori and Ossaka, 1965; Dunning and Cooper, 1969; Kezaaio and Bowler, 1986</td>
</tr>
<tr>
<td>Sinjarite</td>
<td>hydrated halide) 1.8, 1.5, vitreous-resinous, light pink</td>
<td>Found in detritus in a wadi cutting across the Sinjar anticline, Iraq. Highly deliquescent. See also Antarcticite. Also present in hypromaline fluid inclusion in quartz in the meta-evaporites of the western Zambian copper Belt, Africa</td>
<td>Aljubouri and Alldabonbargh, 1980; Eglinger et al., 2014</td>
</tr>
<tr>
<td>Tachyhydrite</td>
<td>(hydrated halide) 2, 1.7, vitreous, colourless, wax yellow to pale yellow, highly deliquescent, very sharp, bitter taste</td>
<td>Is a minor component of some marine evaporite deposits, especially Aptian evaporites in Brazil, Thailand, Laos and China, where its relatively widespread occurrence is tied to MgSO$_4$-depleted world ocean chemistry</td>
<td>Clark et al., 1980; Warren, 2016</td>
</tr>
<tr>
<td>Chlorocalcite</td>
<td>(simple halide) 2.5-3, 2.2, white, tinged violet, deliquescent. Also known as hydrophilite and baemurite.</td>
<td>Cretaceous Maha Sarakham Fm., Thailand and equivalents in Laos and China. Co-association with antarcticite in Bristol Dry Lake, California, intergrown with tachyhydrite in the Desembea potash mine, Leinetal, Prussia and possibly with bischofite at Stassfurt, 34 km south of Magdeburg, Saxony-Anhalt, Germany.</td>
<td>Renner, 1912; Li et al., 2015; Warren, 2017</td>
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Table 1. Natural occurrences of CaCl$_2$ salts.
Saline calcium chloride brines form in sedimentary basins with a thick evaporite near the base of the sediment fill (see article August 11, 2015). But, not all are basins with highly saline CaCl₂ brines co-associated with bedded tachyhydrite occurrences in the buried and dissolving evaporite units (see Part 1).

**Antarcticite**

Antarcticite (CaCl₂·6H₂O) is extremely hygroscopic, colorless with perfect basal cleavage and good to perfect prismatic cleavage, is brittle with a hardness between 2 and 3, and has a specific gravity of 1.715 ± 0.010 (14 °C), and a density of 1.700 g/cm³ (Dunning and Cooper, 1969). The lowest temperature for antarcticite to precipitate is -50 °C and its melting point is 30 °C.

There are only two known modern hypersaline saline deposits where the pure calcium chloride mineral antarcticite (CaCl₂·6H₂O) is present as thin crystal beds and efflorescences; they are, Bristol Dry Lake (BWh) in California and Don Juan Pond (EF) in the Wright Valley, near Lake Vanda in Antarctica (Dunning and Cooper, 1969; Horita, 2009). Both saline lakes possess similar CaCl₂-enriched, MgCl₂-depleted chemistries and are fed in part by hydrothermal waters. In Bristol Dry Lake the concentration process is driven by solar evaporation, while deliquescence and cryogenesis are the primary drivers in Don Juan Pond and its surroundings. Only in Bristol Dry Lake is a CaCl₂ brine is commercially extracted from Quaternary sediments. There is also a minor occurrence as...
isolated small crystals in the Kunteyi Lake of the Tibetan Plateau (Kezao and Bowler, 1986; Zheng and Liu, 2009)

**Don Juan Pond, Antarctica**

Don Juan Pond is a perennial free-standing water body, approximately 300 m long and 100 m wide, surrounded by glacial moraine deposits in the Wright Valley, Antarctica (Figure 2). It defines the outcrop portion of a hypersaline liquid water drainage sump that retains a 10-cm-deep CaCl₂ brine at the surface (Torri and Ossaka, 1965; Marion, 1997; Burt et al., 2003) (Figure 2). This pool contains some of the saltiest free-standing perennial waters on the earth's surface, with concentrations ranging up to 40% (by mass; Dickson et al., 2013). Mean annual precipitation the Don Juan Pond region is 5 to 10 cm and air temperatures range from −55°C to +10°C (Marion, 1997). The pond does not freeze because it is an eutectic brine of H₂O, CaCl₂, and NaCl, with a freezing point of -52°C and a density of approximately 1.4 (Marion, 1997; Burt et al., 2002). Crystals of antarcticite were first found sticking out of the brine at the bottom of the pond, with halite and gypsum fringes at the edges of the pond (Torri and Ossaka, 1965).

Precipitation of antarcticite in this cryogenic environment is the result of the arid climate, ongoing cold temperatures and a CaCl₂ brine chemistry (Torri and Ossaka, 1965). The CaCl₂ brine is in part derived from springs fed by a deep, confined, basaltic aquifer, with a groundwater similar in composition to the surface brine (Harris et al., 1979; Marion, 1997; Burt et al., 2002). The origin of the CaCl₂ is still contentious, but is most likely be related to mineral weathering and periodic deliquescence of calcium chloride held in the surrounding sediments (Dickson et al., 2013).

Brine in the Don Juan Pond is predominantly a CaCl₂ solutions (Figure 3; Marion, 1997). Only Na of the remaining cations contributes significantly to the overall charge balance. Both Mg and K are present at very low concentrations, and SO₄ is usually not detectable. In contrast to low ionic variability in seawater composition, levels of the dominant ions (Ca, Na, and Cl) in the Pond are highly variable (Figure 3). The concentration of the brine varies seasonally, controlled mainly by a complex hydrologic system including groundwater discharge, melting of nearby permafrost, rare precipitation, and evaporation or sublimation (Harris et al., 1979; Dickson et al., 2013). Despite the changes in the absolute concentration of Ca and Cl across an annual cycle, the Ca/Cl molal ratio remained relatively constant over the 23-year sampling period; it varied between 0.432 and 0.506 with an average of 0.462 ± 0.018 (Figure 2; Marion, 1997).

**Bristol Dry Lake, California**

Bristol Dry Lake is a 155 km² continental playa located within a closed Basin and Range valley in the Mojave Desert of southern California (Figure 4a). It is the second known location of natural antarcticite and is thought to this CaCl₂ salt from ponded supersaline lake brines via a lowering of brine temperatures (Dunning and Cooper, 1969). No antarcticite was identified in the nearby

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**Figure 3. Molalities of brines collected at various times from Don Juan Pond, Antarctica (plotted from data in Table 1, Marion, 1997).**
Cadiz or Danby dry lakes. Lake brines first concentrate by solar evaporation beyond halite precipitation. Mountains surrounding Bristol Dry Lake are composed mostly of pre-Cambrian and Mesozoic granite, some Palaeozoic carbonates, and Tertiary and Pleistocene volcanic rocks including Quaternary olivine basalts that erupted from nearby Amboy Crater. Alluvial fans are present between the mountains and the lowest parts of the valley (Dunning and Cooper, 1969; Handford, 1982).

Bristol Dry Lake playa contains more than 300 m of interbedded halite and salt-bearing sands, silts and clay. Halite and gypsum are currently deposited from ephemeral bodies of water under evaporative conditions, with a gypsum pavement surrounding more saline halite-saturated sumps in the central lake depression (Figure 4a; Dunning and Cooper, 1969; Handford, 1982). The primary evaporite minerals at Bristol Dry Lake are gypsum, anhydrite, and halite with rare antarcticite, celestite (SrSO₄), calcite, and possibly chlorocalcite (KCaCl₃). Bristol Dry Lake is mined for its chloride minerals and has been since the 1900s, and so is covered with pits and trenches (Figure 4b).

Antarcticite was identified in one of these previously excavated trenches approximately 9 kilometres south of Amboy, near the road from Amboy to Twenty-nine Palms. Dunning and Cooper (1969) examined this and other trenches during the winters of 1961, 1962, and 1968. Only one trench had antarcticite. The trench was 3 m deep, 20 m long, and contained a 10 to 25 cm deep pool of CaCl₂ brine extending along the length of the trench. At the base of the pit was a massive halite deposit, with acicular groups of antarcticite protruding outward from the halite and within the brine. Antarcticite is not present on the playa surface as no surface brines are present. The only CaCl₂ brines exposed to solar radiation are subsurface brines that have seeped into, and are now exposed within, the excavated trenches.

Dunning and Cooper (1969) suggested that CaCl₂ brines at Bristol Dry Lake originated from chlorine of volcanic origin interacting with calcium carbonate in surrounding
alluvial deposits (Figure 5). Lowenstein et al. (2009) argue that the nearby active magma chamber drives the formation of Ca-Cl brines at elevated temperatures, as well as the thermally-driven transportation of these brines to the surface. Other evidence for the magma chamber involvement in the lake hydrology is the Amboy crater and its associated recent lava flows, which occur directly North of Bristol Lake (Figure 4). Evaporative concentration of this calcium chloride brine, driven by an arid climate and typical surface temperatures below 30°C, encourage antarcticite precipitation (Dunning and Cooper, 1969).

Sinjarite (CaCl\(_2\cdot2\text{H}_2\text{O}\))

Sinjarite is a modern ephemeral precipitate in surficial alluvial fan sediments near Sinjar in Iraq (Figure 6). No natural occurrences of either antarcticite or sinjarite have been documented in ancient salts, except as a volumetrically insignificant mineral phase in brine inclusions in both sediments and igneous rocks (Polozov et al., 2016), even in sedimentary basins containing highly saline CaCl\(_2\)-rich pore fluids.

Sinjarite is an extremely rare pink-tetragonal-hygroscopic mineral that is highly soluble with 117 g dissolving in 100 g of water at 20 °C (Table 1; Aljubouri and Aldabbagh, 1980). The lowest temperature for sinjarite to precipitate is 42.3 °C, while its melting point is 175.5 °C. Theoretical composition of sinjarite is 27.26% Ca, 48.24% Cl, and 24.50% H\(_2\)O but the actual chemistry for sinjarite present at its type locality in Iraq is 25.84% Ca, 46.64% Cl, 26.55% H\(_2\)O, and 0.85% Na with 226 ppm K and trace amounts of Mg, Sr, and Fe (Aljubouri and Aldabbagh, 1980). Properties include; good cleavage, average density of 1.81 g/cm\(^3\), a very deliquescent habit, hardness of 1.5, vitreous to resinosus lustre, white streak, and occurs naturally in massive to granular forms.

Little research has been performed on sinjarite and knowledge of the environment of formation comes from the only place it was discovered. Sinjarite occurs in detritus in a wadi cutting through the Sinjar anticline near the town of Sinjar, Iraq (west of Mosul). Sinjarite precipitates via slow evaporation of groundwater saturated with Ca and Cl ions. CaCl\(_2\) in the groundwater solution must be 3.5 times greater than NaCl for sinjarite to precipitate instead of halite. The extremely deliquescent nature of sinjarite means that the mineral is ephemeral and quickly dissolves in wet seasons or changes to the hexahydrite antarcticite when the temperature is less than 30°C (Aljubouri and Aldabbagh, 1980).

CaCl\(_2\) salts and liquid water flows on current-day Mars

It has been recently proposed that aqueous solutions form seasonally on the current Martian surface, via the periodic deliquescence of hygroscopic salts in contact with atmospheric water vapor. Regions of these hygroscopic salts are thought to be indicated by occurrences of surface features known as recurring slope lineae - RSL (Figure a, b; Chevrier and Rivera-Valentin, 2012). Older studies largely focused on perchlorate species as the most likely set of hygroscopic salts driving the periodic formation of RSLs, but another Mars-relevant set of salts, with similar low eutectic temperatures, relevant to ambient regolith conditions with a significant deliquescence potential, are the calcium chloride hydrates, antarcticite and sinjarite. Gough et al. (2016) propose hydrated calcium chloride salts are linked to RSL formation on Mars. They also note deliquescence of CaCl\(_2\), not perchlorate, is also known to be responsible for the only terrestrial RSL analog known thus far: these are the seasonal water tracks in the McMurdo Dry Valleys, especially in the vicinity of the Don Juan Pond, as documented by Dickson et al., 2013 (Figure 8).
Soluble regolith salts like perchlorate and calcium chloride salts with low eutectic temperatures are likely to deliquesce at low relative humidity (RH) values at a wide range of temperatures (Gough et al., 2016). Deliquescence is the process by which a solid crystalline phase absorbs water vapor to form a saturated aqueous (liquid) solution. This phase transition from solid salt to liquid brine occurs at a deliquescence relative humidity (DRH), the value of which is specific for each hydration state of each salt and often varies with temperature. A salt is expected to be aqueous whenever the temperature is above the eutectic temperature of the salt and the relative humidity is above the DRH, although at much higher RH values ice may form. The low temperature deliquescence of perchlorates has been extensively studied (Gough et al., 2011, 2014; Nuding et al., 2014; Zorzano et al., 2009). Many perchlorate species have deliquescence relative humidity (DRH) values below 40% RH, and so should deliquesce and be

Figure 7. Recurring Slope Linea (RSL) on Mars (images courtesy of NASA and wikiwand.com). A) Dark narrow streaks, called “recurring slope lineae,” emanate seasonally from the walls of Garni Crater on Mars. The view constructed from observations by the High Resolution Imaging Science Experiment (HiRISE) camera on NASA’s Mars Reconnaissance Orbiter. The dark streaks here are up to few hundred yards, or meters, long and are hypothesized by NASA to be formed by flow of briny liquid water on Mars, perhaps due to seasonal deliquescence of CaCl₂ salts. B) 3D reconstruction of RSL on edge of Newton Crater. C) Planet-wide known occurrences of RSLs (blue square), salts (red square) and ice (white square).
stable or metastable liquids under Martian surface conditions (Chevrier et al., 2009), although slow reaction kinetics may limit their formation (Fischer et al., 2014). Not as much attention has been paid to other soluble, deliquescent salts, especially the calcium chloride salts, that may be present in the martian regolith.

Chlorine has been detected by rovers and landers in every Martian soil sample analyzed to date and is found at similar concentrations (≈0.2 to 1%) in all locations (Glavin et al., 2013). The form of the chlorine (i.e. chloride vs. perchlorate) is unknown at some sites, although measurements of the regolith at the Phoenix landing site confirmed chloride, perchlorate (Hecht et al., 2009) and probably chlorate (Hanley et al., 2012). The identity of the associated cation(s) is also generally unknown, although calcium, sodium, magnesium and potassium are the most likely candidates (Hecht et al., 2009). Regionally and globally widespread chloride deposits have also been detected by orbiting spectrometers (Figure 7c; Osterloo et al., 2010; Keller et al., 2006).

The global distribution of chloride deposits across the Martian surface is similar to that of recurring slope lineae (RSL), prompting hypotheses of a relationship between the two (Figure 7c; McEwen et al., 2011; Stillman et al., 2017). Chevrier and Rivera-Valentin (2012) suggest that CaCl$_2$ is one of the best candidates for the formation of RSL, the narrow, dark features that appear and grow seasonally on Mars and appear to be caused by flowing liquid.

Two hydrated chloride salts, MgCl$_2$ and CaCl$_2$, may be the most appropriate salts because the seasonality of observed RSL formation best matches the seasonality of the melting of ice associated with these salts (Chevrier and Rivera-Valentin, 2012). Specifically, these chloride salts have eutectic temperatures less than or equal to the threshold temperature of 250 K that seems to mark the start of RSL activity (McEwen et al., 2011), but the eutectic temperatures of these salts are not so low that brines on Mars would be permanently liquid. Additionally, calculations show that CaCl$_2$ in particular will cause seasonal melting of water ice throughout the top 20 cm of the martian regolith, therefore providing greater potential fluid flow than other salts (Chevrier and Rivera-Valentín, 2012). More recently, hydrated chloride salts (although not specifically calcium chloride) were observed to be present in RSL but not in surrounding regions (Ojha et al., 2015). It is not generally believed that deliquescence could be fully responsible for RSL formation because the small amount of water vapor in the martian atmosphere would limit the condensed phase water that could form. It is certainly possible, however, that salt deliquescence may be involved in the formation of RSL or in their appearance or behavior (McEwen et al., 2011; Ojha et al., 2015; Dickson et al., 2013; Stillman et al., 2017).

In summary, determining whether liquid water exists on the Martian surface is central to understanding the hydrologic cycle and potential for extant life on Mars (Ohja et al., 2015; Stillman et al., 2017). Recurring slope lineae, narrow streaks of low reflectance compared to the surrounding terrain, appear and grow incrementally in the downslope direction during warm seasons when temperatures reach about 250–300 K (−23°C to +26°C), a pattern consistent with the transient flow of a volatile material. Brine flows (or seeps) associated with seasonal deliquescence of hydrated salts (possibly hydrated calcium chloride salts or perchlorates) are proposed to explain the formation of recurring slope lineae. As yet, no direct evidence for either liquid water or actual hydrated salt mineralogies has been found.
Tachyhydrite

Tachyhydrite (CaMg\(_2\)Cl\(_6\).12H\(_2\)O) (occasionally spelled tachydrite or tachhydrite) is a yellow, transparent to translucent, trigonal-rhombohedral mineral with very high solubility. Pure tachyhydrite is composed of 7.74% Ca, 9.39% Mg, 41.10% Cl, 37.09% O, and 4.67% H (Wardlaw, 1972). Its chemical formula is most accurately expressed as \([\text{Mg}(\text{H}_2\text{O})_6]\text{CaCl}_6\) because the structure consists of Mg(H\(_2\)O)\(_6\) octahedra and CaCl\(_6\) octahedra loosely linked together by hydrogen bonds. Physical properties include; good cleavage, vitreous to greasy lustre, white streak, massive habit, bitter taste, deliquescent habit (dissolves or liquefies upon exposure to air), a density of 1.66 g/cm\(^3\), a hardness of 2, and it is hygroscopic (Braitsch, 1971).

Tachyhydrite is extremely soluble with 160 g dissolving in 100 g of water at 20 °C, and its solubility increases with increasing temperature (D’An, 1961; Wardlaw, 1972). Its hygroscopic and extremely deliquescent nature means a crystal becomes liquid by absorbing moisture in the air. On exposure, tachyhydrite quickly alters to a residue of bischofite (MgCl\(_2\).6H\(_2\)O) and a CaCl\(_2\).nH\(_2\)O phase (Wardlaw, 1972). This is why tachyhydrite is typically documented in natural occurrences where a crystal is still encased in halite. Tachyhydrite has a wide thermal stability field from 21.95°C to at least 167°C (Braitsch, 1971; Clark et al., 1980). The lowest temperature for tachyhydrite precipitation is 21.95°C at a concentration of 92.7 mol CaCl\(_2\)/1000 mol H\(_2\)O (450 g CaCl\(_2\)/liter (D’An, 1961; Braitsch, 1971; Wardlaw, 1972). Its lowest temperature of formation increases by 0.0162°C for every atmosphere of pressure (D’An, 1961).

Modern tachyhydrite occurrences

Natural tachyhydrite is documented only in a few modern hypersaline settings and it never forms a bed with primary precipitation textures (Figure 9). It is found in greater quantities in some ancient potash deposits. Tachyhydrite occurs seasonally as a minor interstitial cements and efflorescences, along with antarcticite (the hexahydrate form of calcium chloride), in the modern ephemeral halite crusts, atop sabkhas, of the Gavkhoni Playa (BWk), southeast of Isfahan, Iran (Pakzad and Ajalloeian, 2004), in mine waters in the Salar de Pederales in the andean Altiplano, and perhaps as minor salt efflorescences in the uppermost parts of the Abu Dhabi sabkha (Wood et al., 2005).

Much of the elevated ionic content of various Iranian playas in the Great Kavir is due to salt dissolution of the crests of nearby at- or near-surface diapirs and namakiers, where the mother salt sourced in halokinetic Miocene marine salts (Warren, 2008). These outcropping diapirs have carried carnallite and sylvite remnants into the namakiers that now reside at the surface (Rahimpour-Bonab and Kalantarzadeh, 2005). Tachyhydrite is also found as white feathery efflorescences within waste piles at an abandoned borate working along the southwestern margin of Salar de Pederales, Chile (BWk Koeppen climate location very near the ET climate boundary; Ericksen et al., 1989).

It seems that tachyhydrite’s high solubility means it has little or no preservation potential as a solid salt in any modern at-surface depositional setting; in the Peruvian case, it is a winter precipitate that disappears with the end of winter. In Abu Dhabi it, along with other highly soluble salts in the salty surface efflorescences, can disappear in morning dew (Warren, pers. obs.). In both the Iranian

Figure 9. Documented natural occurrences of tachyhydrite, modern and ancient. Extracted with permission from the SaltWork Database Version 1.7.
and the Peruvian settings the climate is cool and elevated. It seems the arid desert environments where bedded subaqueous-textured tachyhydrite accumulated in the drawn-down Aptian seepage basins of the opening Atlantic were very different to its occasional rare occurrence in the evaporite settings of today.

Cretaceous of Brazil & W. Africa

Lower Cretaceous (Aptian) evaporite deposits in Sergipe, Brazil, and Gabon and Congo in western Africa contain significant amounts of tachyhydrite in halite-carnallite beds, along with other SO$_4$-poor bitterns (Figure 10; Wardlaw, 1972; Borchert, 1977; de Ruiter, 1979; Hardie, 1990; Garrett, 1995; Zhang et al., 2017). These evaporite basins formed during the early Cretaceous rifting of Africa and South America. In each basin, potash-rich halite-dominant evaporites are transitional between older continental pre-rift and rift siliciclastics and younger post-rift marine shales and carbonates (Wardlaw, 1972, Borchert, 1977; de Ruiter, 1979; Szatmari et al., 1979; Hardie, 1990; Garrett, 1996).

The basic salt cycle of the Gabon and Congo basins includes from bottom to top: (1) thin black shale, (2) halite, (3) combination of halite and carnallite (carnallitite), and (4) bischofite and/or tachyhydrite (Figure 10; de Ruiter, 1979; Zhang et al., 2017). Although variations exist, a similar sequence is present in Sergipe, Brazil comprising the Ibura Member of the Muribecca Formation. The Ibura Member includes from bottom to top: (1) halite, (2) carnallite, (3) tachyhydrite, (4) sylvinite (KCl) and halite, and (5) anhydrite (CaSO$_4$) (Wardlaw, 1972; Borchert, 1977; Garrett, 1996). Tachyhydrite is located within the central and deepest portions of the Sergipe basins (Wardlaw, 1972; Borchert, 1977; Szatmari et al., 1979).

The origin of the evaporite sequences in Sergipe, Gabon and Congo is controversial with some authors suggesting a marine origin (Wardlaw, 1972; de Ruiter, 1979; Szatmari et al., 1979) or diagenetic origin (Borchert, 1977). More recent literature discussing Sergipe, Gabon, Congo, and other similar tachyhydrite deposits cite a non-marine/hydrothermal origin based on geochemical and textural studies (Lowenstein et al., 1989; Hardie, 1990; Garrett, 1996; El Tabakh et al., 1999). Yet other recent authors indicate a marine source based on its dominance in beds with a CaCl$_2$ oceanic timing (Warren, 2016; Zhang et al., 2017).

The brine that tachyhydrite precipitated from must have been high in Ca because in waters with more SO$_4$ than Ca present, the Ca is used-up by gypsum or anhydrite. Only if the Ca level is greater than SO$_4$ in the early stages of precipitation will Ca stay in the brine allowing for potential precipitation of tachyhydrite (Wardlaw, 1972; Hardie 1990). The CaCl$_2$-rich brine that produced the tachyhydrite and other potash salts is thought to have formed either by the interaction of hot meteoric groundwater with rift-related sediment and bedrock, or an influx of seawater at a time of a MgSO$_4$-depleted ocean. Based on figure 1, Hardie (1990) suggests heated seawater could also have interacted with sediment and/or bedrock to produce a CaCl$_2$ brine. This hot CaCl$_2$ brine was perhaps driven to the surface by thermal circulation (Hardie, 1990). Alternatively, without arguing that the proportions of major ions in seawater change over time, the fact that modern marine water cannot precipitate tachyhydrite precludes it being the dominant mother brine in the Sergipe, Congo, and Gabon Basin evaporite basins, (Lowenstein et al., 2014; Warren 2016).

Textures recovered in core, and visible in mine walls in Brazil, indicate Sergipe tachyhydrite was a primary bedded precipitate in those circum-Atlantic Cretaceous evaporite basins with stratiform tachyhydrite units in potash beds (Figure 10; Wardlaw, 1972). The Cretaceous world ocean at the time this tachyhydrite precipitated was typified by Mg-SO$_4$-free marine bitterns. Figure 9 shows tachyhydrite does not occur as a bittern phases in many other potash sequences deposited in basinwide settings at other times of CaCl$_2$ oceans (e.g. the Devonian of Canada, the Silurian of the Michigan Basin). This has led to the argument that stratabound tachyhydrite in potash beds indicates an additional hydrothermal/basinal source for the mother brine. If so, the presence of tachyhydrite is not solely indicative of a MgSO$_4$-depleted marine feed to the basin (Hardie 1990).
Cretaceous occurrences in Thailand

Another significant tachyhydrite occurrence is within mid Cretaceous (Cenomanian) evaporites of the Maha Sarakham Formation on the Khorat Plateau of northeastern Thailand (Figure 11). The majority of the Maha Sarakham Formation consists of alternating anhydrite and halite, separated by mudstone and siltstone “redbeds”. A 10- to 75-m-thick salt unit overlies a lower halite unit and underlies mudstone red beds. Carnallite is most abundant, but sylvite and halite are also abundant. Tachyhydrite is present with halite and carnallite, but not with sylvite and is perhaps concentrated more in former basin centre or sump positions (El Tabakh et al., 1999; Warren, 2016). Hite and Japakasetr (1979) estimated that tachyhydrite comprises less than 30% of the total carnallite deposit, but tachyhydrite does form pure layers up to 16 m thick. Tachyhydrite crystals are euhedral and average 1 mm in size (El Tabakh et al., 1999). Sylvite and halite are also associated with accessory amounts of hilgardite \((\text{Ca,BCl(OH)}_2)\) and boracite \((\text{Mg}_3\text{ClB}_2\text{O}_5)_m\).

The origin of the Maha Sarakham Formation evaporites is still contentious; Hite and Japakasetr (1979) advocate a purely marine origin (highly restricted and concentrated sea), Hardie (1990) advocating an exclusively non-marine origin (hydrothermal \(\text{CaCl}_2\) brines), and El Tabakh et al. (1999) advocate an alternating marine and non-marine origin. They envisage an inland basin that was periodically inundated by the rising sea and at the time of tachyhydrite deposition received an additional influx of hydrothermal \(\text{CaCl}_2\) brines. Hardie (1990) states that formation of Maha Sarakham evaporites may have been similar to that of tachyhydrite formation in the Cretaceous basins of Brazil and western Africa, although he offers no evidence for the origin of the hydrothermal \(\text{CaCl}_2\) brines. El Tabakh et al. (1999) suggested that hydrothermal \(\text{CaCl}_2\) waters entered the restricted marine basin and created the right conditions for tachyhydrite precipitation and they cite contemporaneous granitic intrusions as possible evidence of thermal activity during the time of tachyhydrite formation.

**Hydrothermal oceanic \(\text{CaCl}_2\) brine**

Today, large volumes of relatively dilute, oceanic \(\text{CaCl}_2\) brines form via hydrothermal circulation and thermal-driven alteration of mid-ocean ridge (MOR) lithosphere. These \(\text{CaCl}_2\) waters occur in and near active fracture zones, wherever seawater interacts with labile basalt (oceanic crust) at elevated temperatures and converts the circulating fluid from a Na–Mg–Cl water into a low-salinity Na–Ca–Cl brine, depleted in Mg and SO\(_4\). Similar hydrothermally-driven alteration of continental basalts via deeply circulated seawater interactions forms modern \(\text{CaCl}_2\)-rich brine seeps, for example, within the thermally active continental Danakil rift valley (Hardie, 1990).

**Tachyhydrite is a 'Swift Water' mineral**

There may be an additional factor at work in terms of our recognition of tachyhydrite’s basin-by-basin distribution across the Phanerozoic. That factor is tachyhydrite’s high solubility in most subsurface waters and drilling muds. Even the name, tachyhydrite, was chosen from the Greek tachy hydros for “swift water” to indicate its rapid dissolution on exposure to atmospheric conditions. This property means that any ground-up remains (rock chips) of tachyhydrite in a return mudstream in a conventional drilling operation typically do not make it to the surface. Ancient tachyhydrite has only been found encased in halite in recovered cores and mine walls, never in drill cuttings, and its presence or absence can be easily misinterpreted in wireline logs, especially when drilling through thick salt masses in the search for oil and gas (companies tend to run a more limited log suite in thick salt units). So, as most
oil companies prefer not to core evaporites when drilling for hydrocarbons trapped beneath salt, there may be more tachyhydrite occurrences in deeply buried basin evaporites than the few currently documented.

Tachyhydrite’s lack of shear strength and extremely high solubility makes mining any associated potash beds difficult; it presence leads to head beam and floor stability problems in conventional underground mines in Brazil and West Africa. Holle, a West African potash mine in the 1970s, was never economical and was lost to flooding after a few years of conventional mining and the Brazilian mine has ongoing floor and wall stability problems ties to tachyhydrite-induced heave. Today, solution mining is proposed as a more efficient means to exploit areas of Cretaceous potash associated with tachyhydrite beds, as in Aptian halite-potash associations on both sides of the Atlantic. High levels of tropical humidity mean at-surface potash evaporation pans are not viable in either area, so brine concentration and processing will probably require a more expensive option involving motorised dryers.

Not only is tachyhydrite highly soluble, but it is also highly reactive whenever in comes into contact with subsurface bitterns. Based on its occurrence in the Permian Stassfurt series in Germany, D’Ans (1961) suggested that much of the widespread polyhalite found in the CaCl₂, brine-rich parts of the Zechstein Basin was a reaction product indicating former tachyhydrite. He noted that, at temperatures higher than room, there is a reaction between gypsum/anhdydrite, sylvite and tachyhydrite-bischofite, or their dissolution-related brines, which removes tachyhydrite to form diagenetic polyhalite and calcium chloride brines;

\[
\text{CaMgCl}_2\cdot12\text{H}_2\text{O}+4\text{KCl}+8\text{CaSO}_4 \rightarrow 2\text{CaSO}_4 \cdot \text{Mg(SO}_4)_2(\text{H}_2\text{O})_2 + 5\text{CaCl}_2 + 4\text{H}_2\text{O}
\]

This was the mechanism suggested by Manheim (1974) to explain the lack of tachyhydrite, and the formation CaCl₂-rich brines that characterise hydrothermal pore waters circulating in sediments associated with buried Miocene evaporites along the deep axial trough of the Red Sea.

Terrestrial CaCl₂ minerals across time

The high solubility of CaCl₂ minerals means that, with the exception of some parts of the Aptian Atlantic Potash association, even in past times of likely CaCl₂-rich oceans, calcium chloride minerals are relatively rare as primary-textured occurrences in solid salt beds. On the other hand, as we saw in part 1, CaCl₂ brines are commonplace in basinal or formation waters in many Phanerozoic sedimentary basins entraining thick sequences of dissolving ancient salt. For example, since 1914, CaCl₂ brines have been extracted from Silurian strata adjacent to Salina Salt of the Michigan Basin USA, yet there are no significant volumes of tachyhydrite documented in the Michigan Basin (Garrett, 2004).

Historically, before micro-inclusion studies of chevron halite showed that the ionic proportions of seawater likely varied across the Phanerozoic, the various CaCl₂ basin brines occurrences in Silurian and Cretaceous strata were explained as an indicator of widespread dolomitisation and other diagenetic reactions, which preferentially extracted magnesium from pore waters. Since then, some authors have argued that CaCl₂ enrichments in many ancient basin brines, including brines in the Detroit group are partial leftovers of primary seawater chemistries (Lowenstein and Timofeff, 2008). That is, Ca-enriched (MgSO₄-depleted) pore brines are indicators of ancient CaCl₂ oceans, with the pore brines being remnants from time the enclosing evaporitic and marine sediments were deposited (relict or connate brines).

Others, such as Houston et al. (2011), conclude this is not necessarily so, they agree that there are two end-members typifying highly saline subsurface brines. But they conclude that end-member chemistries relate to either substantial subsurface halite dissolution, or to preservation of early reflux-related seawater. Houston et al. (2011) go on to argue that CaCl₂-enriched formation water chemistries from many basins worldwide, including the Michigan Basin, do not support an interpretation of variation in ionic proportions in seawater across the Phanerozoic. They find that CaCl₂-rich brines formed either by dissolving bittern salts in the subsurface, or simply lost water in the subsurface after significant rock-fluid interaction had taken place. Water loss might be achieved by interaction with a gas phase at the elevated temperatures of deep burial or, alternatively, water may have been lost to clays. Both these mechanisms would have the effect of dehydrating (concentrating) the brine.

However, whatever the mechanism, it does seem that there is a Quaternary continental/pre-Quaternary marine dichotomy in the nature and distribution of CaCl₂ brines and the associated antarcticite/tachyhydrite minerals, much as there is for the world’s potash deposits (MgSO₄-enriched versus MgSO₄-depleted). On Earth, there are no documented examples of pre-Quaternary bedded antarcticite. The situation may be different on Mars.

Today terrestrial antarcticite either precipitates in the hot-arid Bristol Dry Lake or the icecap-polar setting of Don Juan Pond, neither is associated with brine sourced in seawater or derived by the recycling of older (“connate”) marine evaporite successions. Rather the occurrence of the calcium chloride minerals is in part a reponse to low temperatures and regolith cycling. Other present-day examples of regions with somewhat enriched levels of CaCl₂ surface waters, lack both tachyhydrite and antarcticite precipitates, and contain higher levels of Mg that are tied to...
deeply circulated marine/hydrothermal waters and variable interactions with MgSO₄-enriched marine salts (e.g., Lake Asal and the Dallol Salt Pan). CaCl₂ brines of the Dead Sea and the Red Sea show even more elevated levels of MgCl₂ as they are derived, at least in part by the fractionated dissolution of bedded and halokinetic Miocene marine evaporites. The Mg-rich clay palygorskite is co-associated with these CaCl₂ brines in the subsurface of the Red Sea and the Dallol.

In contrast, tachyhydrite in some ancient marine-fed basin-wide evaporite associations is found as somewhat rare, but at times bedded, units in the bittern-rich portions of the halite succession, as in the Cretaceous basinwide evaporites of Brazil, the Congo and Thailand, and as a cementing phase in the Permian Stassfurt 2 in the Zechezien (where it is commercially extracted in association with MgCl₂ brines).

All the ancient tachyhydrite examples mentioned above, are associated with the presence of widespread potash salts within adjacent salt beds. However, there are many other even larger and richer ancient potash deposits, such as the intracratonic Alberta basin (Devonian) and the Kama basins (Permian) where no tachyhydrite is documented. It seems that the terrestrial precipitation of bedded tachyhydrite is not just favoured by times of CaCl₂ oceans, it also requires additional input from saline hydrothermal/basin al waters. Such settings are most likely in the transition phases in an actively-opening hydrothermally-influenced continental rift as passes into the marine seepage realm at a time when the adjacent ocean was a MgSO₄-depleted system.

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