Introduction

In the previous two articles in this series on potash exploitation, we looked at the production of either MOP or SOP from anthropogenic brine pans in modern saline lake settings. Crystals of interest formed in solar evaporation pans and dropped out of solution as: 1) Rafts at the air-brine interface, 2) Bottom nucleates or, 3) Syn-depositional cements precipitated within a few centimetres of the depositional surface. In most cases, periods of more intense precipitation tended to occur during times of brine cooling, either diurnally or seasonally (sylvite, carnallite and halite are prograde salts). All anthropogenic saline pan deposits examples can be considered as primary precipitates with chemistries tied to surface or very nearsurface brine chemistry.

In contrast, this article discusses ancient potash deposits where the post-deposition chemistries and ore textures are responding to ongoing alteration processes in the diagenetic realm. Unlike the modern brine pans where brines chemistries and harvested mineralogies are controllable, at least in part, these ancient deposits show ore purities and distributions related to ongoing natural-process overprints.

Table 1 lists some modern and ancient potash deposits and prospects by dividing them into Neogene and Pre-Neogene deposits (listing is extracted and compiled from SaltWork® database Version 1.7). The Neogene deposits are associated with a time of MgSO₄-enriched seawaters while a majority of the Pre-Neogene deposits straddle times of MgSO₄ enrichment and depletion in the ocean waters. Ionic proportions in the feed brines to modern MOP brine factories in the Dead Sea and the Qaidam sump most closely resemble those of ancient MgSO₄-depleted oceans, while SOP factories in Great Salt Lake and Lop Nur have chemistries more enriched in MgSO₄.

Incongruent dissolution in burial

Many primary evaporite salts dissolve congruently in the diagenetic realm; i.e., the composition of the solid and the dissolved solute stoichiometrically match, while the dissolving salt goes entirely into solution (Figure 1a). This situation describes the typical subsurface dissolution of anhydrous evaporite salts such as halite or sylvite. However, some evaporite salts, typically hydrated salts, such as gypsum or carnallite, dissolve incongruently in the diagenetic realm, whereby the composition of the solute in solution does not match that of the solid (Figure 1b). This solubilisation or mineralogical alteration is defined by the
transformation of the "primary solid" into a secondary solid phase, typically an anhydrous salt, along with the loss of water formerly held in the lattice structure. The resulting solution generally also carries some ions away in solution.

More than a century ago, van’t Hoff (1912) suggested that much subsurface sylvite is the result of incongruent solution of carnallite yielding sylvite and a Mg-rich solution. According to Braitsch (1971, p. 120), the incongruent alteration (dissolution) of carnallite is perhaps the most crucial process in the alteration of subsurface potash salts and the formation of diagenetic (secondary) sylvite.

Widespread burial-driven incongruent evaporite reactions in the diagenetic realm include the burial transition of gypsum to anhydrite via dehydration (reaction 1)

$$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} \quad \text{(1)}$$

or the in-situ conversion of carnallite to sylvite via the loss of magnesium chloride in aqueous solution (reaction 2)

$$\text{KMgCl}_6 \cdot 6\text{H}_2\text{O} \rightarrow \text{KCl} + \text{Mg}^{2+} + 2\text{Cl}^- + 6\text{H}_2\text{O} \quad \text{(2)}$$

Typically, with incongruent dissolution a new solid mineral remains and the related complex solubility equilibrium creates a saline pore water that may, in turn, drive further alteration or dissolution as it leaves the reaction site (Warren, Chapters 2 and 8). Specifically for ancient potash, reaction 2 generates magnesium and chloride in solution and has been used to explain why diagenetic bischofite and carnallite have a tendency to form in lake brines.

![Table1](Table 1. Potash occurrences, listed by age, reserves listed in thousand metric tons (kt), million tons (mt), or billion (Gt) metric tons of K₂O equivalent. SOP = Sulphate of Potash, MOP = Muriate of Potash (Listing is extracted from SaltWork® Database Version 1.7; for overviews of the geology of the deposits see Garrett, 2004; Prud'homme and Krukowski, 2006; Warren, 2010, 2016 and references therein).]

<table>
<thead>
<tr>
<th>Location, country, main product</th>
<th>Age</th>
<th>Köppen</th>
<th>Brine source</th>
<th>Target unit</th>
<th>Comments/key reference</th>
</tr>
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<tbody>
<tr>
<td>Quill Lake, Canada SOP</td>
<td>Quat.</td>
<td>Dfb</td>
<td>Nonmarine</td>
<td>Lake brine</td>
<td>Saline depression in Quaternary glacial outwash. Supratill, sodium sulphate salts in lake floor beds, lake brine pumping and winter processing brine then combined with SOP (truck in) to produce SOP (Estok, 1987).</td>
</tr>
<tr>
<td>Salar de Atacama brine, Chile SOP/MOP</td>
<td>Quat.</td>
<td>BWk</td>
<td>Nonmarine</td>
<td>Lake brine</td>
<td>Brine Processing. Sylvite, MOP and SOP is recovered as byproducts of lithium carbonate production (830,000 metric tons potash in 2016). Situated in Andean Altiplano at 2250m above sealevel.</td>
</tr>
<tr>
<td>Lop Nur, China SOP</td>
<td>Quat.</td>
<td>BWk</td>
<td>Non Marine</td>
<td>Lake brine</td>
<td>Natural lake evaporites are a nonmarine assemblages of mirabilite-glauberite-polyhalite-bloedite-gypsum-halite. Recent evaporitic stages of the lake fill in Lop Nur contain massive amounts of glauberite and polyhalite, compared to the other salts present. Their predominance, is indicative of pervasive back-reactions, as is the presence of very minor amounts of carnallite and sylvite. Lake waters are processed to produce SOP (Ma et al., 2010; Dong et al., 2012). Annual capacity 1.7 million tonnes SOP. Largest set of salt ponds in world.</td>
</tr>
<tr>
<td>Dabuxum Lake, Qahran Playa, Qaidam Basin, China SOP/MOP</td>
<td>Quat.</td>
<td>BWk</td>
<td>Nonmarine</td>
<td>Lake brine</td>
<td>Carnallite (via solar processing of lake brine along with bischofite). Transtensional basin at 2675m elev. The Qahran playa region is main local supplier of potash to Chinese market (annual production of 1.2 Mt K₂O). Other Quaternary K-rich lakes in Qaidam Basin include Seni Lake and Tuanjie Playa (Duan and Hu, 2001).</td>
</tr>
<tr>
<td>Dead Sea brines, Israel and Jordan MOP (due to inflow brine mostly dissolving older marine evaporites)</td>
<td>Quat.</td>
<td>BSh</td>
<td>Nonmarine</td>
<td>Holocene anthrop.</td>
<td>Brine Processing (carnallite ppt. and converted to KCl) of lake brine pumped into a series of processing pans at southern end of Dead Sea. The Dead Sea brine contains an estimate 2 Gt of dissolved KCl, 1 Gt of MgBr₂ and 20 Gt of MgCl₂, Annual production of KCl = 3.4 Mt (MgCl₂ is coprocess) Subsealevel transtensional basin with brine surface some 415 m below sealevel. (Recent) (Zak, 1997, Garrett, 2004).</td>
</tr>
<tr>
<td>Great Salt Lake region, Utah, USA SOP</td>
<td>Quat.</td>
<td>Csa</td>
<td>Nonmarine</td>
<td>Lake brine</td>
<td>Processing of lake brines in North Arm of lake and of shallow brines in Great Salt Lake desert (Bonneville Basin) at Wendover (MgCl₂ is coprocess). Lake surface is 1270 m above msl. (Bingham, 1980; Garrett, 2004).</td>
</tr>
<tr>
<td>Paradox Potash Basin, Utah, USA MOP (due to inflow dissolving older marine evaporites)</td>
<td>Quat.</td>
<td>BSh</td>
<td>Nonmarine</td>
<td>Lake brine from Paradox Fm.</td>
<td>Solution mining of Paradox Fm. in converted conventional mine on Coke Creek anticline at a depth of 850 m. Middle Pennsylvanian collision basin related to Mara-thy-Ourichta orogeny, 18 of 20 halite cycles contain potash, mostly sylvite, (Moscovian) Tachyhydrite present (Desmoinian). (Hite, 1961; Williams-Stroud, 1994).</td>
</tr>
<tr>
<td>Daloll Saline pan, Ethiopia SOP</td>
<td>Quat.</td>
<td>BWh</td>
<td>Marine</td>
<td>Lake brine</td>
<td>Three members; uppermost is sylvite member up to 10 thick; intermediate is 3-24 m thick with carnallite throughout, (sylvite at its top and kainite at its base) and lower member is kainite that is 4-13 m thick. It is a Pleistocene marine-fed unit that now lies beneath continental halite in a subsaline (-115 m) hydrographically-isolated marine-fed rift valley, region of active volcanism and hydrothermal overprints. (Garrett, 2004; Bastow et al., 2018).</td>
</tr>
<tr>
<td>Sicilian Basin, Italy SOP</td>
<td>Mio., Late</td>
<td>-</td>
<td>Marine</td>
<td>Saltifera Series</td>
<td>Inactive since mid 1990s. Kainite was dominant ore mineral (manufactured potassium sulphate). Other minerals in ore were sylvite, kieserite, and bischofite in 2-30m thick beds dipping to 60°. Piggy-back basin in thrust belt. (Messinian) (Adamo, 1992).</td>
</tr>
<tr>
<td>Carpathian foredeep, Ukraine MOP/SOP</td>
<td>Mio., Middle</td>
<td>-</td>
<td>Marine</td>
<td>Tyanas Series</td>
<td>Stebник mine and Kaliush-Golyn region: Four evaporite cycles upper three with potash; exploited potash units composed of kainite, langbeinite, kainite-langbeinite, sylvite and carnallite rocks with layers of rock salt or interbedded clays and carbonates. Fourth bed is polyhalite. (Burdigalian-Helvetian), (Hryv et al., 2007).</td>
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### Table 1 continued

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<tbody>
<tr>
<td>Mulhouse Potash Basin, Rhine rift, France MOP</td>
<td>Eoc.-Olig.</td>
<td>-</td>
<td>Marine</td>
<td>Upper Salt Group</td>
<td>Main potash target is primary sylvinite bed in Salit IV in Oligocene Rupelian succession at depths between 420 and 1100m. Basin was a consequence of Paleogene collision between European and African plates. Periodically mined for carnallite/sylvinite ore. Subsaealevel rift graben was active along western sidewall of the Alpine orogen during collision of the Apulian indenter with the European passive margin. (Sanninoiser) (Cendon et al., 2008)</td>
</tr>
<tr>
<td>Catalonina and Navarra Potash Basins, Spain MOP</td>
<td>Eoc.-Upper</td>
<td>-</td>
<td>Marine to continental</td>
<td></td>
<td>Transitional from marine evaporite to continental, deposited in two depositions in Southern Pyrenean foreland. Sylvinite-halite at base of unit, carnallite + halite toward top (Bartonian). Lower sylvinite member is ore bed. MgSO₄-free. (Rosell and Ortí, 1981; Cendon at al., 2003)</td>
</tr>
<tr>
<td>Khorat &amp; Sakhon Nakphon Potash Basins, Thailand, Laos (prospect, likely MOP)</td>
<td>Cret. - Upp.</td>
<td>-</td>
<td>Marine</td>
<td>Maha Sarakham Fm.</td>
<td>Possible sylvinite target on basin margin. Widespread massive halite, carnallite (with local zones of sylvinitie), tachyhydrite and bischofite traces of priceite/boracite. Unconformable base, interbedded with three continental redbed successions and overlain by continental deposits. Variably halokinetic toward basin centre. (Albian-Cenomanian?) (Hite and Japakaseth, 1979; E. Tabak et al., 1999; Warren, 2000c)</td>
</tr>
<tr>
<td>Congo and Gabon basins, Africa (Congo, Zaire, Angola) (prospect, likely MOP)</td>
<td>Cret. - Low.</td>
<td>-</td>
<td>Marine</td>
<td>Koulou horizons</td>
<td>Carnallite, sylvinitie in halite host, variable tachyhydrite (Aptian). Previously mined at Holle Mine (Republic of Congo) in 2 variable layers of 1.9 m and 3 m thickness with K₂O contents of 18% and 38% respectively with mineable reserves of 17 mt and 26 mt K₂O respectively. Mine lost to flooding (brecchia zone) in 1977. Future projected solution mine targeting of K and Mg brines in Koulou evaporite horizons. (De Ruitfer, 1979)</td>
</tr>
<tr>
<td>Neuquén and Mendoza Basins, Andes, Argentina (prospect)</td>
<td>Cret. -</td>
<td>-</td>
<td>Marine</td>
<td>Potash interval</td>
<td>Possible future solution mine. Sylvinite ore divided into 2 zones, upper zone about 3 m thick and lower about 11 m thick, average grade 20-25% K₂O. A 1000m depth and high formation temperature (&gt;50°C) precludes conventional mine (Prud’hommee and Kruckowski, 2006).</td>
</tr>
<tr>
<td>Salado Potash Basin, NM, USA historically MOP/increasingly SOP</td>
<td>Perm.-Upp. Lower Trias.</td>
<td>-</td>
<td>Marine</td>
<td>Salado Fm.</td>
<td>Resource now largely depleted, 12 potash horizons in part of Delaware Basin known as McNutt Zone (sylvinite ore), few mines still active. Ore zones contain sylvinitie, carnallite, lesser amounts of sulphate minerals such as polyhalite and langbeinite (Tatarian - Olenekian). (Lowerstein,1988)</td>
</tr>
<tr>
<td>English Zecheztien Potash Basin, UK MOP, to polyhalite</td>
<td>Perm. - Upp.</td>
<td>-</td>
<td>Marine</td>
<td>Zechstein 3</td>
<td>Boulby Mine in UK extracts sylvinite ore from two 6-8 m beds at depths between 1000 and 2700m, essentially no MgSO₄ phases. Water inflow and instability problems (Tatarian). (Smith, 1996; Woods, 1979)</td>
</tr>
<tr>
<td>Zecheztien Potash Basin, Germany (MOP, minor SOP)</td>
<td>Perm. - Upp.</td>
<td>-</td>
<td>Marine</td>
<td>Zechstein Group</td>
<td>Actively mined at depths between 300-800m, Zechstein comprises four evaporite cycles, with potash as five ore horizons in lower three (Thuringen, Hessen, Slaasfurt, Ronnenberg and Riedel) (Tatarian). Tachyhydrite present in Slaasfurt. (Smith and Crosby, 1979; Richter-Bernig, 1986)</td>
</tr>
<tr>
<td>Solikamsk depression, Russia MOP</td>
<td>Perm. - Upp.</td>
<td>-</td>
<td>Marine</td>
<td>Iren horizon</td>
<td>Bezeneski and Solingenkine mines, potash interval lies at depths of 200-500m and is divided into lower sylvinite and upper sylvinite-carnallite, little to no MgSO₄ salts. Av. lower interval thickness 21 m, upper interval 60m. (Kungurian) (Zharkov, 1984)</td>
</tr>
<tr>
<td>Amazonas Basin, Brazil (prospect, MOP)</td>
<td>Upp. Carb.-Perm. Low.</td>
<td>-</td>
<td>Marine</td>
<td>Nova Olinda Fm.</td>
<td>Two potential potash deposits (sylvinite cap to uppermost of 7 evaporite cycles) near Manaus = 1000m depth, with average thickness of 2.7 m and grade 16.5% K₂O. (Ufimian - Olenekian) (Szatmari et al., 1979)</td>
</tr>
<tr>
<td>Pripyat Depression, Belarus MOP</td>
<td>Dev. - Upp.</td>
<td>-</td>
<td>Marine</td>
<td>Liven and Elets horizons</td>
<td>Livet (Frasnian) interval made up of four potash horizons with areas between 130 to 1500 sq. km. Sylvinite ore with minor carnallite in beds 4cm to 1.5m thick interbedded with muddy halite. Elets (Famennian) interval &gt; 60 potash beds over 5,000 sq. km. at depth of 200 to 3,000m. Major potash production from Elets at average depth 480m, grade 18% K₂O. (Zharkov, 1984)</td>
</tr>
<tr>
<td>Alberta Potash Basin, Canada MOP</td>
<td>Dev. - Middle</td>
<td>-</td>
<td>Marine</td>
<td>Prairie Fm</td>
<td>Actively mined, some ten mines (2 solution mines) at depths between 800-1000m, region is world’s major supplier of potash ore. Three potash horizons (sylvinite, carnallite, halite) 20-25m thick in upper part of Prairie Fm. (Esterhayzy, Belle Plain and Patience Lake members). Dips gently to south at 1-8km/km with potash level some 600-2500m below surface. Prairie Evaporite basin is a marine-fed foreland basin situated behind foreland bulge created by Antlerian orogen. (Cowan) (see text)</td>
</tr>
<tr>
<td>Michigan Basin, MI, USA MOP</td>
<td>Sil. - Low. - Upp.</td>
<td>-</td>
<td>Marine</td>
<td>Salina A-1 Evap.</td>
<td>Sylvinite and carnallite ore within central part of an intracratonic sag basin. Potash zone &gt; 30m thick in central part of basin but ore concentration is erratic locally up to 40% K₂O and as deep as 2,550m but only solution mining is possible at these depths. (Wenlockian-Ludlovian). Tachyhydrite present. (Matthews and Egleson, 1979)</td>
</tr>
<tr>
<td>Eastern Siberia Potash Basin, Russia (MOPprospect)</td>
<td>Camb. - Lower</td>
<td>-</td>
<td>Marine</td>
<td>Chara horizon</td>
<td>Potash lies at depths of 600-900m and contains some ore-grade sylvinite intervals (&gt;30% K₂O) in Usolye and Angara Fm. Not currently exploited. (Botoman - Angman) (Zharkov, 1984)</td>
</tr>
</tbody>
</table>
Carnallite’s crystal structure is built of Mg(H₂O)₆ octahedra, with the K⁺ ions are situated in the holes of chloride ion packing meshworks, with a structural configuration similar to perovskite lattice types (Voigt, 2015). Potassium in the carnallite lattice can be substituted by other large single-valence ions like NH₄⁺, Rb⁺, Cs⁺ or Li(H₂O)₄⁺ in the carnallite lattice. Such substitutions change the lattice symmetry from orthorhombic in the original carnallite to monoclinic.

In the lab, the decomposition of carnallite in an undersaturated aqueous solution is a well-documented example of incongruent dissolution (Emons and Voigt, 1981; Xia et al., 1993; Hong et al., 1994; Liu et al., 2007; Cheng et al., 2015, 2016). When undersaturated water comes into contact with carnallite, the rhombic carnallite crystals dissolve and, because of the common ion effect, small cubic KCl crystals form in the vicinity of the dissolving carnallite. As time passes, the KCl crystals grow into larger sparry subhedral forms and the carnallite disappears.

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When interpreting the genesis of ancient potash deposits and solutions, the elemental segregation in the lattice means trace element contents of bromide, rubidium and caesium in primary carnallite versus sylvite daughter crystals from incongruent dissolution can provide valuable information. For example, in a study by Wardlaw, (1968), a trace element model was developed for sylvite derived from carnallite that gave Br and Rb concentration ranges of 0.10–0.90 mg/g and 0.01–0.18 mg/g, respectively. In a later study of sylvite derived by fresh-water leaching of magnesium chloride under isothermal conditions at 25 °C, Cheng et al. (2016), defined a model whereby primary sylvites precipitated from MgSO₄-deficient sea water, gave Br and Rb concentration ranges of 2.89–3.54 mg/g and 0.017–0.02 mg/g, respectively (no evaporation occurred at saturation with KCl). In general, they concluded sylvite derived incongruently from carnallite will contain less Br and more Rb than primary sylvite (Figure 2; Cheng et al., 2016).

Figure 2. Primary sylvite (red squares and white triangles has higher Br than incongruent sylvite. That is, sylvite formed by incongruent conversion creates low Br and high Rb concentrations in sylvite as secondary sylvite from the carnallite precursor (after Cheng et al., 2016).

Subsurface examples

The burial-driven mechanism widely cited to explain the incongruent formation of sylvite from carnallite is illustrated in Figure 3 (Koehler et al., 1990). Carnallite precipitating from evaporating seawater at time 1 forms from a solution at 30°C and atmospheric (1 bar) pressure, and so plots as point A, which lies within the carnallite stability field (that is, it sits above the dashed light brown line). With subsequent burial, the pressure increases so that the line defining carnallite-sylvite boundary (solid dark brown line) moves to higher values of K. By time 2, when the pressure is at 1 Kbar (corresponds to a lithostatic load equivalent to 2-3 km depth), the buried carnallite is thermodynamically unstable and so is converting to sylvite + solution (as the plot field now lies in the sylvite + solution field (Figure 3). If equilibrium is maintained the carnallite reacts incongruently to form further sylvite and MgCl₂-solution. Thus, provided the temperature does not rise substantially, increasing pressure as a result of burial will favour the breakdown of carnallite to sylvite. However, as burial proceeds, the temperature may become high enough to favour once again the formation of carnallite...
Sylvite, interpreted to have formed from incongruent dissolution of primary carnallite, is reported from the Late Permian Zechstein Formation of Germany (Borchert and Muir, 1964), Late Permian Salado Formation of New Mexico (Adams, 1970), Early Mississippian Windsor Group of Nova Scotia (Evans, 1970), Early Cretaceous Muribeca Formation of Brazil and its equivalents in the Gabon Basin, West Africa (Wardlaw, 1972a, b; Wardlaw and Nicholls, 1972; Szatmari et al., 1979; de Ruiter, 1979), Late Cretaceous of the Maha Sarakham Formation, Khorat Plateau, Thailand and Laos (Hite and Japakasetr, 1979), Pleistocene Houston Formation, Danakil Depression, Ethiopia (Holwerda and Hutchinson, 1968), and Middle Devonian Prairie Formation of western Canada (Schwerdtner, 1964; Wardlaw, 1968) (See Table 1).

This well-documented literature base supports a long-held notion that there is a problem with sylvite as a primary (first precipitate) marine bittern salt, especially if the mother seawater had ionic proportions similar to those present in modern seawater (see Lowenstein and Spencer, 1990 for an excellent, if 30-year-old, review). We know from numerous evaporation experiments, that sylvite does not crystallise during the evaporation of modern seawater at 25°C, except under metastable equilibrium conditions (Braitsch, 1971; Valyashko, 1972; Hardie, 1984). The sequence of bitterns crystallising from modern seawater bitterns was illustrated in the previous Salty Matters article in this series (see Figure 1 in October 31 2018).

Across the literature documenting sylvite-carnallite associations in ancient evaporites, the dilemma of primary versus secondary sylvite is generally solved in one of three ways. Historically, many workers interpreted widespread sylvite as a diagenetic mineral formed by the incongruent dissolution of carnallite (Explanation 1). Then there is the interpretation that some sylvite beds, perhaps associated with tachyhydrite, were precipitated in the evaporite bittern part of a basin hydrology that was fed by CaCl₂-rich basinal hydrothermal waters (Explanation 2: see Hardie, 1990 for a good discussion of this mechanism). Then there is the third, and increasingly popular explanation of primary or syndepositional sylvite at particular times in the chemical evolution of the world oceans (MgSO₄-depleted oceans).

Changes in the relative proportions of magnesium, sulphur and calcium in the world’s oceans are well supported by brine inclusion chemistry of co-associated chevron halite (Figure 4). Clearly, there are vast swathes of times in the earth’s past when the chemistry of seawater changed so that MgSO₄ levels were lower than today and it was pos-
sible that sylvite was a primary marine bittern precipitate (see Lowenstein et al., 2014 for an excellent summary).

In my opinion, there is good evidence that all three explanations are valid within their relevant geological contexts but, if used exclusively to explain the presence of ancient sylvite, the argument becomes somewhat dogmatic. I would say that that, owing to its high solubility, the various textures and mineralogical associations of carnallite/sylvite and sulphate bitterns found in ancient potash ore beds reflect various and evolving origins. Ambient textures and mineralogies are dependent on how many times and how pervasively in a potash sequence’s geological burial history an evolving and reactive pore brine chemistry came into contact with parts or all of the extent of highly reactive potash beds (Warren, 2000; 2010; 2016). In my experience, very few ancient examples of economic potash show layered textures indicating primary precipitation on a brine lake floor, instead, most ancient sylvite ores show evidence of at least one episode of alteration.

In other words, various forms and textures of potash may dissolve, recrystallise and backreact with each other from the time a potash salt is first precipitated until it is extracted by coring or mining. The observed textural and mineralogical evolution of a potash ore association depends on how open was the hydrology of the potash system at various stages during its burial evolution. Alteration can occur syn-depositionally, in brine reflux, or later during flushing by compactional or thermobaric subsurface waters or during re-equilibration tied to uplift and telogenesis. Tectonism (extensional and compactional) during the various stages of a basin’s burial evolution acts as a bellows driving fluid flow within a basin, so forcing and speeding up the focused circulation of potash-altering waters.

A similar, but somewhat less intense, textural evolution tied to incongruent alteration is seen in the burial history of other variably hydrated evaporite salts. For example, CaSO₄ can flip-flop from gypsum to anhydrite and back again depending on temperature, pore fluid salinity and the state of uplift/burial. Likewise, with the more complicated double salt polyhalite, there are mineralogical changes related to whether it formed in a MgSO₄ enriched or depleted world ocean and the associated chemistry of the syndepositional reflux brines across extensive evaporite platforms (for a more detailed discussion of polyhalite see Salty Matters, July 31, 2018). Kainite–kieserite–carnallite also shows evidence of ongoing incongruent interactions. This means that, as in gypsum/anhydrite/polyhalite or kainite/kieserite sequences, there will be primary and secondary forms of both carnallite and sylvite that can alternate during deposition, during burial and any deep meteoric

Figure 5. Sylvinite ore (Ci in Salt IV) in the Oligocene Mulhouse Basin, Rhine Graben. A) Photograph (metre-scale) of mine wall showing lateral continuity of layering in the sylvinite units. B) Close-up (cm-scale) showing tripartite and vertically-segregated nature of ore body layering (clayey dolomite-halite-sylvite). C) Interpreted photomicrograph of layering (in part after Lowenstein and Spencer, 1990).
flushing and then again with uplift. In Quaternary brine factories these same incongruent chemical relationships are what facilitate the production of MOP (sylvite) from a carnallitite feed or SOP from kainite/kieserite/schoenite feed (see articles 1 and 2 in this series).

To document the three end-members of ancient sylvite-carnallite decomposition/precipitation we will look at three examples; 1) Oligocene potash in the Mulhouse Basin where primary sylvite textures are commonplace, 2) Devonian potash ores in western Canada, where multiple secondary stages of alteration are seen, and 3) Igneous-dyke associated sylvite in east Germany where thermally-driven volatisation (incongruent melting) forms sylvite from dehydrated carnallite.

Oligocene Potash, Mulhouse Basin France

Moving back into deep time, this 34 Ma mined potash deposit contains some of the first indications of well preserved primary marine-fed sylvinite (MOP) textures, exemplified by laterally-continuous mm-scale alternations of potash, halite layers and clay lamina (Figure 5a–c). Interestingly, all solid-state potash deposits laid down in the post-Oligocene period contain increased proportions of MgSO₄ salts, making them much more difficult to economically mine and process (see Table 1 and Salty Matters, May 12, 2015).

From 1904 until 2002, potash was conventionally mined in France from the Mulhouse Basin (near Alsace, France). With an area of 400 km², the Mulhouse Basin is the southernmost of a number of Lower Oligocene evaporite basins that occupied the upper Rhine Graben, which at that time was a narrow adiabatic-arid rift valley (Figure 6a). The graben was a consequence of the collision between European and African plates during the Paleogene. It is part of a larger intrакontinental rift system across Western Europe that extended from the North Sea to the Mediterranean Sea, stretching some 300 km from Frankfurt (Germany) in the north, to Basel (Switzerland) in the south, with an average width of 35 km (Cendon et al., 2008). The southern extent of the graben is limited by a system of faults that place Hercynian massifs and Triassic materials into contact with the Paleogene filling. Across the north, a complex system of structures (including salt diapirs) put the basin edges in contact with Triassic, Jurassic and Permian materials. In the region of the evaporite basins, the Paleogene fill of the graben lies directly on the Jurassic basement. The sedimentary filling of this rift sequence is asymmetrical with the deeper parts located at the southwestern and northeastern sides of the Graben (Rouchy, 1997).

Palaeogeographical reconstructions place the potential marine-seaway or seepage-feed to the north or perhaps also southeast of the Mulhouse Basin, while marginal continental conglomerates tend to preclude any contemporaneous hydrographic connection with Oligocene ocean water (Blanc-Valleron, 1991; Hinsken et al., 2007; Cendon et al., 2008). At the time of its hydrographic isolation, some 34 Ma, the basin was located 40° north of the equator. Total fill of Oligocene lacustrine/marine-fed sediments in the graben is some 1,700m thick. The saline stage is dominated by anhydrite, halite and mudstone. The main saline sequence is underlain by non-evaporitic Eocene continental mudstones, with lacustrine fossils and local anhydrite beds. Evaporite bed continuity in the northern part of the basin is disturbed by (Permian-salt cored) diapiric and or erosional/fault movement. Consequently, these northern basins are not considered suitable for conventional potash mining (Figure 6a).

The Paleogene fill of the basin is divided into 6 units; a pre-evaporitic series, Lower Salt Group (LSG), Middle Salt Group (MSG), an Upper Salt Group (USG - with potash), Grey Marls Fm., and the Niederroedern Fm (Figure 7; Cendon et al., 2008). The LSG and lower section of

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**Figure 6.** Mulhouse Basin, Rhine Graben. A) Regional distribution of salt basins showing how the potash dominant section is the southernmost of a number of small saline lacustrine deposits in the graben. B) Detail of the Mulhouse (Alsace) Basin show how the exploited bedded potash area lay to the southeast of a more disturbed and Permian salt-cored diapiric zone (after Blanc-Valleron and Schuler, 1997).
the MSG are interpreted as lacustrine in origin, based on the limited paleontologic and geochemical data. However, based on the presence of Cenozoic marine nannoplankton, shallow water benthic foraminifera, and well-diversified dinocyst assemblages in the fossiliferous zone below Salt IV, Blanc-Valleron (1991) favours a marine influence near the top of the MSG, while recognising the ambiguity of marine proportions with brackish faunas. Many marine-seepage fed brine systems have salinities that allow halotolerant species to flourish in marine-fed basins with no ongoing marine hydrographic connection (Warren, 2011). According to Blanc-Valleron and Schuler (1997), the region experienced a Mediterranean climate with long dry seasons during Salt IV member deposition.

In detail, the Salt IV member is made up of some 210 m of evaporitic sequence, with two relatively thin potash levels (Ci and Cs). The stratigraphy associated with this potash zone is, from base to top (Figure 7):

- **S2 Unit**: 11.5 m thick with distinct layers of organic-rich marls, often dolomitic, with dispersed anhydrite layers.

- **S1 Unit**: 19 m thick, evenly-bedded and made up of alternating metre-scale milky (inclusion-rich) halite layers, with much thinner marls and anhydrite layers (Figure 5a). Marls show a sub-millimetric lamination formed by micritic carbonate laminae alternating with clay, quartz, and organic matter-rich laminae. Hofmann et al. (1993a, b) interpreted these couplets as reflecting seasonal variations. Anhydrite occasionally displays remnant swallowtail ghost textures, which suggest that at least part of the anhydrite first precipitated as subaqueous gypsum. Halite shows an abundance of growth-aligned primary chevron textures, along with fluid-inclusion banding suggesting halite was subaqueous and deposited beneath shallow brine sheets (Lowenstein and Spencer, 1990).

- **S Unit**: Is 3.7 m thick and consists of thin marl layers and anhydrite, similar to the S2 Unit, with a few thin millimetric layers of halite.

- **Mi Unit**: With a thickness of 6 m, it is mostly halite with similar characteristics to the S1 Unit. Sylvite was detected in one sample, but its presence is probably related to the evolution of interstitial brines (Cendon et al., 2008).

- **Ci Unit (“Couche inférieure”)**: Is formed by 4 m of alternating marls/anhydrite, halite, and sylvite beds (Figure 7).

The Ti unit consists of alternating beds of halite, marl and anhydrite. The top of the interval is the T unit, which is similar to the S unit and consists of alternating beds of marl and anhydrite. Above this is the Ms or upper Marl, near identical to the lower marl Mi. The Mi is overlain by the upper potash bed (Cs), a thinner, but texturally equivalent, bed compared to the sylvinitic Ci unit.

![Figure 7. Potash stratigraphy in the Mulhouse Basin, Rhine Graben, France (after Cendon et al., 2008)](www.saltworkconsultants.com)
Thus, the Oligocene halite section includes two thin, formerly mined, potash zones: the Couche inferieure (Ci; 3.9m thick), and Couche superieure (Cs; 1.6m thick), both occur within Salt IV of the Upper Salt group (Figures 5, 7). Both potash beds are made up of stacked, thin, parallel-sided cm-dm-thick beds (averaging 8 cm thickness), which are in turn constructed of couplets composed of grey-coloured halite overlain by red-coloured sylvite (Figure 5b). Each couplet has a sharp base that separates the basal halite from the sylvite cap of the underlying bed. In some cases, the separation is also marked by bituminous partings. The bottom-most halite in each dm-thick bed consists of halite aggregates with cumulate textures that pass upward into large, but delicate, primary chevrons and cornets. Clusters of this chevron halite swell upward to create a cm-scale hummocky boundary with the overlying sylvite (Figure 5c; Lowenstein and Spencer, 1990).

The sylvite member of a sylvinite couplet consists of granular aggregates of small transparent halite cubes and rounded grains of red sylvite (with some euhedral sylvite hoppers) infilling the swales in the underlying hummocky halite (Figure 5b, c). The sylvite layer is usually thick enough to bury the highest protuberances of the halite, so that the top of each sylvite layer, and the top of the couplet, is flat. Dissolution pipes and intercrystalline cavities are noticeably absent, although some chevrons show rounded coigns, implying shallow bittern-brine sheets controlled potash deposition. Intercalated marker beds, formed during times of brine pool freshening, are composed of a finely laminated bituminous shale, with dolomite and anhydrite.

The sylvinite-halite couplets record combinations of unaltered settle-out and bottom-nucleated growth features, indicating primary chemical sediment accumulating in shallow perennial brine pools (Lowenstein and Spencer, 1990). Based on the crystal size, the close association of halites with sylvite layers, their lateral continuity and the manner in which sylvite mantles overlie chevron halites, the sylvites are interpreted as primary precipitates. Sylvite first formed at the air-brine surface or within the uppermost brine mass and then sank to the bottom to form well-sorted accumulations. As sylvite is a prograde salt it, like halite, probably grew during times of cooling of the brine mass (Figure 8a). These times of cooling could have been diurnal (day/night) or weather-front induced changes in the above-brine air temperatures. Similar cumulate sylvite deposits form as ephemeral bottom accumulations on the floor of modern Lake Dabuxum in China during its more saline phases.

The subsequent mosaic spar textural overprint seen in many of the Mulhouse sylvite layers was probably produced by postdepositional modification of the crystal boundaries, much in the same way as mosaic halite is formed by recrystallisation of raft and cumulate halite during shallow burial. Temperature-based inclusion studies in both the sylvite and the halite average 63°C, suggesting solar heating of surface brines as precipitation took place (Figure 8b; Lowenstein and Spencer, 1990). Similar high-at-surface brine temperatures are not unusual in many modern brine pools, especially those subject to periodic density stratification and heliothermometry (Warren 2016; Chapter 2).

Mineralogically, potash evaporites in the Mulhouse Basin in the Rhine Graben (also known as the Alsatian (Alsace) or Wittelsheim Potash district) contain sylvite with subordinate carnallite, but lack the abundant MgSO₄ salts characteristic of the evaporation of modern seawater. The Rhine graben formed during the Oligocene, via crustal extension, related to mantle upwelling. It was, and is, a continental graben typified by high geothermal gradients along its rift axis. In depositional setting, it is not dissimilar to the pre-120,000-year potash fill stage in the Quaternary Danakil Basin or the Dead Sea during deposition of potash salts in the Pliocene Sedom Fm. The role of a high-temperature geothermal inflow in defining the CaCl₂ nature of the potash-precipitating brines, versus a deriva-
tion from a MgSO₄-depleted marine feed, is considered significant in the Rhine Graben deposits, but is poorly understood and still not resolved (Hardie, 1990; Cendón et al., 2008). World ocean chemistry in the Oligocene is on a shoulder between the MgSO₄-depleted CaCl₂-rich oceans of the Cretaceous and the MgSO₄-enriched oceans of the Neogene (Figure 4).

Cendón et al. (2008) conclude brine reaction processes were the most important factors controlling the major-ion (Mg, Ca, Na, K, SO₄, and Cl) evolution of Mulhouse brines (Figure 9a-d). A combined analysis of fluid inclusions in primary textures by Cryo-SEM-EDS with sulphate-δ³⁴S, δ¹⁸O and δ³⁶Sr/δ³⁰Sr isotope ratios revealed likely hydrothermal inputs and recycling of Permian evaporites, particularly during the more advanced stages of evaporation that laid down the Salt IV member. Bromine levels imply an increasingly concentrated brine at that time (Figure 9a). The lower part of the Salt IV (S2 and S1) likely evolved from an initial marine input (Figure 9b-d).

Throughout, the basin was disconnected from direct marine hydrographic connection and was one of a series of sub-basins formed in an active rift setting, where tectonic variations influenced sub-basin interconnections and chemical signatures of input waters. Sulphate-δ³⁴S shows Oligocene marine-like signatures at
the base of the Salt IV member (Figure 9c, d). However, enriched sulphate-$\delta^{18}$O reveals the importance of synchronous re-oxidation processes.

As evaporation progressed, other non-marine or marine-modified inputs from neighbouring basins became more important. This is demonstrated by increases in K concentrations in brine inclusions and Br in halite, sulphate isotopes trends, and $^{87}$Sr/$^{86}$Sr ratios (Figure 9b, c). The recycling (dissolution) of previously precipitated evaporites of Permian age was increasingly important with ongoing evaporation. In combination, this chemistry supports the notion of a connection of the Mulhouse Basin with basins situated north of Mulhouse. The brine evolution eventually reached sylvite precipitation. Hence, the chemical signature of the resulting brines is not 100% compatible with global seawater chemistry changes. Instead, the potash phase is tied to a hybrid inflow, with significant but decreasing marine input.

There was likely an initial marine source, but this occurred within a series of rift-valley basin depressions for which there was no direct hydrographic connection to the open ocean, even at the time the Middle Salt Member (potash-entraining) was first deposited (Cendon et al., 2008). That is, the general hydrological evolution of the primary textured evaporites in the Mulhouse basin sump is better explained as a restricted sub-basin with an initial marine-seepage stage. This gradually changed to $\approx 40\%$ marine source near the beginning of evaporite precipitation, with the rest of hydrological inputs being non-marine. There was a significant contribution of solutes from recycled, Permian evaporites, likely remobilised by the tectonics driving the formation of the rift valley (Hinsken et al., 2007; Cendon et al., 2008). The general proportion of solutes did not change substantially over the time of evaporite precipitation. However, as the basin restriction increased, the formerly marine inputs changed to continental, diapiric or marine-modified inputs, perhaps fed from neighbouring basins north of Mulhouse basin. As in the Ethiopian Danakil potash-rift, it is likely brine interactions occurred both during initial and early post-depositional reflux overprinting of the original potash salt beds.

**West Canadian potash (Devonian)**

The Middle Devonian (Givetian) Prairie Evaporite Formation is a widespread potash-entraining halite sequence deposited in the Elk Point Basin, an early intracratonic phase of the Western Canada Sedimentary Basin (WCSB) (Figure 10; Chipley and Kyser, 1989). Economic levels of bedded potash were first intersected in 1946 by the gas exploration well Verbata No. 2 well, near the town of Unity, Saskatchewan. At a depth around 1050 m the well penetrated 140 metres of salt, and recovered core grade was 21.6 per cent K$_2$O over 3.35 metres. This core was the first indication of potash beds with commercial grade, and with a depth of 1056 metres meant shaft mining (as opposed to
solution mining) was feasible (Fuzesy, 1982). However, it was the thickness, purity and the availability of water and natural gas that made solution mining with hot crystallisation processing of the halite beds an attractive proposition. Plans were made by the Prairie Salt Company, a subsidiary of Dominion Tar and Chemical Company, to brine the salt. (Other substances brought to the surface during solution mining were to remain the property of the Crown.) After further test drilling a salt refinery was erected and production began in 1949.

Today, the Prairie Evaporite is the world’s predominant source of MOP fertiliser (Warren, 2016; Chapter 11). The flexure that formed the WCSB basin and its subsealevel accommodation space was a distal downwarp to, and driven by, the early stages of the Antler Orogeny (Root, 2001). Texturally and geochemically the potash layers in the thick bedded halites of the Prairie Evaporite Formation show the effects of multiple alterations and replacements of its potash minerals, especially interactions between sylvite and carnallite in a variably recrystallised halite host.

Regionally halite constitutes a large portion of the four formations that make up the Devonian Elk Point Group (Figure 10): 1) the Lotsberg (Lower and Upper Lotsberg Salt), 2) the Cold Lake (Cold Lake Salt), 3) the Prairie Evaporite (Whitkow and Leonard Salt), and 4) the Dawson Bay (Hubbard Evaporite). Today the remnants of the Middle Devonian Prairie Evaporite Formation constitute a bedded unit some 220 metres thick, which lies atop the irregular topography of the platform carbonates of the Winnipegosis Fm. Extensive solutioning of the various salts has given rise to an irregular thickness to the formation and the local absence of salt within the main salt mass and a periphery of anhydritic solution residues (Figure 11a). Interestingly, the positions of the various active potash mines lie near the the dissolution edge of the current extent of the evaporite (Figure 11c). This positioning relates to shallower zones with depths appropriate for mining (700-1000m) being nearer the shallow salt edge and to reworking/alteration of the potash by a variety of subsurface water crossflows.
The Elk Point Group was deposited within what is termed the Middle Devonian “Elk Point Seaway,” a broad intracratonic sag basin extending from North Dakota and northeastern Montana at its southern extent north through southwestern Manitoba, southern and central Saskatchewan, and eastern to northern Alberta (Figure 11a). Its Pacific coast was near the present Alberta-British Columbia border, and the basin was centred at approximately 10°S latitude. To the north and west the basin was bound by a series of tectonic ridges and arches; but, due to subsequent erosion, the true eastern extent is unknown (Mossop and Shetsen, 1994). In northern Alberta, the Prairie Evaporite is correlated with the Muskeg and Presqu’ile formations (Rogers and Pratt, 2017).

Hydrographic isolation of the intracratonic basin from its marine connection resulted in the deposition of a drawn-down sequence of basinwide (platform-dominant) evaporites with what is a uniquely high volume of preserved potash salts deposited within a clayey halite host. The potash resource in this basin far exceeds that of any other known potash basin in the world.

Potash geology

Potash deposits mined in Saskatchewan are all found within the upper 60-70 m of the Prairie Evaporite Formation, at depths of more than 400 to 2750 metres beneath the surface of the Saskatchewan Plains. Within the Prairie Evaporite, there are four main potash-bearing members, in ascending stratigraphic order they are: Esterhazy, White Bear, Belle Plaine and Patience Lake members (Figure 11b). Each member is composed of various combinations of halite, sylvite, sylvinite, and carnallite, with occurrences of sylvite versus carnallite reliably definable using wireline signatures (once the wireline is calibrated to core or mine control - Figure 12; Fuzesy, 1982).

The Patience Lake Member is the uppermost Prairie Evaporite member and is separated from the Belle Plaine by 3-12 m of barren halite (Holter, 1972). Its thickness ranges from 0-21 m and averages 12 m, its top 7-14 m is made up of clay bands and stratiform sylvite. This is the targeted ore unit in conventional mines in the Saskatoon and Lanigan areas and is the solution-mined target, along with the underlying Belle Plaine Member, at the Mosaic Belle Plaine potash facility. The Belle Plaine member is separated from the Esterhazy by the White Bear Marker beds made up of some 15 m of low-grade halite, clay seams and sylvinite. The Belle Plaine Member is more carnallite-prone than the Patience Lake member (Figure 12). It is the ore unit in the conventional mines at Rocanville and Esterhazy (Figure 11b) where its thickness ranges from 0-18 m and averages around 9 m. In total, the Prairie Evaporite Formation does not contain any significant MgSO₄ minerals (kieserite, polyhalite etc.) although some members do contain abundant carnallite. This mineralogy indicates precipitation from a Devonian seawater/brine chemistry somewhat different from today’s, with inherently lower relative proportions of sulphate and lower Mg/Ca ratios (Figure 4).

Figure 12. Typical ore grades, thicknesses and wireline characteristics of the potash members in the Upper Prairie Evaporite (After Fuzesy, 1982).
The Prairie Evaporite Fm. is nonhalokinetic throughout the basin, it is more than 200 m thick in the potash mining district in Saskatoon and 140 m thick in the Rocanville area to the southeast (Figure 11a; Yang et al., 2009). The Patience Lake member is the main target for conventional mining near Saskatoon. The Esterhazy potash member rises close to the surface in the southeastern part of Saskatchewan near Rocanville and on into Manitoba. This is a region where the Patience Lake Member is thinner or completely dissolved (Figure 11b). Over the area of mineable interest in the Patience Lake Member, centred on Saskatoon, the ore body currently slopes downward only slightly in a westerly direction, but deepens more strongly to the south at a rate of 3-9 m/km. Mines near Saskatoon are at depths approaching a kilometre and so are nearing the limits of currently economic shaft mining.

The main shaft for the Colonsay Mine, which took IMC Global Inc. more than five years to complete through a water-saturated sediment column, finally reached the target ore body at a depth of 960 metres. Such depths and a southerly dip to the ore means that the conventional shaft mines near Saskatoon define a narrow WNW-ESE band of conventional mining activity (Figure 11c). To the south potash is recovered from greater depths by solution mining; for example, the Belle Plaine operation leaches potash from the Belle Plaine member at a depth of 1800m.

The Prairie Evaporite typically thins southwards in the basin; although local thickening occurs where carnallite, not sylvite, is the dominant potash mineral (Worsley and Fuzesy, 1979). The Patience Lake member is mined at the Cory, Allan and Lanigan mines, and the Esterhazy Member is mined in the Rocanville area (Figure 11c). Ore mined from the 2.4 m thick Esterhazy Member in eastern Saskatchewan contain minimal amounts of insolubles (=1%), but considerable quantities of carnallite (typically 1%, but up to 10%) and this reduces the average KCl grade value to an average of 25% K₂O. The converse is true for ore mined from the Patience Lake potash member in western Saskatchewan near Saskatoon, where carnallite is uncommon in the Cory and Allan mines. The mined ore thickness is a 2.74-3.35 metre cut off near the top of the 3.66-4.57 metre Prairie Lake potash member. Ore grade is 20-26% K₂O and inversely related to thickness (Figure 12). The insoluble content is 4-7%, mostly clay and markedly higher than in the Rocanville mines.
A typical sylvinite ore zone in the Patience Lake member can be divided into four to six units, based on potash rock-types and clay seams (Figures 12, 13a; M1-M6 of Boys, 1990). Units are map-pable and have been correlated throughout the PCS Cory Mine with varying degrees of success, dependent on partial or complete loss of section from dissolution. Potash deposition appears to have been early and related to short-term brine seaway cooling and syndepositional brine reflux. So the potash layering (M1-M6) is cyclic, expressed in the repetitive distribution of hematite and other insoluble minerals (Figure 13). Desiccation polygons, desiccation cracks, subvertical microkarst pits and chevron halite crystals indicate that the Patience Lake member that encompasses the potash ore was deposited in and just beneath a shallow-brine, salt-pan environment (Figure 13b; Boys, 1990; Lowenstein and Spencer, 1990; Brodlyo and Spencer, 1987; pers. obs).

Clay seams form characteristic thin stratigraphic segregations throughout the potash ore zone(s) of the Prairie Evaporite, as well as disseminated intervals, and constitute about 6% of the ore as mined. For example, the insoluble minerals found in the PCS Cory samples are, in approximate order of decreasing abundance: dolomite, clay [illite, chlorite (including swelling-chlorite/chlorite), and sepiolite], quartz, anhydrite, hematite, and goethite. Clay minerals make up about one-third of the total insolubles: other minor components include: potassium feldspar, hydrocarbons, and sporadic non-diagnostic palynomorphs (Figure 13; Boys, 1990).

In all mines, the clays tend to occur as long continuous seams or marker layers between the potash zones and are mainly composed of detrital chlorite and illite, along with authigenic sepiolite, montmorillonite and sepiolite (Mossman et al., 1982; Boys, 1990). Of the two chlorite minerals, sepiolite is the more thermally stable. The sepiolite, sepiolite and vermiculite very likely originated as direct products of settle-out, syndepositional dissolution or early diagenesis under hypersaline conditions from a precursor that was initially eolian dust settling to the bottom of a vast brine seaway. The absence of the otherwise ubiquitous sepiolite from Second Red Beds west of the zero-edge of the evaporite basin supports this concept (Figure 9, 10).

**Potash Textures**

Texturally, at the cm-scale, potash salt beds in the Prairie Evaporite (both carnallitite and sylvinite) lack the lateral continuity seen in primary potash textures in the Oligocene of the Mulhouse Basin (Figure 14). Prairie potash probably first formed as syndepositional secondary precipitates and alteration products at very shallow depths just beneath the sediment surface. These early prograde precipitates were then modified to varying degrees by ongoing fluid flushing in the shallow burial environment. The cyclic depositional distribution of disseminated insolubles as the clay marker beds was possibly due to a combination of source proximity, periodic enrichment during times of brine freshening and the strengthening of the winds blowing detritals out over the brine seaway. Possible intra-potash disconformities, created by dissolution of overlying potash-bearing salt beds, are indicated by an abundance of residual hematite in clay seams with some cutting subvertically into the potash bed. Except in, and near, dissolution levels and collapse features, the subsequent redistribution of insolubles, other than iron oxides, is not significant.

In general, halite-sylvite (sylvinite) rocks in the Prairie Evaporite ore zones generally show two end member
textures; 1) the most common is a recrystallised polygonal mosaic texture with individual crystals ranging from millimetres to centimetres and sylvite grain boundaries outlined by concentrations of blood-red halite (Figure 14a). 2) The other end member texture is a framework of euhedral and subhedral halite cubes enclosed by anhedral crystals of sylvite (Figure 14b). This is very similar to ore textures in the Salado Formation of New Mexico interpreted as early passive precipitates in karstic voids.

Petrographically, the halite-carnallite (carnallitite) rocks display three distinct textures. Most halite-carnallite rocks contain isolated centimetre-sized cube mosaics of halite enclosed by poikilitic carnallite crystals (Figure 14c); 1) Individual halite cubes are typically clear, with occasional cloudy crystal cores that retain patches of syndepositional growth textures (Lowenstein and Spencer, 1990). 2) The second texture is coarsely crystalline halite-carnallite with equigranular, polygonal mosaic textures. In zones where halite overlies bedded anhydrite, most of the halite is clear with only the occasional crystal showing fluid inclusion banding.

Bedded halite away from the ore zones generally retains a higher proportion of primary depositional textures typical of halite precipitation in shallow ephemeral saline pans (Figure 14d; Brodylo and Spencer, 1987). Crystalline growth fabrics, mainly remnants of vertically-elongate halite chevrons, are found in 50-90% of the halite from many intervals in the Prairie Evaporite. Many of the chevrons are truncated by irregular patches of clear halite that formed as early diagenetic cements in syndepositional karst.

In contrast, the halite hosting the potash ore layers lacks well-defined primary textures but is dominated by intergrown mosaics. From the regional petrology and the lower than expected Br levels in halite in the Prairie Evaporite Formation, Schwerdtner (1964), Wardlaw and Watson (1966) and Wardlaw (1968) postulated a series of recrystallisation events forming sylvite after carnallite as a result of periodic flushing by hypersaline solutions. This origin as a secondary precipitate (via incongruent dissolution) is supported by observations of intergrowth and overgrowth textures (McIntosh and Wardlaw, 1968), collapse and dissolution features at various scales and timings (Gendzwill, 1978; Warren 2017), radiometric ages (Baadsgaard, 1987) and palaeomagnetic orientations of the diagenetic hema...
tite linings associated with the emplacement of the potash (Koehler, 1997; Koehler et al., 1997).

Dating of clear halite crystals in void fills within the ore levels shows that some of the exceptionally coarse and pure secondary halites forming pods in the mined potash horizons likely precipitated during early burial, while other sparry halite void fills formed as late as Pliocene-Pleistocene (Baadsgard, 1987). Even today, alteration and remobilisation of the sylvite and carnallite and the local precipitation of bischofite, is an ongoing process, related to the encroachment of the contemporary dissolution edge or the ongoing stoping of chimneys fed by deep artesian circulation (pers obs.).

Fluid inclusion studies support the notion of primary textures (low formation temperatures in chevron halite in the Prairie evaporite and an associated thermal separation of non-sylvite and sylvite associated halite (Figure 15; Chipley et al., 1990). Most fluid inclusions found in primary, fluid inclusion-banded halite associated with the Prairie potash salts contain sylvite daughter crystals at room temperature or nucleate them on cooling (e.g. halite at 915 and 945 m depth in the Winsal Osler well; Lowenstein and Spencer, 1990). In contrast, no sylvite daughter crystals have been observed in fluid inclusions outlining primary growth textures from chevron halites away from the potash deposits.

The data illustrated as Figure 15 clearly show that inclusion temperatures in primary halite chevrons are cooler than those in halites collected in intervals nearer the potash levels. Sylvite daughter crystal dissolution temperatures from fluid inclusions in the cloudy centres of halite crystals associated with potash salts are generally warmer (Brodylo and Spencer, 1987; Lowenstein and Spencer, 1990). Sylvite and carnallite daughter crystal dissolution temperatures from fluid inclusions in fluid inclusion banded halite from bedded halite-carnallite are the hottest. This mineralogically-related temperature schism establishes that potash salts occur in stratigraphic intervals in the halite where syndepositional surface brines were warmer. In the 50° – 70°C temperature range there could be overlap with heliothermal brine lake waters. Even so, these warm-

![Figure 16. K-Ar dates from sylvites with haematite, so allowing measurement of co-associated magnetic declination (after Koehler 1997). Compiled from data in Table 1.](image)

![Figure 17. Fluid chemistry in Prairie Evaporite. A) Brine inclusion chemistry (K vs Br) from halite samples in mines and waters collected from seeps at mine levels compared to the concentration trend seen during evaporation of modern seawater (after Horita et al., 1996). B) Chemical compositions of seepage waters collected from mine-shafts and at mine-levels (plotted on a normalized Janecke Na-K-Mg diagram.) The stability fields are shown for halite, sylvite and carnallite in contact with a solution (after Wittrup and Kyser, 1990).](image)
er potash temperatures imply parent brines would likely be moving via a shallow reflux drive and are not the result of primary bottom nucleation (in contrast to primary sylvite in the Mulhouse Basin). Whether the initial Prairie reflux potash precipitate was sylvite or carnallite is open to interpretation (Lowenstein and Hardie, 1990).

Fluid evolution from mineral and isotope chemistry

Analysis of subsurface waters from various Canadian potash mines and collapse anomalies in the Prairie Evaporite suggest that, after initial potash precipitation, a series of recrystallising fluids accessed the evaporite levels at multiple times throughout the burial history of the Prairie Formation (Chiple, 1995; Koehler, 1997; Koehler et al., 1997). Likewise, the isotope systematics and K-Ar ages of sylvite in both halite and sylvite layers indicate that the Prairie Evaporite was variably recrystallised during fluid overprint events (Table 2; Figure 16). These event ages are all younger than original deposition (=390Ma) and likely correspond to ages of various tectonic events that influenced subsurface hydrology along the western margin of North America.

Chemical compositions of inclusion fluids in the Prairie Evaporite, as determined by their thermometric properties, reveal at least two distinct waters played a role in potash formation: a Na-K-Mg-Ca-Cl brine, variably saturated with respect to sylvite and carnallite; and a Na-K-Cl brine (Horita et al., 1996). That is, contemporary inclusion water chemistry is a result in part of ongoing fluid-rock interaction. The ionic proportions in some halite samples are not the result of simple evaporation of seawater to the sylvite bittern stage (Figure 17a; Horita et al., 1996). There is a clear separation of values from chevron halites in samples from the Lanigan and Bredenbury (K-2 area) mines, which plot closer to the concentration trend seen in halite from modern seawater and values from clear or sparry halite. The latter encompass much lower K and higher Br related to fractionation tied to recrystallisation. Likewise, the influence of ongoing halite and potash salt dissolution is evident in the chemistry of shaft and mine waters with mine level waters showing elevated Mg and K values, (Figure 17b; Wittrup and Kyser, 1990; Chiple, 1995). What is more, the mine waters of today show substantial overlap with waters collected more than thirty years ago (Jensen et al., 2006).

This notion of ongoing fluid-rock interaction controlling the chemistry of mine waters is supported by δD and δ18O values of inclusion fluids in both halite and sylvite, which range from -146 to 0‰ and from -17.6 to -3.0‰, respectively (Figure 18). Most of the various preserved isotope values are different from those of evaporated seawater, which should have δD and δ18O values near 0‰.

Furthermore, the δD and δ18O values of inclusion fluids are probably not the result of precipitation of the evaporite minerals from a brine that was a mixture of seawater and meteoric water. The low latitude position of the basin during the Middle Devonian (10-15° from the equator), the required lack of meteoric water to precipitate basin-wide evaporites, and the expected δD and δ18O values of any meteoric water in such a setting, make this an unlikely explanation. Rather, the δD and δ18O values of inclusion fluids in the halites reflect ambient and evolving brine chemistries as the fluids in inclusions in the various growth layers were intermittently trapped during the subsurface
evolution of the Prairie Formation in the Western Canada Sedimentary Basin. They also suggest that periodic migration of nonmarine subsurface water was a significant component of the crossflowing basinal brines throughout much of the recrystallisation history (Chipley, 1995).

**Prairie carnallite-sylvite alteration over time**

Ongoing alteration of carnallite to sylvite and the reverse reaction means a sylvite-carnallite bed must be capable of gaining or losing fluid at the time of alteration. That is, any reacting potash beds must be permeable at the time of the alteration. By definition, there must be fluid egress to drive incongruent alteration of carnallite to sylvite or fluid ingress to drive the alteration of sylvite to carnallite. There can also be situations in the subsurface where the volume of undersaturated fluid crossflow was sufficient to remove (dissolve) significant quantities of the more soluble evaporite salts. Many authors looking at the Prairie evaporite argue that the fluid access events during the alteration of carnallite to sylvite or the reverse, or the complete leaching of the soluble potash salts was driven by various tectonic events (Figure 16). In the early stages of burial alteration (few tens of metres from the landsurface) the same alteration processes can be driven by varying combinations of brine reflux, prograde precipitation and syndepositional karstification, all driven by changes in brine level and climate, which in turn may not be related to tectonism (Warren, 2016; Chapters 2 and 8 for details).

In the potash areas of the Western Canada Sedimentary Basin, the notion of 10-100 km lateral continuity is a commonly stated precept for both sylvite and carnallite units across the extent of the Prairie Evaporite. But when the actual distribution and scale of units are mapped based on mined intercepts, there are numerous 10-100 metre-scale discontinuities (anomalies) present indicating fluid ingress or egress (Warren, 2017).

Sometimes ore beds thin and alteration degrades the ore level (Section A-A, A, A$_2$), other times these discontinuities can locally enrich sylvite ore grade (B-B; Figure 19). Discontinuities or salt anomalies are much more widespread in the Prairie evaporite than mentioned in much of the potash literature (Figure 19). Mining for maintenance of ore grade shows that unexpectedly intersecting an anomaly in a sylvite ore zone can have a range of outcomes ranging from the inconsequential to the catastrophic, in part because there is more than one type of salt anomaly or "salt horse" (Warren, 2017).

Figure 20 summarises what are considered the three most common styles of salt anomaly in the sylvite ore beds of the Prairie Evaporite, namely 1) Washouts, 2) Leach

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Figure 19. Salt anomalies mapped in an ore level in a potash mine near Saskatoon, Canada (after Baar 1974; Warren, 2017). A) Subsurface distribution of small scale salt anomalies mapped during mining. B) Scaled cross sections of salt anomalies and associated K$_2$O values.
anomalies, 3) Collapse anomalies. These ore bed disturbances and their occurrence styles are in part time-related. Washouts are typically early (eogenetic) and defined as... “salt-filled V- or U-shaped structures, which transect the normal bedded sequence and obliterate the stratigraphy” (Figure 20a; Mackintosh and McVittie, 1983, p. 60). They are typically enriched in, or filled by, insoluble materials in their lower one-third and medium–coarse-grained sparry halite in the upper two thirds. Up to several metres across, when traced laterally they typically pass into halite-cemented paleo-sinks and cavern networks (e.g. Figure 20b). Most washouts likely formed penecontemporaneous to the potash beds they transect, that is, they are preserved examples of synkarst, with infilling of the karst void by a slightly later halite cement. They indicate watertable lowering in a potash-rich saline sump. This leaching was followed soon after by a period of higher watertables and brine saturations, when halite cements occluded the washouts and palaeocaverns. Modern examples of this process typify the edges of subcropping and contemporary evaporite beds, as about the recently exposed edges of the modern Dead Sea. As such, “washouts” tend to indicate relatively early interactions of the potash interval with undersaturated waters, they may even be a part of the syn-depositional remobilisation hydrology that focused, and locally enriched, potash ore levels.

In a leach anomaly zone, the stratabound sylvinite ore zone has been wholly or partially replaced by barren halite, without significantly disturbing the normal stratigraphic sequence (clay marker beds) which tend to continue across the anomaly (Figure 20b). Some loss of volume or local thinning of the stratigraphy is typical in this type of salt anomaly. Typically saucer-shaped, they have diameters ranging from a few metres up to 400m. Less often, they can be linear features that are up to 20 m wide and 1600 m long. Leach zones can form penecontemporaneously due to depressions and back-reactions in the ore beds, or by later low-energy infiltration of Na-saturated, K-undersaturated brines. The latter method of formation is also likely on the margins of collapse zones, creating a hybrid situation typically classified as a leach-collapse anomaly (Mackintosh and McVittie, 1983; McIntosh and Wardlaw, 1968).

Of the three types of salt anomaly illustrated, leach zone processes are the least understood. Historically, when incongruent dissolution was the widely accepted interpretation for loss of unit thickness in the Prairie Evaporite, many leach anomalies were considered metasomatic. Much of the original metasomatic interpretation was based on decades of detailed work in the various salt mines of the German Zechstein Basin. There, in an endemic halokinetic terrane, evaporite textures were considered more akin to metamorphic rocks, and the term metasomatic alteration was commonly used when explaining leach anomalies (Bochert and Muir, 1964, Braitsch, 1971). In the past two decades, general observations of the preservation of primary chevron halite in most bedded evaporites away from the potash layers in the Prairie Evaporite have led to reduced use of notions of widespread metamorphic-like metasomatic or solid-state alteration processes in bedded evaporites. There is just too much preserved primary texture in the bedded salt units adjacent to potash beds to invoke pervasive burial metasomatism of the Prairie Evaporite.

So how do leach anomalies, as illustrated in Figure 20b, occur in nonhalokinetic settings? One possible explanation...
is given by the depositional textures documented in anomalies in the Navarra Potash Province (Figure 21). There, the underlying and overlying salt stratigraphy is contiguous, while the intervening sylvite passed laterally into a syn-depositional anomaly or “salt horse” created by an irregular topography on the salt pan floor prior to the deposition of onlapping primary sylvinite layers (see Warren 2016, 2017 for detailed discussion).

On the other hand, in halokinetic situations (which characterises much Zechstein salt) solid-state alteration via inclusion related migration in flowing salt beds is a well-documented set of texture-altering processes (diffusion metasomatism). Most workers in such halokinetic systems would agree that there must have been an original stratiform potassium segregation present during or soon after deposition related to initial precipitation, fractional dissolution and karst–cooling precipitation. But what is controlling potassium distribution now in the Zechstein salts is a recrystallised and remobilised set of textures, which preserve little or no crystal-scale evidence of primary conditions (Warren, 2016; Chapter 6). The complex layering in such deposits may preserve a broad depositional stratigraphy, but the decimetre to metre scale mineral distributions are indications of complex interactions of folds, overfolds, and disaggregation with local flow thickening. We shall return to this discussion of Zechstein potash textures in the next section dealing with devolatisation of hydrated salts such as carnallite. in zones of local heating

Collapse zones in the Prairie Evaporite are characterized by a loss of recognizable sylvinite ore strata, which is replaced by less saline brecciated, recemented and recrystal-\textit{ized material, with the breccia blocks typically made of the intrasalt or roof lithologies (Figure 20c), so angular fragments of the Second Red beds and dolostones of the Dawson Bay Formation are the most conspicuous components of the collapse features in the Western Canada Sedimentary Basin. When ore dissolution is well developed, all the halite can dissolve, along with the potash salts, and the overlying strata collapse into the cavity (these are classic solution collapse features). Transitional leached zones typically separate the collapsed core from normal bedded potash. Such collapse structures indicate a breach of the ore layers by unsaturated waters, fed either from below or above. For example, in the Western Canada Sedimentary Basin, well-developed collapse structures tend to occur over the edges and top Devonian mud mounds, while in the New Mexico potash zone the collapse zones are related to highs in the underlying Capitan reef trend (Warren, 2017). Leaching fluids may have come from below or above to form collapse structures at any time after initial deposition. When connected to a water source, these are the subsurface features that when intersected can quickly move the mining operation out of the salt into an adjacent aquifer system, a transition that led to flooding in most of the mine-lost operations listed earlier.

Identifying at the mine scale the set of processes that created a salt anomaly in a sylvite bed also has implications in terms of its likely influence on mine stability and whatever decision is made on how to deal with it as part of the ongoing mine operation (Warren, 2016, 2017). Syndepositional karst fills and leach anomalies are least likely to be problematic if penetrated during mining, as the aquifer system...
that formed them is likely no longer active. In contrast, penetration or removal of the region around a salt-depleted collapse breccia may lead to uncontrollable water inflows and ultimately to the loss of the mine.

Unfortunately, in terms of production planning, the features of the periphery of a leach anomaly can be similar if not identical to those in the alteration halo that typically forms about the leached edge a collapse zone. The processes of sylvite recrystallisation that define the edge of collapse anomaly can lead to local enrichment in sylvite levels, making these zones surrounding the collapse core attractive extraction targets (Boys 1990, 1993). Boundaries of any alteration halo about a collapse centre are not concentric, but irregular, making the prediction of a feature’s geometry challenging, if not impossible. The safest course of action is to avoid mining salt anomalies, but longwall techniques make this difficult and so they must be identified and dealt with (see Warren 2017).

Cooking sylvite: Dykes & sills in potash salts

In addition to; 1) primary sylvite and 2) sylvite/carnallite alteration via incongruent transformation in burial, there is a third mode of sylvite formation related to 3) igneous heating driving devolatisation of carnallitite, which can perhaps be considered a form of incongruent melting (Warren, 2016; Chapter 16). And so, at a local scale (measured in metres to tens of metres) in potash beds cut by igneous intrusions, there are a number of documented thermally-driven alteration styles and thermal haloes. Most are created by the intrusion of hot doleritic or basaltic dykes and sills into cooler salt masses, or the outflow of extrusive igneous flows over cooler salt beds (Knipping, 1989; Grishina et al, 1992, 1998; Gutsche, 1988; Steinmann et al., 1999; Wall et al., 2010). Hot igneous material interacts with somewhat cooler anhydrous salt masses to create narrow, but distinct, heat and mobile fluid-release envelopes, also reflected in the resulting salt textures. At times, relatively rapid magma emplacement can lead to linear magma emplacement can lead to linear breakout trends outlined by phreatomagmatic explosion craters, as imaged in portions of the North Sea (Wall et al., 2010) and the Danakhil/Dallol potash beds in Ethiopia (Salty Matters, May 1, 2015).

Based on studies of inclusion chemistry and homogenization temperatures in fluid inclusions in bedded halite near intrusives, it seems that the extent of the influence of a dolerite sill or dyke in bedded salt is marked by fluid-inclusion migration, evidenced by the disappearance of chevron structures and consequent formation of clear halite with a different set of higher-temperature inclusions. Such a migration envelope is well documented in bedded Cambrian halites intruded by end-Permian dolerite dykes in the Tunguska region of Siberia (Grishina et al., 1992).

Defining \( b \) as the thickness of the dolerite intrusion in these salt beds, and \( d \) as the distance of the halite from the edge of the intrusion, then the disappearance of chevrons occurs at greater distances above than below the intrusive sill. For \( d/b < 0.9 \) below the intrusion, \( \text{CaCl}_2, \text{CaCl}_3, \text{KCl} \) and \( n\text{CaCl}_2, m\text{MgCl}_2 \) solids occur in association with water-free and liquid-CO\(_2\) inclusions, with \( \text{H}_2\text{S}, \text{SCO} \) and orthorhombic or glassy \( \text{S}_x \). For a \( d/b \) of 0.2-2 above the intrusion, \( \text{H}_2\text{S} \)-bearing liquid-CO\(_2\) inclusions are typical,

<table>
<thead>
<tr>
<th>Salt</th>
<th>Formula</th>
<th>Decomposition/Melt point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halite</td>
<td>( \text{NaCl} )</td>
<td>804°C anhydrous melt</td>
</tr>
<tr>
<td>Gypsum</td>
<td>( \text{CaSO}_4.2\text{H}_2\text{O} )</td>
<td>100-150°C loss of water</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>( \text{CaSO}_4 )</td>
<td>1460°C anhydrous melt</td>
</tr>
<tr>
<td>Carnallite</td>
<td>( 3\text{MgCl}_2.6\text{H}_2\text{O} )</td>
<td>150-180°C loss of water</td>
</tr>
<tr>
<td>Sylvite</td>
<td>( \text{KCl} )</td>
<td>750-790°C anhydrous melt</td>
</tr>
<tr>
<td>Bischofite</td>
<td>( \text{MgCl}_2.6\text{H}_2\text{O} )</td>
<td>&gt;118°C loss of water</td>
</tr>
<tr>
<td>Epsomite</td>
<td>( \text{MgSO}_4.7\text{H}_2\text{O} )</td>
<td>&gt;70-80°C loss of water</td>
</tr>
<tr>
<td>Kieserite</td>
<td>( \text{MgSO}_4.\text{H}_2\text{O} )</td>
<td>150-200°C loss of water</td>
</tr>
<tr>
<td>Trona</td>
<td>( \text{Na}_4\text{H}_2\text{CO}_3.3\text{H}_2\text{O} )</td>
<td>&gt;70°C loss of water</td>
</tr>
<tr>
<td>Nahcolite</td>
<td>( \text{NaHCO}_3 )</td>
<td>270°C anhydrous melt</td>
</tr>
</tbody>
</table>

**Typical magma/eruption temperatures**

<table>
<thead>
<tr>
<th>Type</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Picritic</td>
<td>1400 - 1500°C</td>
</tr>
<tr>
<td>Basaltic</td>
<td>1100 - 1200°C</td>
</tr>
<tr>
<td>Rhyolitic</td>
<td>800 - 900°C</td>
</tr>
<tr>
<td>Natrocarbonatite</td>
<td>500 - 600°C</td>
</tr>
</tbody>
</table>

Table 3. Decomposition and melting points of selected salts and typical ranges of magma temperatures (after Warren 2016).
with various amounts of water. Thus, as a rule of thumb, an alteration halo extends up to twice the thickness of the dolerite sill above the sill and almost the thickness of the sill below (Figure 22).

In a series of autoclavation laboratory experiments, Fabricius and Rose-Hampton (1988) found that: 1) at atmospheric pressure carnallite melts incongruently to sylvite and hydrated MgCl2 at a temperature of 167.5°C. 2) the melting/transformation temperature increase to values in excess of 180°C as the pressure increases (Figure 23).

A similar situation occurs in the dyke-intruded halite levels exposed in the mines of the Werra-Fulda district of Germany (Steinmann et al., 1999; Schofield, et al., 2014). There the Herfa-Neurode potash mine is located in the Werra-Fulda Basin in the Hessian district of central Germany (Figure 24a). The targeted ore levels consist of the carnallite-rich Kaliftöz Hessen (K1H) and Kaliftöz Thüringen (K1Th) intervals, which form part of the Zechstein 1 (Z1) bedded Werra salt succession (Warren, 2016). In the mine the K1H and K1Th units range in thickness from 2 m to 10 m, are generally subhorizontal and occur at a depth of 650–710 m below the present-day surface.

In the later Tertiary, basaltic melts intruded these Zechstein evaporites as numerous sub-vertical dykes, but only a few dykes attained the Miocene landsurface. Basaltic melt production was related to regional volcanic activity some 10 to 25 Ma. Basalts exposed in the mine walls, where it cuts non-hydrus units of halite or anhydrite, are typically subvertical dykes, rather than subhorizontal sills. The basalts are phonolitic tephrites, limburgites, basanites and olivine nephelinites. Dyke margins are usually vitrified, forming a microlitic limburgite glass along dyke edges in contact with halite (Figure 24b; Knipping, 1989). At the contact on the evaporite side of the glassy rim, there is a cm-wide carapace of high-temperature salts (mostly anhydrite and ferroan carbonates). Further out, the effect of the high-temperature envelope is denoted by transitions to clear halite, with higher temperature fluid inclusions (Knipping 1989). All of this metre-scale alteration is an anhydrous alteration halo, the halite did not melt (melting temperature of 804°C), rather than migrating, the fluid driving recrystallisation was mostly from entrained brine gas inclusions. The dolerite/basalt interior of the basaltic dyke is likewise altered and salt soaked, with clear, largely inclusion-free halite typically filling vesicles in the basalt.

Heating of hydrated (carnallitic) salt layers, adjacent to a dyke or sill, tends to drive off the water of crystallisation (chemical or hydration thixotropy) at much lower temperatures than that at which anhydrous salts, such as halite or anhydrite, thermally melt (Figure 24c; Table 3). For example, in the Fulda region, the thermally-driven release of water of crystallisation within carnallitic beds creates thixotropic or subsurface “peperite” textures as carnallitite alters to sylvinite layers. These are layers where heated water of crystallisation escaped from the hydrated-salt intervals and the intrusive is sub-vertical to steeply dipping (Figure 24b versus 24c).

Accordingly, away from the immediate vicinity of the direct thermal aureole, heated and overpressured dehydration waters can enter carnallite halite bed, and drive the creation of extensive soft sediment deformation and peperite textures in hydrated layer (Figure 24c). Mineralogically, sylvite and coarse recrystallised halite dominate the salt fraction in the peperite intervals of the Herfa-Neurode mine. Sylvite in the altered zone is a form of dehydrated carnallite, not a primary-textured salt. Across the Fulda region, such altered zones and deformed units can extend along former carnallite layer to tens or even a hundred or more metres from the dyke feeder. Ultimately, the deformed potash bed passes back out into the unaltered
bed, which retains abundant inclusion-rich halite and carnallite (Schofield et al., 2014).

That is, nearer the basalt dyke, the carnallite is largely transformed into inclusion-poor halite and sylvite, the result of incongruent flushing of warm saline fluids mobilised from the hydrated carnallite crystal lattice as it was heated by dyke emplacement. During Miocene salt alteration/thermal metamorphism in the Fulda region, NaCl-fluids were mixed with fluids and gases originating from thermally-mobilised crystallisation water in the carnallite, as it converted to sylvite. This brine/gas mixture altered the basalts during post-intrusive cooling, an event which numerical models suggest was quite rapid (Knipping, 1989): a dyke of less than 0.5 m thickness probably cooled to temperatures less than 200°C within 14 days of dyke emplacement.

The contrast in alteration extent between anhydrous and hydrous salt layers shows alteration effects are minimal wherever the emplacement temperature of the magma is below that of the anhydrous salt body as it is next to a basalt dyke. If this is the mechanism driving entry of igneous-related volatiles (gases and liquids) into a salt body, then the distribution of products (including CO₂) will be highly inhomogeneous and related to the mineralogy of the salt unit adjacent to the intrusive. Worldwide, dykes intersecting salt beds tend to widen to become sills in two zones: 1) along evaporite units within the halite mass that contain hydrated salts, such as carnallite or gypsum (Figure 24c) and, 2) where rising magma has ponded and so created laccoliths at the upper or lower halite contact with the adjacent nonsalt strata or against a salt wall (Figure 22 vs 24). The first is a response to a pulse of released water as dyke-driven heating forces the dehydration of hydrated salt layers. The second is a response to the mechanical strength contrast at the salt-nonsalt contact.

In summary, sylvite formed from a carnallite precursor during Miocene salt alteration/thermal metamorphism in the Fulda region, NaCl-fluids were mixed with fluids originating from thermally-mobilised crystallisation water in the carnallite, as it converted to sylvite. This brine mixture altered the basalts during post-intrusive cooling, an event which numerical models suggest was quite rapid (Knipping, 1989): a dyke of less than 0.5 m thickness probably cooled to temperatures less than 200°C within 14 days of dyke emplacement.

**How to produce economic potash salts**

Over this series of three articles focused on current examples of potash production, we have seen there are two main groups of potash minerals currently utilised to make fertiliser, namely, muriate of potash (MOP) and sulphate.
of potash (SOP). MOP is both mined (generally from a Pre-Neogene sylvinite ore) or produced from brine pans (usually via processing of a carnallitite slurry). In contrast, large volumes of SOP are today produced from brine pans in China and the USA but with only minor production for solid-state ore targets. Historically, SOP was produced from solid-state ores in Sicily, the Ukraine, and Germany but today there are no conventional mines with SOP as the prime output in commercial operation (See Salty Matters, May 12, 2015).

The MgSO$_4$-enriched chemistry of modern seawater makes the economic production of potash bitterns from a seawater-feed highly challenging. Today, there is no marine-fed plant anywhere in the world producing primary sylvite precipitates. However, sylvite is precipitating from a continental brine feed in salt pans on the Bonneville salt flat, Utah. There, a brine field, drawing shallow pore waters from saltflat sediments, supplies suitably low-MgSO$_4$ inflow chemistry to the concentrator pans. Sylvite also precipitates in solar evaporator pans in Utah that are fed brine circulated through the abandoned workings of the Cane Creek potash mine (Table 1).

Large-scale production of MOP fertiliser from potash precipitates created in solar evaporation pans is taking place in perennially subaqueous saline pans of the southern Dead Sea and the Qaidam Basin. In the Dead Sea, the feed brine is pumped from the waters of the northern Dead Sea basin, while in the Qaidam sump the feed is from a brine field drawing pore brines with an appropriate mix of river and basinal brine inputs. In both cases, the resulting feed brine to the final concentrators is relatively depleted in magnesium and sulphate. These source bitterns have ionic proportions not unlike seawater in times of ancient Mg-SO$_4$-depleted oceans. Carnallitite slurries, not sylvinite, are the MOP precipitates in pans in both regions. When feed chemistry of the slurry is low in halite, then the process to recover sylvite is a cold crystallisation technique. When halite impurity levels in the slurry are higher, sylvite is manufactures using a more energy intensive, and hence more expensive, hot crystallisation technique. Similar sulphate-depleted brine chemistry is used in Salar Atacama, where MOP and SOP are recovered as byproducts of the production of lithium carbonate brines.

Significant volumes of SOP are recovered from a combination of evaporation and cryogenic modification of sulfate-enriched continental brines in pans on the edge of the Great Salt Lake, Utah, and Lop Nur, China. When concentrated and processed, SOP is recovered from the processing of a complex series of Mg–K–SO$_4$ double salts (schoenitic) in the Ogden pans fed brines from the Great Salt Lake. The Lop Nur plant draws and concentrates pore waters from a brine field drawing waters from glau-berite-polyhalite-entraining saline lake sediments.

All the Quaternary saline lake factories supply less than 20% of the world’s potash; the majority comes from the conventional mining of sylvinite ores. The world’s largest reserves are held in Devonian evaporites of the Prairie Evaporite in the Western Canada Sedimentary Basin. Textures and mineral chemistry show that the greater volume of bedded potash salts in this region is not a primary sylvite precipitate. Rather the ore distribution, although stratiform and defined by a series of clay marker beds, actually preserves the effects of multiple modifications and alterations tied to periodic egress and ingress of basinal waters. Driving mechanisms for episodes of fluid crossflow range from syndepositional leaching and reflux through to tectonic pumping and uplift (relogenesis). Ore distribution and texturing reflect local-scale (10–100 metres) discontinuities and anomalies created by this evolving fluid chemistry. Some alteration episodes are relatively benign in terms of mineralogical modification and bed continuity. Others, generally tied to younger incidents (post early Cretaceous) of undersaturated crossflow and karstification, can have substantial effects on ore continuity and susceptibility to unwanted fluid entry. In contrast, ore textures and bed continuity in the smaller-scale sylvinite ores in the Oligocene Mulhouse Basin, France, indicate a primary ore genesis.

What makes it economic?

Across the Quaternary, we need a saline lake brine systems with the appropriate brine proportions, volumes and climate to precipitate the right association of processable potash salts. So far, the price of potash, either MOP or SOP, and the co-associated MgSO$_4$ bitterns, precludes industrial marine-fed brine factories.

In contrast, to the markedly nonmarine locations of potash recovery from the Quaternary sources, almost all pre-Quaternary potash operations extract product from marine-fed basinwide ore hosts during times of MgSO$_4$-depleted and MgSO$_4$-enriched oceans (Warren, 2016; Chapter 11). This time-based dichotomy in potash ore sources with nonmarine hosts in the Quaternary deposits and marine evaporite hosted ore zones in Miocene deposits and older, reflects a simple lack of basinwide marine deposits and appropriate marine chemistry across the Neogene (Warren, 2010). As for all ancient marine evaporites, the depositional system that deposited ancient marine-fed potash deposits was one to two orders of magnitude larger and the resultant deposits were typically thicker stacks than any Quaternary potash settings. The last such “saline giant” potash system was the Solifèra series in the Sicilian basin, deposited as part of the Mediterranean “salinity crisis,” but these potential ore beds are of the less economically attractive MgSO$_4$-enriched marine potash series.

So, what are the factors that favour the formation of, and hence exploration for, additional deposits of exploitable
ancient potash? First, large MOP solid-state ore sources are all basinwide, not lacustrine deposits. Within the basinwide association, it seems that intracratonic basins host significantly larger reserves of ore, compared to systems that formed in the more tectonically-active plate-edge rift and suture association. This is a reflection of: 1) accessibility – near the shallow current edge of a salt basin, 2) a lack of a halokinetic overprint and, 3) the setup of longterm, stable, edge-dissolution brine hydrologies that typify many intracratonic basins. Known reserves of potash in the Devonian Prairie evaporite in West Canadian Sedimentary Basin (WCSB) are of the order of 50 times that of next largest known deposit, the Permian of the Upper Kama basin, and more than two orders of magnitude larger than any other of the other known exploited deposits (Table 1).

Part of this difference in the volume of recoverable reserves lies in the fact that the various Canadian potash members in the WCSB are still bedded and flat-lying. Beds have not been broken up or steepened, by any subsequent halokinesis. The only set of processes overprinting and remobilising the various potash salts in the WCSB are related to multiple styles and timings of aquifer encroachment on the potash units, and this probably took place at various times since the potash was first deposited, driven mainly by a combination of hinterland uplift and subrosion. In contrast, most of the other significant potash basins listed in Table 1 have been subjected to ongoing combinations of halokinesis and groundwater encroachments, making these beds much less laterally predictable. In their formative stages, the WCSB potash beds were located a substantial distance from the orogenic belt that drove flexural downwarp and creation of the subscalevel sag depression. Like many other intracratonic basins, the WCSB did not experience significant syndepositional compression or rift-related loading.

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