Polyhalite: Geology of an alternate low-chloride potash fertiliser

**Introduction**

Polyhalite is the hydrated sulfate of potassium, calcium and magnesium, with the formula \((K_2Ca,Mg(SO_4)\cdot2H_2O)\). Polyhalite crystallises in the triclinic system, but individual euhedral crystals are very rare in nature where the usual habit is fibrous to massive. It is typically colourless, grey to white, although the natural colour in some evaporite deposits tends to brick red due to iron oxide inclusions. Primary (syndepositional) precipitates can be layered at a mm to cm scale. Its Mohs hardness is 3.5 with a specific gravity of 2.8. It was first described from a Salzburg mine in 1818 and the name comes from a Latin root that refers to the "many salts" evident in its chemical formula.

Polyhalite is relatively easy to distinguish from associated evaporites by simple field tests. Its hardness separates it from most evaporite salts, other than anhydrite. It has a bitter taste and is water soluble (incongruent dissolution), with remnants of gypsum and syngenite \((K_2Ca(SO_4)\cdot2H_2O)\), which is also soluble, leaving behind a final residue of gypsum (unlike sylvite and halite which dissolve wholly and congruently in fresh water). Polyhalite is not deliquescent, unlike carnallite, and gives a purple flame result when held in a gas flame due to its potassium content, unlike the non-potassium salts. Table 1 lists the constituents of the various evaporite salts mentioned in this article.

The complete equilibrium evaporation of modern seawater at 25°C produces the mineral sequence: CaCO₃ (calcite and aragonite), CaSO₄ (gypsum and anhydrite), halite \((NaCl)\), other sulphates (glauberite, polyhalite, epsomite, hexahydrite, and kieserite) and chlorides (carnallite and bischofite). Halite is the dominant mineral because of the high concentration of Na and Cl in seawater (Figure 1; after Harvie et al., 1980).

This mineral sequence with abundant sulphate bitterns reflects the relatively high concentration of sulphate in modern seawater (molar SO₄ > Ca), which, following evaporation and precipitation of CaCO₃ and CaSO₄, produces a SO₄-rich, Ca-depleted brine at halite saturation and beyond, from which Mg-sulphate bitterns precipitate. Polyhalite can form syndepositionally at temperatures below 30 °C, via back-reaction of the evaporating K-Mg-SO₄ brine with early-formed gypsum or anhydrite (Hardie 1984). Mg and Cl reach high concentrations during the latest bittern stages of evaporation resulting in the precipitation of carnallite and bischofite (Figure 1).

**Utilisation**

Today polyhalite is mined as a prime ore target in only one place in the world, the Israel Chemical Limited (ICL)-owned Boulby Mine, located below the North Sea, off the North Yorkshire coast of the UK. Currently, ICL-UK distributes around 500 kt/y from its Boulby mine as a direct application fertiliser or bulk-blend/compound NPK additive and is in the process of expanding its polysulphate output as it downgrades its MOP operations. A second major polyhalite mine, located near the Boulby Mine, is proposed by Sirius Minerals PLC. This renewed interest in polyhalite as an economical source of potash fertiliser is why I am writing this article.

Sulphate of Potash (SOP) fertiliser was initially derived from polyhalite/langbeinite in the US during the first half of the twentieth century. But then during the 1940s, after its discovery in vast quantities by prospectors searching for oil in Saskatchewan, the focus for the world’s potash fer-

<table>
<thead>
<tr>
<th>Anhydrite</th>
<th>CaSO₄</th>
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<tr>
<td>Bischofite</td>
<td>MgCl₂·6H₂O</td>
</tr>
<tr>
<td>Broedite</td>
<td>Na₂Mg(SO₄)₂·7H₂O</td>
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<tr>
<td>Epsomite</td>
<td>MgSO₄·7H₂O</td>
</tr>
<tr>
<td>Glauberite</td>
<td>CaSO₄·Na₂SO₄</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
</tr>
<tr>
<td>Halite</td>
<td>NaCl</td>
</tr>
<tr>
<td>Hexahydrite</td>
<td>MgSO₄·6H₂O</td>
</tr>
<tr>
<td>Kainite</td>
<td>KMg(SO₄)Cl·3H₂O</td>
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<tr>
<td>Kieserite</td>
<td>MgSO₄</td>
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<tr>
<td>Langbeinite</td>
<td>K₂Mg(SO₄)₂</td>
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<tr>
<td>Leonite</td>
<td>K₂Mg(SO₄)₂·6H₂O</td>
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<tr>
<td>Schoenite (picromerite)</td>
<td>K₂Mg(SO₄)₂·6H₂O</td>
</tr>
<tr>
<td>Polyhalite</td>
<td>K₂Ca,Mg(SO₄)₂·2H₂O</td>
</tr>
<tr>
<td>Sylvite</td>
<td>KCl</td>
</tr>
<tr>
<td>Syngenite</td>
<td>K₂Ca(SO₄)₂·6H₂O</td>
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Table 1. Sulphate and other evaporite minerals mentioned in this article.
tiliser supply moved to Canada and the mining of sylvite (muriate of potash- KCl), (Warren, 2016). The geology of SOP was discussed in an earlier Salty Matters article (May 15, 2015). All aspects of SOP and MOP geology and mining are discussed in detail in Chapter 11, Warren (2016).

ICL currently markets crushed and processed polyhalite from the Boulby mine as polysulphate (Table 2). The purity of the Polysulphate product from the Boulby mine is very high (95% polyhalite) with <5% sodium chloride (NaCl) and traces of boron (B) and iron (Fe) at 300 and 100 ppm, respectively (Yermiyahu et al., 2017). The declared minimum analysis of polyhalite for S, K, Mg and Ca is 48% sulphur trioxide (SO$_3$), 14% potassium oxide (K$_2$O), 6% magnesium oxide (MgO) and 17% calcium oxide (CaO), respectively. This compares to a K$_2$O content of contains 60–63% in MOP and around 50% in SOP.

Polyhalite’s make up in terms of K, Mg, S and Cl proportions is similar to the other major potassium-magnesium-sulphate (SOPM) fertilisers: Langbeinite, Schöenite and Patentkali® (Table 2). All are marketed as low-chloride potash fertilisers with additional magnesium and sulphur components. ICL-UK markets polyhalite as a multi-nutrient, low-chloride fertiliser under the brand name Polysulphate®. Sirius plans to market its polyhalite as POLY4®.

CRU estimates the global consumption of potassium-magnesium-sulphate (SOPM) fertilisers in 2017 at 1.7 Mt total product; a comparatively small total compared to the widely traded 65.5 Mt potassium chloride (MOP) market (https://www.crugroup.com “Will polyhalite disrupt the fertiliser industry?” published online April 2018; last accessed 12 July 2018). Polyhalite accounts for around 450-460 kt of current SOPM fertilisers. ICL-UK is cur-

<table>
<thead>
<tr>
<th>Product</th>
<th>Manufacturer (Brand)</th>
<th>% K$_2$O</th>
<th>% MgO</th>
<th>% SO$_3$</th>
<th>% Cl</th>
</tr>
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<tbody>
<tr>
<td>Polyhalite</td>
<td>ICL-UK (Polysulphate®)</td>
<td>14</td>
<td>6</td>
<td>48</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Langbeinite</td>
<td>Mosaic (K-Mag®)</td>
<td>22</td>
<td>18</td>
<td>55-66</td>
<td>1-3</td>
</tr>
<tr>
<td>Hartsalz</td>
<td>K+S (Magnesia-Kainit®)</td>
<td>11</td>
<td>5</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>Schoenite</td>
<td>Chinese producers</td>
<td>21-24</td>
<td>5-6</td>
<td>35-40</td>
<td>2-3</td>
</tr>
<tr>
<td>Blends</td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>MOP +Kieserite</td>
<td>K+S (Kom-Kal®)</td>
<td>40</td>
<td>6</td>
<td>12</td>
<td>38</td>
</tr>
<tr>
<td>SOP + Kieserite</td>
<td>K+S (Patentkali®)</td>
<td>30</td>
<td>10</td>
<td>42</td>
<td>&gt;3</td>
</tr>
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Table 2. Listing of the main manufacturers of SOPM fertilisers currently available, along with K$_2$O contents.
rently ramping-up production to 1 Mt/y (140 kt/y K2O) by 2020, as it simultaneously phases out MOP production at the Boulby mine. At current production levels, this will be equivalent to almost 40% of the current SOPM market in K2O terms.

Sirius Minerals’ planned Phase I mine capacity (10 Mt/y product) is on a different scale altogether; around four times larger than the current SOPM market in K2O terms. This volume is almost the same size as the current global potassium sulphate (SOP) market, which is the most popular low-chloride potash fertiliser, outside China. The success of any future expanded SOPM application in agriculture is contentious; the majority of SOPM consumption has traditionally been concentrated close to production sites, nurtured by the local marketing efforts of producers. The proposed worldwide expansion will be tied to increasing acceptance by the agricultural community of polyhalite as an acceptable cheaper substitute for SOP and perhaps MOP.

**Polyhalite as a fertiliser.**

In the last few years, the use of polyhalite as an agricultural fertiliser has been tested successfully in a number of studies supported by Sirius minerals (Mello et al., 2018; Pavuluri et al., 2017). Polyhalite supplies four nutrients, is less water soluble than the more conventional potassium sources and may conceivably provide a slower release of nutrients. Studies comparing polyhalite to other K and Mg fertilisers have shown that polyhalite is at least as effective as potassium sulphate (K2SO4) as a slow release source of K, and at least as effective as potassium chloride (KCl) plus magnesium sulphate (MgSO4) as a source of K and Mg (Barbarick, 1991).

The possibility of successful use of polyhalite as a fertiliser is illustrated by the positive effects of its application on the growth of a potato crop at Tapira Brazil (Figure 2; Mello et al., 2017). Its impact on tuber starch and tuber dry matter exceeded that of either MOP or SOP applications. *Cultivar Asterix* at Tapira is mainly used for frying and chip-making (fries) in the food processing industry. High dry matter and starch content improve texture, and lower sugar contents result in less darkening of fries which is desirable. High dry matter percentage enables lower oil absorption while frying, resulting in lower oil usage per unit product. Tuber firmness is essential to handle mechanical stresses that may occur during tuber harvesting, transport, and storage. Crunchiness and hardness are positively related to starch and dry matter contents and specific gravity.

It seems polyhalite products are probably suitable as a low chloride fertiliser replacement of sylvite in some agricultural applications especially in arid acid, infertile soils as found in parts of Israel and other dry growing areas in the Middle East where salinisation due to fertiliser residues is a known problem. Yermiyahu et al., 2017, found the transport and leaching of Ca, Mg, K and S in soil following polyhalite application is lower than following the application of the equivalent sulphate salt fertilisers. The residual effect of polyhalite fertiliser on the subsequently grown crop is higher than the impact from the equivalent sulphate salts, especially regarding Ca, Mg and S. Irrigation management, as determined by the leaching fraction, has a substantial effect on the efficiency of polyhalite as a source of K, Ca, Mg and S for plant nutrition.

**Geology of polyhalite**

Polyhalite is a common constituent of many ancient evaporite sequences, especially in Permian and Neogene deposits, due to evaporation of Na–K–Mg–Cl–SO4 marine brines. These sulphate bittern assemblages correspond to periods of MgSO4-enriched ocean chemistries (Lowen-
The presence of syndepositional polyhalite in the supratidal evaporite flats around the Ojo de Liebre lagoon was first discovered by Holser (1966), who attributed its origin to the diagenesis of gypsum by interstitial marine brines. A large part of this area is now occupied by artificial salt ponds. However, some remnants of the ancient evaporite flats are still accessible, for example, on the southeast coast of the evaporitic complex, where sedimentological, chemical and isotopic investigations were performed on evaporitic sediments and interstitial solutions (Figure 3a, Pierre, 1983). In May 1979, the evaporitic succession was mainly composed of gypsum; a few centimetres below the surface, polyhalite was present in the form of small nodules that were partially replacing former gypsum crystals (Figure 3b,c). In May 1980, this evaporitic succession was drastically modified, since polyhalite replaced gypsum sediments lying below the water table. This gives an exact timing for the mineral transformation from gypsum to halite of one year to replace 10cm thick interval of gypsum with a 10cm interval of polyhalite, which points to a chemical evolution of the solutions permeating the sediments.

During this one-year period, ionic concentrations of interstitial brine increased from thirteen to 18 times with respect to seawater concentration (Pierre, 1983). SO$_4$ levels of interstitial solutions in the sabkha were higher than in normal marine brine and progressively increased in a landward direction, suggesting gypsum dissolution by groundwater crossflows.

Isotope study suggests both water and aqueous sulphate in the mud-flat porewater have a mixed marine and continental origin (Figure 4). Thus, it appears that sulphate ions are provided in part by marine brines, in part by continental waters which have dissolved Pleistocene interstitial gypsum present at depth. The replacement of gypsum by polyhalite requires not only high Mg$^{2+}$ and K$^+$, but also high SO$_4$ concentrations in the crossflowing solutions (Braitsch, 1971).

The polyhalite in Ojo de Liebre mudflats is diagenetic but also penecontemporaneous with the crystallisation of gypsum. However, in brines with temperatures >30°C, polyhalite may also be a primary co-precipitate with halite, as is occurring in recent saltworks near Santa Pola, SE Spain (as observed by B.C. Schreiber), and in cool-zone (cryogenic) salt lakes associated with widespread mira-
bilite-glauberite such as in Karabogazgol (Andriyasova, 1972).

Polyhalite is also a minor but widespread phase associated with glauberite in the Late Pleistocene-early Holocene sediments of Lop Nur China (Ma et al., 2016). There, the natural lake evaporites are nonmarine assemblages of mirabilite-glauberite-polyhalite-bloedite-gypsum-halite. The evaporitic stages of the lake fill contain massive amounts of glauberite and polyhalite compared to the other salts present. Polyhalite in the upper 40 m of the lake column and its predominance, is indicative of pervasive back-reactions, as is the presence of very minor amounts of carnallite and sylvite in the same section (Ma et al., 2010; Dong et al., 2012).

Ancient occurrences

Most ancient occurrences are interpreted as early diagenetic, formed in shallow brine crossflows as replacement of anhydrite or gypsum. Even so, there is a direct association between higher volumes of polyhalite in marine evaporite basins and times of MgSO₄ enrichment of ocean waters.

Neogene polyhalite

Polyhalite is not found as a widespread primary precipitate in rocks of this age even though ocean chemistries are MgSO₄-enriched. Instead, polyhalite is typically a minor but extensive early burial replacement of anhydrite or gypsum. The better-documented examples of this type of replacement polyhalite are found in association with gypsum and thenardite/glauberite in various Tertiary lacustrine basins of Spain. For example, below the exploited thenardite beds in the Madrid (Tajo) basin, Spain, the succession in the upper part of the lower Miocene unit is characterised by glauberite layers made up of a mixture of glauberite (45.8 %) and halite (41.7 %), with a minor polyhalite (7.8 %), dolomite (2.1 %), and clay minerals (1.8 %) (Herrero et al., 2015).

The Madrid Basin is a large Tertiary intra-cratonic depression that contains some of the largest fossil sodium sulphate and sepiolite deposits in the world. Bedded sodium sulphates (glauberite and thenardite) are restricted to the Lower Saline Unit, where they are associated with anhydrite, halite, magnesite, polyhalite and minor clays. Glauberite and thenardite are thought to have been deposited in the most central part of a permanent saline lake. The accumulation of thenardite might have taken place during a stage of contraction of the lake system at the beginning of the middle Aragonian (middle Miocene).

Polyhalite occurs as a diagenetic saline phase related both to calcium and sodium sulphates occurrences. Both sepiolite and bentonite deposits are widely distributed within peripherally in distal fan and marginal lacustrine sequences in the so-called Intermediate Unit of the Miocene (middle to upper Aragonian). Thick beds of nearly pure sepiolite were deposited in ponds extended at the toes of arkosic alluviums. Sepiolite is also found within calcrite profiles in these environments. Minor amounts of sepiolite are commonly recognised along with palygorskite in open lacustrine areas. On the other hand, Mg-bentonites characteristically occur associated with dolostones and fine micaceous sands in sequences that provide evidence of fluctuations in the lake level. Polyhalite typically occurs as felty and spherulitic aggregates that alternate with centimetre-thick halite layers or millimetre-thick glauberite laminae in the Lower Saline Unit (Figure 5). The polyhalite

![Figure 5. Measured section from a borehole with early diagenetic polyhalite in the Saline Unit of the Madrid Basin (After Ordonez et al., 1991)](image-url)
crystals are always associated with micritic magnesite). In its turn, the felty polyhalite may be related to skeletal glauberite crystals. The halite crystals commonly exhibit chevron-type morphologies. The thickness of the individual layers of halite ranges from 1 to 6 cm.

Similar polyhalite proportions are entrained in a number of glauberitic mineral assemblage in gypsiferous Neogene continental basins across the Iberian Peninsula, such as those of the Zaragoza (Salvany et al., 2007) or Lerín gypsum units (Salvany and Ortí, 1994), both occurrences are in the Ebro basin. In all cases, the polyhalite tends to be either massive or more typically a fibrous rim on large glauberite crystals.

Polyhalite also occurs as a minor phase in some potash regions the Messinian evaporites of the Mediterranean. In the mined succession exposed in the Realmonde mine, (southern Sicily) the halite unit is approximately 400 m-thick. From the bottom to the top, it consists of irregular anhydrite and marly mudstone breccia layer up to 2 m thick followed by units A to D (Figure 6; Lugli et al., 1999). Unit A, up to 50 m thick, contains evenly laminated halite with anhydrite nodules and laminae passing upward to massive halite beds with irregular mudstone bed some decimeters thick. Unit B (approximately 100m thick) consists of massive even layers of halite inter-bedded with thin kainite laminae, along with millimeter to centimetre-thick layers dominated by polyhalite spherulites and anhydrite laminae Figure 7; Garcia-Veigas et al., 1995). It may well be that along with kainite, the layers of polyhalite spherulites are primary co-precipitates at the potash bittern stage. The upper part of the succession contains several kainite layers up to 12 m thick. The 70–80 m thick unit C, consists of halite 10 to 20 cm thick lay-

![Figure 6. Polyhalite in the Messinian of Sicily A) Schematic showing potash stratigraphy in Realmonde Mine, Agrigento. B) Regional section showing structure in Realmonde region (after Decima and Wezel, 1971, 1973; Lugli, 1999).](image)

![Figure 7. Messinian polyhalite in the Realmonde Mine, Sicily (after Garcia-Veigas et al., 1995. A) Photomicrograph of radial spherulitic aggregates composed of fibrous polyhalite crystals that grew within a halite rock host (black) collect in Unit C (crossed polars. B) Fibrous prismatic polyhalite that grew in a halite host (Unit C) and partially replaced it. Replacement started at the halite grain boundaries (crossed polars). C) Radial spherulitic composed of fibrous polyhalite (centre of photomicrograph) that grew at the boundary among three halite grains. Unit C partially crossed polars.](image)
ers separated by irregular mud laminae and it too contains minor polyhalite and anhydrite. Unit D, up to 60 m thick, begins with a grey anhydrite-rich mudstone passing to an anhydrite laminate sequence, followed by halite millimetre- to centimetre-thick layers intercalated with anhydrite laminae and decimetre-thick halite beds.

Lugli et al. (1999) proposed that these lithologies, including the early diagenetic polyhalite, reflect the shallowing and the desiccation of the evaporitic basin resulting from a possible combination of factors: (1) uplift of the basin floor by thrust activity, (2) simple evaporitic drawdown and (3) a basin-wide drop of the Mediterranean sea level.

Polyhalite is also common as a potash contributor along with, in the highly deformed bittern series in the Badenian (Middle Miocene) ores of the Carpathian Foredeep Figure 8a). These beds are highly distorted and host former potash mines extracting a kainite-langbeinite ore target (Figure 8b). These potash-entraining salt deposits occur in western Ukraine within two structural terranes: 1) Carpathian Foredeep (rock and potash salt) and (II) Transcarpathian trough (rock salt) (Figure 8a). Deposits differ in the thickness and lithology, depending on the regional tectonic location (Czapowski et al., 2009). In the Ukrainian part of Carpathian Foredeep, three main tectonic zones are distinguished (Figure 8a): (I) outer zone (Bilde-Volytsya Unit), in which the Miocene molasse deposits overlie the Mesozoic platform basement discordantly at a depth of 10-200 m, and in the foredeep they subsided under the overthrust of the Sambir zone and are at depths of 1.2-2.2 km (Bukowski and Czapowski, 2009; Hryniv et al., 2007); (II) central zone (Sambir Unit), in which the Miocene deposits were overthrust some 8-12 km onto the external part of the Foredeep deposits of the external zone occur at depths of 1.0-2.2 km; (III) internal zone (Boryslav-Pokuttya Unit), where Miocene deposits were overthrust atop the Sambir Nappe zone across a distance of some 25 km (Hryniv et al., 2007).

Potash evaporites of the Carpathian Foredeep host an interesting sulphates group that includes about 20 sulphate evaporite minerals. Exploited potash deposits of the foredeep are composed of kainite, langbeinite, kainite-langbeinite, sylvite, polyhalite and carnallite rocks with layers of rock salt or interbedded clays and rock salt. In the areas of salt-bearing breccia, a polyhalite-anhydrite layer occurs along the contact with the potash salts bed. Halite, langbeinite and kainite dominated targeted ore levels in these potash deposits. Kieserite, polyhalite, anhydrite, sylvite and carnallite were present in smaller but significant quantities. These deposits, once a source of sulphate of potash, are no longer mined.

A study of sulphur isotopic composition of 10 of the sulphate minerals from the Kalush-Holyh and Stebnyk pot
ash deposits shows that only the basal Ca-sulphates (anhydrite) from the Kalush–Holyn potash deposits has \( \delta^{34}S_{\text{CD}} \) values typical of Neogene marine evaporites (+21.0‰; Hryniv et al., 2007). Potash minerals related to the ore-associations in the deposits (polyhalite, anhydrite, kainite, langbeinite and kieserite) show \( \delta^{34}S_{\text{CD}} \) values from +15.28‰ to +17.54‰, while weathering zone minerals (picromerite, leonite, bloedite, syngenite and gypsum) in the Dombrovo Quarry show values ranging from +14.73‰ to +18.22‰ (Table 3).

According to Hryniv et al. (2007) the recorded depletion of sulphur isotopic composition of the salt minerals in the Ukrainian potash deposits (and their weathering zone) was probably caused by one or more factors as follow: 1) bacterial reduction of sulphate, 2) effect of crystallisation and 3) inflow of surface waters containing sulphates enriched in light sulphur isotopes due to pyrite oxidation. Accordingly, the observed sulphur isotopic composition of minerals from these potash deposits demonstrates the depletion of the original marine brines and continual inflow of new (concentrated) seawater and later meteoric access. The preponderance of lighter sulphur isotopic values recorded in the Stebnyk deposit can be explained by a more intensive inflow of surface waters from the Carpathian nappes or by the oxidation of a part of the pyrite hosted in the sediments. Whatever the case, it seems that once again polyhalite is an early diagenetic mineral.

### Permian polyhalite

Permian polyhalite deposits are much more impressive in terms of volume and extent, compared to the Neogene, and are exemplified by massive occurrences in the USA and Europe.

### Permian polyhalite in West Texas and New Mexico

Polyhalite deposits are by far the most abundant, most numerous, and widespread of all potash mineral occurrences in the Delaware Basin of Texas and New Mexico (Jones 1972; Lowenstein, 1988; Harville and Fritz, 1986). However, langbeinite and sylvinite are the economically important potash minerals and have been the focus of many studies, rather than polyhalite documentation (Figure 9a).

Permian polyhalite in the Delaware Basin occurs both as massive and disseminated deposits in anhydrite and salt beds and less often in clay beds. Typically, massive deposits and all veins and lenses are composed predominantly of polyhalite, in distinctly compact units that have sharp, clear-cut outlines. Disseminated deposits generally are less defined, shapeless bodies of spherules as cleavage-parallel growths in a host rock, chiefly in halite. Disseminated occurrences are many times more numerous than the massive deposits, but the amount of polyhalite present is minor in comparison with that present in most massive deposits in anhydrite beds.

Massive polyhalite occurrences outline a crude oval-shaped area in the basin, extending over a region about 325 km long and 220 km wide, covering practically the whole southern half of the area between the Pecos River and the eastern limit of salt in the Ochoa Series (Figure 9a). Occurrences range stratigraphically from low in the Tansill Formation (upper part of Guadalupe Series) in the North-western shelf to near the middle of the Rustler Formation in the north-east corner of the Delaware basin (Figure 9b). Polyhalite beds reach their highest number and size in the Salado Formation (Ochoan), where they have a wide distribution over much of the Delaware and Midland basins and adjacent platform and shelf areas (Figure 9). In the Salado Fm., thick clay seams occur as basal strata
that underlie massive polyhalite/anhydrite beds (Harville and Fritz, 1986; Lowenstein, 1988). By virtue of the wide extent and number of massive deposits, polyhalite ranks next to halite and anhydrite among the major constituents of the Salado Formation. Sections with layered halite and polyhalite cover areas of 95,000 km² and 70,000 km², respectively (Jones 1972).

Massive polyhalite units are typically compact and fine-grained, exhibiting a variety of colours (grey to red) and textures (irregular to layered to laminated and fibrous to equigranular prismatic). Significant volumes are replacements of anhydrite beds, and although they may have almost any shape, most tend to be lenticular to sheet-like masses that spread out along the bedding and replace practically the entire section of anhydrite. Polyhalite units in the McNutt Potash zone, east of Carlsbad, have lateral continuities sufficient to act as marker beds, which separate and define layering in the sylvite-langbeinite ore zones (Figure 10).

As a general rule, sheet-like to crudely tabular polyhalite bodies occur in anhydrite layers where stacked polyhalite units are a few centimetres to a metre thick. Deposits that are more irregular in shape occur mostly in thicker beds (>1m). In most cases the polyhalite is pseudomorphous after growth-aligned subaqueous and nodular anhydrite beds (Figure 11). Practically all the deposits enclose residual strips and irregular remnants of magnesitic anhydrite, which are mottled and streaked with halitic and anhydritic pseudomorphs after gypsum. Commonly polyhalite crystals and multigrain aggregates project into the magnesitic anhydrite remnants either as elongate crystals and veinlike tongues or as aggregates having scalloped margins convex toward anhydrite.

In many places in the Carlsbad district and nearby parts of the north-western shelf, many of the massive polyhalite deposits grade laterally to an anhydritic harsalz unit with ore grade levels of sylvite. This is the area known as

![Figure 9. Distribution of massive potash deposits in evaporites of the Ochoan (Salado) Series in Texas and New Mexico. A) polyhalite has a wide extent, while the economic sylvite-langbeinite layers are restricted to a smaller area known as the McNutt Zone located to the east of Carlsbad (Jones 1972). B) stratigraphic section in southeastern New Mexico showing distribution of bedded sylvite-langbeinite mineralization with the polyhalite interval of the Salado Fm (after Bates, 1969).](www.saltworkconsultants.com)
the McNutt Member or the McNutt potash zone (Figures 9a, 10). The change from polyhalite to hartsalz coincides with a shift from unmineralized to sylvinitic rock peppered with sparse grains and veinlets of carnallite and other magnesium-bearing bittern minerals, such as langbeinite and polyhalite.

In 1988, Lowenstein recognised two types of metre-scale depositional cycles (Type I and Type II) within the McNutt Potash Zone (Figure 11). Both cycles record progressive drawdown and concentration of brine in a shallow, marginal marine drawdown basin. "Type I" cycles have a base of carbonate-siliciclastic mudstone, overlain by anhydrite-polyhalite that is pseudomorphous after primary bedded gypsum. This, in turn, is overlain by bedded halite and capped by muddy halite. Lowenstein (1988) concluded the McNutt Zone of the Salado Formation consists entirely of these two types of metre-scale sequences, variably stacked one upon another (Figure 11).

All units are interpreted as mostly marine-brine dominated units precipitated by evaporation of massive volumes of brines fed by marine seepage or periodic overflows of the Permian ocean water. The upper cap to Type II cycles influenced by inflows of continental groundwater (Figure 11).

A basal mudstone grades upsection into anhydrite-polyhalite that is commonly laminated. Laminae are defined by couplets of anhydrite or polyhalite separated by magnesite-rich mud (Figure 12a-c). The most significant feature of the anhydrite/polyhalite interval is the large number of crystal outlines that occur in the anhydrite-polyhalite laminae. These crystals are now composed of anhydrite, polyhalite, halite, or sylvite but are all interpreted as replacement pseudomorphs after primary gypsum because of their close similarity to typical bottom-nucleated subaqueous gypsum crystal habits such as "swallow-tail twins" (Figure 11). In some occurrences, the polyhalite is forming early diagenetic spherules in magnesite layers (Figure 13a). Elsewhere

Figure 10. Stratigraphy of the McNutt Potash zone in the Salado Fm, showing polyhalite marker beds, focused on the main ore zone near Hobbs New Mexico (comments on mineralogy from Griswold, 1982).
Polyhalite directly replaces bottom-nucleated subaqueous gypsum or halite (Figures 12a, c, ), while yet elsewhere it grows as spherular clusters in halite that already has pseudomorphed aligned gypsum crystals (Figure 12c). In other places, rippled gypsum beds are replaced by polyhalite and anhydrite. Syndepositional brine reflux likely drove replacement of subaqueous gypsum by anhydrite-polyhalite, in a fashion similar to that described by Hovorka (1992) for halite replacing growth-aligned gypsum.

At the microscopic scale, it is evident that polyhalite forms as a replacement (Figure 13). One of the most common modes of occurrence across the Salado Formation is coalescing spherules growing in relatively undisturbed magnesite layers (Figure 13a). Elsewhere, coarser mm-scale polyhalite prisms have poikilotopically enclosed anhydrite crystals (Figure 13b). Felted fibrous polyhalite also surrounds euhedral halite (Figure 13c) or forms a replacement rim to halite in the langbeinite-sylvite ore layers (Figure 13d).

"Type II" cycles, lacking the basal mudstone and polyhalite/anhydrite beds, occur between Type I cycles and contain additional halite units (with thinly layered polyhalite) overlain transitionally by muddy halite (also with dispersed polyhalite). Complete brining-upward Type I and Type II cycles record a temporal evolution of depositional environment from a shallow saline lake to an ephemeral salt-pan-saline mudflat complex. The uppermost muddy halite unit interpreted as a continental-dominated sequence, sourced by meteoric inflow from surrounding land areas that mixed with variable amounts of seawater, either from residual pore waters or introduced into the Salado Basin by seepage.

Periodic invasions of seawater best explain the vertical stacking of Type I cycles in the Salado basin, perhaps coincident with eustatic sea-level rises (Lowenstein, 1988). The continental-dominated upper parts of Type I and II cycles formed during intervening periods of eustatic sea-level fall and low stand when nonmarine waters exerted more in-
fluence on the brine chemistry. According to Lowenstein (1988), the maximum time interval between major marine incursions averages 100,000 years. The layered nature of the polyhalite replacement implies that this occurred in each eustatic cycle, that is, the replacement was an integral part of the eogenetic hydrolology and was not a burial diagenetic (mesogenetic) process.

Permian Polyhalite in Poland and Russia

According to Peryt et al., 2005 (and references therein) there are four polyhalite deposits in the Zechstein of northern Poland, and more than ten polyhalite-bearing areas in the adjacent part of Russia (Figure 14). In addition, K-Mg chlorides are found locally both in Poland and Russia. The K-Mg salts originated during the last stages of chloride accumulation within small, actively subsiding isolated salt basins of the salina type, which were probably tectonically controlled.

The paragenetic sequence in one polyhalite deposit in the Zechstein of Poland was the result of a very early - penecontemporaneous polyhalitisation of anhydrite that had already pseudomorphed gypsum, much as is seen in the Delaware basin (Peryt et al. 1998). There polyhalite formed by altering anhydrite during crossflows of concentrated brines that were also responsible for potash deposition in local salt basins, while the sulphate-rich brines supplied by the dissolution of emergent parts of the sulfate platform (Peryt et al. 1998).

The timing of the polyhalitisation can be inferred from a
S–O isotope crossplot (Figure 15; Peryt et al., 1998). The isotopic compositions of sulphate evaporites indicate that marine solutions were the only source of sulphate ions supplied to the Zechstein basin. The more negative oxygen values associated with the polyhalite compared to its anhydrite precursor indicates somewhat warmer solutions that drove the conversion to polyhalite. These solutions were more saline than those driving the initial shallow anhydritisation that replaced platform gypsum by a reaction with refluxing brines.

**Polyhalite in the Zechstein of the UK**

Polyhalite in the Boulby Mine and the proposed York mine both occur within the Permian Fordon Formation, of the 2nd Zechstein cycle (Z2) in north-east England (Figure 16; Table 4; Stewart 1963; Smith et al., 1986; Kemp et al., 2016). Although initially discovered in 1939, the deeper, polyhalite-bearing Fordon (Evaporite) Formation was largely overlooked until recently. ICL-UK operations at the Boulby Mine have largely depleted the sylvinite target in the Boulby Potash Member, so the mine is now transitioning into polyhalite extraction from the Fordon (Evaporite) Formation (Table 4). The historical output from the Boulby Mine was around 1 Mt/yr of refined KCl product and 0.6 Mt of road salt (Kemp et al., 2016). Polyhalite beds in the proposed York (Whitehall) mine are considered to be so high grade that they can be mined and marketed as SOPM fertiliser with no processing except crushing and sizing (Kemp et al., 2016).

Five evaporite cycles (EZ1–EZ5) are developed in the northwestern corner of the main Permian Zechstein basin where it comes onshore in the UK between Teesside and Lincolnshire (Table 2, Figures 16, 17).

The relationship between the evaporite sequence in the main Zechstein basin and its onshore, lateral gradation into shelf and then semi-continental clastic strata was described by Smith et al., (1986). Potash salts are known from cycles EZ2, EZ3, and EZ4, and Britain’s only potash producer, the Boulby mine, exploits sylvinite from the EZ3 Boulby Potash Member. Sylvinite-bearing horizons are also known in the EZ2 cycle, but the key potash resource therein is polyhalite, first discovered in 1939 in the E2 oil exploration hole at Eskdale, Whitby (Stewart, 1949). The only known occurrence of potentially economic volumes of polyhalite in the UK is in the EZ2 Fordon (Evaporite) Formation in this area.
Mineral zonation in the Fordon (Evaporite) Formation was first described in detail by Stewart (1949, 1963) from the Eskdale and Fordon boreholes. Polyhalite was described as partly primary, but mostly a replacement of syndepositional anhydrite. Three subcycles were recognised at Fordon. The Lower subcycle was deposited in a basin that still displayed considerable topographic variation from a shallow-water shelf to a deepwater basin (Figure 17). It contains no known potash occurrences. The Middle subcycle, in which the polyhalite occurs, includes a large volume of basin-fill evaporites, chiefly halite, that filled accommodation space and smoothed out the shelf-basin geometry. Consequently, it shows considerable lateral variation in thickness. The Upper subcycle formed in uniformly shallow-water conditions with no clear distinction between shelf and basin. It hosts a persistent sylvite-bearing horizon known as the Gough Seam. Colter and Reed (1980) showed that Stewart's mineral zones could be projected far beyond the Fordon borehole and were recognisable throughout much of the British section of the North Sea basin (Doornenbal and Stevenson, 2010).

The description of mineral zones at Eskdale and Fordon by Stewart (1949, 1963) relate to boreholes drilled through the shelf and basin, respectively. The precise correlation of the polyhalite-bearing sulfate deposits between these two environments, or zones, remains ambiguous (Kemp et al., 2016). At present, the polyhalite deposit is referred to as the Shelf seam in the Shelf zone, and the Basin seam in the Basin zone, with a Transition zone across the ramp and in its vicinity where great thicknesses of polyhalite and anhydrite occur with varying amounts of early diagenetic, displacive halite. In borehole SM2 there was solid evidence for overlapping Shelf and Basin seams, separated by 82 m of "sulphatic halite". Both the shelf and basin polyhalite seams are considered to be of mineable thickness and grade in their relevant sectors, averaging over 12 m in thickness for high-grade sections of >85% polyhalite.

Kemp et al. (2016) argue that the polyhalite is almost entirely secondary, resulting from replacement reactions between freshly deposited anhydrite muds on the seabed, with dense, bottom flowing, K-Mg-rich brines. A sylvite-bearing bittern salt horizon is locally present near the top of the Middle subcycle in both the Basin and the Shelf Zechstein cycle.

Table 4. Permian lithostratigraphical units in northeastern England (after Smith et al., 1986). EZ = English Zechstein units.

<table>
<thead>
<tr>
<th>Zechstein cycle</th>
<th>North East England onshore lithostratigraphy</th>
</tr>
</thead>
<tbody>
<tr>
<td>EZ5 Eskdale Group</td>
<td>Littlebeck (Anhydrite) Fm. Sileights (Siltstone) Fm.</td>
</tr>
<tr>
<td>EZ4 Staintondale Group</td>
<td>S neutron (Halite) Fm. Sherburn (Anhydrite) Fm. Upgang (Limestone) Fm. Carnallitic Marl Fm. S neutron Potash Mbr</td>
</tr>
<tr>
<td>EZ3 Teesside Group</td>
<td>Boulby (Halite) Fm.Billingham (Anhydrite) Fm. Brotherton (Mg limestone) Fm. Grauer Saltzon Boulby Potash Mbr</td>
</tr>
<tr>
<td>EZ2 Aislaby Group</td>
<td>Fordon (Evaporite) Fm. Kirkham Abbey (Limestone) Fm. Polyhalite unit</td>
</tr>
<tr>
<td>EZ1 Don Group</td>
<td>Hayton (Anhydrite) Fm. Cadeby (Limestone) Fm. Marl Slate Fm.</td>
</tr>
</tbody>
</table>

Figure 17. Conceptual geologic model for the Fordon (Evaporite) Formation in the York Potash Ltd area of interest (after Kemp et al., 2016).
(though less commonly) and is referred to here as the Pasture Beck seam, after the borehole (also known as SM1) where it was first cored and characterised (Figure 16).

Another sylvite-bearing bittern salt horizon is more commonly present near the top of the Upper subcycle in both Basin and Shelf and is referred to here as the Gough seam; described in the SM4 borehole, where it was first cored and characterised as containing relatively high-grade sylvite. It is not clear why this and the Pasture Beck potash seam are so localised and patchy in distribution, but they may result from bittern brine pools of limited area, cut off from each other as the aggrading basin filled up at the end of each subcycle.

At an even more local scale in the polyhalite ore intervals in the Boulby Mine, there are metre-scale domal structures interpreted as a form of tepee structure (Figures 18; Abbott, 2017). The height of the domal-shaped structures exposed in the mine workings varies between 0.4 m and 1.5 m (average = 0.9±0.1 m) and widths ranging from ~2.3 m to 10.5 m (average = 5.3±0.5 m).

Unlike the highly deformed halokinetic flow textures in the overlying sylrite of the Boulby Potash Member, it seems much of the polyhalite ore preserves mostly syn-depositional diagenetic alteration structures. Most of the domal features do not show the overthrust brittle ridge crests that define most tepees (Kendall and Warren, 1987). Instead, the domal peak tends to be a fractured and folded local anticlinal culmination. Whether one calls these anticlinal deformations domes in the polyhalite a true tepee, depends on which definition of a tepee one chooses to use. The domal features are thought to be a soft sediment deformation features, formed via polyhalite dewatering, coupled with penecontemporaneous precipitation of halite in opening fractures and below anticline crests in shallow burial. Deformation was driven by fluid crossflows and escapes, as anhydrite converted to polyhalite.

**Forming polyhalite?**

Nowhere is the present or the past is there evidence of direct primary precipitation of polyhalite. By primary, I mean that to be considered a primary polyhalite, the crystals should drop out of a concentrating at-surface brine either as bottom-nucleated or foundered brine-surface crystals. Such primary textures are widespread in gypsum and halite units but not in polyhalite. Instead, polyhalite textures and isotopic signals indicate polyhalite forms via replacement of gypsum or anhydritised gypsum.

In the modern salt flats of Ojo de Liebre, we see polyhalite replacing gypsum. Likewise, in various Tertiary lacustrine basins in Spain, polyhalite is found in association with gypsum and thenardite, and it is replacing a CaSO4
phase. In the Badenian marine evaporites of the Carpathian fore-deep, the polyhalite is part of the kainite-langbeinite ore sequence. It is in the Permian of the UK and West Texas and New Mexico that the volumes of polyhalite become sufficient for it to become a potential ore target in its own right. Once again all the textural and isotopic evidence indicates polyhalitisation of anhydrite rather than primary precipitation. But this replacement is more likely to be eogenetic (driven by nearsurface hydrologies that were active in the depositional setting) rather than mesogenetic (burial).

The most likely driven mechanism was brine reflux moving highly saline seawater through shallowly buried units of platform or basinal gypsum and anhydrite. This shallow subsurface emplacement occurred while the gypsum anhydrite was still permeable, and so allowed the preservation of pristine texture (pseudomorphs) of the CaSO₄ precursors.

Polyhalitisation of basinal and platform gypsum units in the mega-sulphate stages of a saline giant are driven by time separate hydrologies, tied to the changing brine levels in the drawdown basin (Figure 19; Warren, 2016). Marine-derived brine reflux through basinal anhydrites occurs during maximum drawdown in the mega-sulphate basin (blue arrow positions stage b in Figure 19), while reflux through the upper (marginal salt-ern) parts of a sulphate platform is a response to a relative highstand (blue arrow positions in stage c Figure 19; Warren, 2016 - Chapter 5). The likely loss of permeability as one goes deeper in a sulphate platform and the associated lessening in the volume brine crossflow probably explains why there is an interval of sub-economic polyhalitic sulphates separating the basinal from the shelfal ore zones. The sequence stratigraphic fill model also explains why the patchy potash intervals are located higher in the stratigraphy at the "fill and spill stage" of a hyperarid climate (stage e in Figure 19; Warren 2016).

A drawdown model encompassing two stages of polyhalitisation explains why much of the textures seen in the

![Figure 19. Times and positions of hydrologies suitable for polyhalitisation via brine reflux is indicated by the position of blue arrows in holomictic gypsum saturation hydrologies, in a hydrographically isolated marine-seepage saline giant. The basinal sulphates are converted to polyhalite at time b, while the platform sulphates are converted at time c. The sequence stratigraphic model driving the seepage positioning is based on the sequence stratigraphic model of Warren 2016.](www.saltworkconsultants.com)
The saline giants of the Neogen, which is also a time of MgSO₄-enriched waters. Polyhalite is never present in the gypsumiferous units of the Messinian or Badenian saline giants in the same volumes we see in the Permian. Then again, the extreme hyper-arid hydrologies we see in arid climate belts across the Pangean supercontinent are also unusual. But the seawater chemistry was not too different to that of today (Lowenstein et al., 2005).

**References**


If the layer and laminate gypsum-anhydrite is interlayered with units of bottom-aligned gypsum or its anhydritised “ghosts,” as in west Texas and Poland, then the depositing waters in both units were shallow.

We can now take this reflux model for polyhalitisation and explain why the two polyhalite ore seams in the Forden Evaporite Formation are separated by a low quality "sulphatic halite-anhydrite" unit (Figure 20). At time 1 the basin is at its maximum lowstand and dense reflux brines are sinking into the basinal gypsum units. Water depths below the holomictic brine mass in the basin lows are relatively shallow. At time two the brine levels in the basin are much higher, and a gypsum platform is prograding into the basin. Water depths above the platform are shallow, while they are deep in the basin centre. When the water column is holomictic, brine reflux is occurring across the platform and out into the basin. However descending brines cannot penetrate into all parts of the platform due to compaction and earlier reflux of halite-saturated cements. Brines must pass beyond halite saturation to reach polyhalite (Figure 1). This early loss of permeability created a core of less altered anhydrite below the polyhalite replacement interval.

But we must now ask, why did polyhalitisation of large parts of sulphate platforms reach its zenith in the Permian. A pseudomorphing process with a halite-gypsum focus is seen throughout the rock record (Chapter 5, 7; Warren, 2016). But the volumes of polyhalite we see in the Permian saline giants are different to the much smaller volumes of


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