SYNDEPOSITIONAL ORIGIN OF POTASH EVAPORITES: PETROGRAPHIC AND FLUID INCLUSION EVIDENCE

TIM K. LOWENSTEIN* and RONALD J. SPENCER**

ABSTRACT. The major potash salt sylvite (KCl) formed syndepositionally in three ancient evaporite deposits (Oligocene Rhine Graben, Alsace, France; Permian Salado Formation, New Mexico; Devonian Prairie Formation, Saskatchewan, Canada). Most sylvite in ancient evaporites has been interpreted as a secondary diagenetic mineral formed by the incongruent dissolution of carnallite (MgCl₂ · KCl · 6H₂O). The evidence for the formation of syndepositional sylvite casts doubt on these previous interpretations.

Fluid inclusions in primary subaqueous “chevron” and “cumulate” halites associated with potash salts in the Rhine Graben, Salado, and Prairie evaporites contain daughter crystals of sylvite, which establishes the existence of syndepositional surface brines capable of precipitating sylvite without further brine concentration. Sylvite daughter crystals from fluid inclusions in halite dissolve at moderately high temperatures (avg of 63°C for Rhine Graben, 71°C for Salado, and 39°C in Prairie). These results indicate that halite crystallized from warm surface brines rich in KCl. Cooling of these brines at or just below the surface is a major mechanism by which to achieve supersaturation with respect to sylvite.

Sylvite layers in the Rhine Graben evaporites consist of fine-grained, well sorted equigranular mosaics. The sylvites are interpreted as primary cumulates, originally crystallized at the air-brine interface of a perennial saline lake by the mechanism of brine cooling. Sylvite in the Salado Formation occupies areas equivalent to the void spaces in modern saline pan halites and is thus interpreted as an early diagenetic pore-filling cement. The sylvite cement formed just beneath the surface of an ephemeral saline pan. Warm, KCl-rich surface brines would slowly drop below the sediment-air interface upon desiccation of the saline pan. The groundwater brines so produced would become, when cooled, highly supersaturated with respect to sylvite, leading to the growth of sylvite cements. It also appears that the Prairie Formation sylvites formed by cooling of syndepositional brines as they sank into the shallow subsurface.

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INTRODUCTION

A long recognized problem in evaporite geochemistry is the failure of ancient evaporites, which contain the very soluble “potash” or “bittern” salts, to match the mineralogical sequences predicted by the evaporation of modern seawater. Indeed, in only one deposit (the Stassfurt Series of the Permian Zechstein Formation) is the vertical sequence of salts that predicted by the equilibrium evaporation of modern seawater at 25°C (Harvie and others, 1980: Eugster, Harvie, and Weare, 1980; Hardie, 1984). No other known potash evaporite in the geologic record has the distinctive seawater evaporation sequence. However, practically every ancient potash evaporite has been interpreted as marine, and there is general consensus that the major element chemistry of seawater did not change significantly during the Phanerzoic (Rubey, 1951; Chave, 1960; Kramer, 1965: Holland, 1972; Holland, Lazar, and McCaffrey, 1986). The discrepancy between predicted versus observed potash-bearing mineral sequences has been explained by:

1. syndepositional modification of seawater composition by biological processes, such as sulfate reduction (Borchert and Muir, 1964; Braitsch, 1971; Wardlaw, 1972b; Sonnenfeld, 1984);

2. syndepositional modification of seawater by mixing with non-marine inflows, composed of meteoric (D’Ans, 1947: Stewart, 1963: Wardlaw, 1972b; Valyashko, 1972), diagenetic, volcanogenic, or hydrothermal waters (Hardie, 1984);

3. non-marine parent waters (Hardie, 1984);

4. metastable equilibrium or non-equilibrium conditions that prevented precipitation of the normal seawater sequence (Valyashko, 1972); and

5. syndepositional or post-depositional processes (thermal metamorphism, metasomatic alteration) which have modified the primary marine sequence by cementation, mineral replacements, recrystallization, and formation of high temperature salts (Stewart, 1963: Borchert and Muir, 1964; Wardlaw, 1968; Evans, 1970; Braitsch, 1971; Holser, 1979; Hardie, Lowenstein, and Spencer, 1985). In fact, Stewart (1963, p. 4) concludes that “most large evaporite bodies have suffered widespread metasomatic changes since their original formation.”

Metastable equilibrium or non-equilibrium precipitation (option 4 above) is difficult to assess in an ancient evaporite and will not be considered further (see however, Valyashko, 1972; and Hardie, 1984, p. 206–207). Thus, for the purposes of this paper, hypotheses on the origins of the “anomalous” potash evaporite sequences can be divided into those involving departures of the parent waters from seawater composition (options 1, 2, and 3 above) and those invoking diagenetic alteration of the original primary mineral sequence (option 5).

This paper treats the timing of precipitation of potash evaporites based on petrographic textures, fluid inclusions in associated halites, sedimentary structures, and comparisons with modern and Quaternary
evaporites. The potash salt sylvite (KCl) is emphasized because it is the most common potash mineral in ancient "marine" evaporites (Stewart, 1963; Holser, 1979). Primary potash evaporites, formed syndepositionally, during or just after deposition by processes controlled by the existing depositional environment, are distinguished from secondary potash evaporites that are diagenetic mineral assemblages controlled by the subsurface burial environment (Hardie, Lowenstein, and Spencer, 1985). Evidence is presented for a syndepositional origin of the potash salts in the Oligocene Rhine Graben of Alsace, France, the Permian Salado Formation of New Mexico, and the Devonian Prairie Formation of Saskatchewan, Canada. Furthermore, the Rhine Graben potash evaporites formed primarily as a bedded subaqueous deposit, whereas the Salado and Prairie potash evaporites formed syndepositional diagenetic cements by the mechanism of cooling of surface brines.

METHODS

Observations of petrographic textures, sedimentary structures, and fluid inclusion data are from core material and mine samples. Petrographic textures and sedimentary structures are compared with a variety of modern and ancient examples (Hardie, Lowenstein, and Spencer, 1985; Lowenstein and Hardie, 1985). There is virtually no published work that describes modern potash evaporites in detail. Therefore we have relied on modern and Quaternary halites as analogs for the halites that coexist with the ancient potash deposits in the same bed or in overlying and underlying layers.

Halite crystals in ancient evaporites commonly contain well defined fluid inclusion banding (fig. 1A). The fluid inclusion bands occur in (1) vertically oriented, vertically elongated chevron halite (Wardlaw and Schwerdtner, 1966) and (2) cumulate halite, consisting of accumulations of pyramidal hopper crystals (Dellwig, 1955), equant cubes, and rectangular and square-shaped plates (Artherton, 1973; Lowenstein and Hardie, 1985). In both cases, fluid inclusion banding is clearly parallel to halite crystal growth faces. In transmitted light, dark bands rich in fluid inclusions are commonly 100 to 250 μm thick but may be up to 1 mm thick. The dark bands alternate with clear bands that contain fewer fluid inclusions. Individual fluid inclusions in the bands are negative crystals (cubes). In most samples the length of one side of an inclusion is from less than 1 to about 40 μm (fig. 1B). This distinct banding is similar to growth banding seen in halite grown in modern salt pans and in the laboratory. We, and many before us, interpret the inclusions as primary features and their enclosed fluids as syndepositional brines (Wardlaw and Schwerdtner, 1966; Roedder, 1984; Knauth and Beeunas, 1986).

Fluid inclusions in halite associated with potash salts in the Salado, Prairie, and Rhine Graben evaporites contain cubic, isotropic daughter crystals of sylvite (fig. 1B). These fluid inclusions were analyzed using a Fluid Inc. U.S.G.S. adapted gas-flow heating/freezing system. Some inclusions contain sylvite daughter crystals at room temperature,
Fig. 1(A) Thin section photomicrograph of vertically oriented halite “chevron.” Dark bands rich in fluid inclusions alternate with lighter bands containing fewer fluid inclusions. Sample from McNutt Potash Zone, Salado Formation. Scale bar is 1 mm long.

(B) Thin section photomicrograph of fluid-inclusion banding in chevron halite. Inclusions are negative crystals (cubes) that range in size from less than 1 μm to greater than 40 μm (length of one side of cube). Each fluid inclusion contains a single cubic daughter crystal of sylvite (arrows). Sample from McNutt Potash Zone, Salado Formation. Scale bar is 100 μm long.
Syndepositional origin of potash evaporites

Table 1

Dissolution temperatures of sylvite daughter crystals (Tsylvite) in fluid inclusions in laboratory-grown crystals of halite in system NaCl-KCl-H₂O compared with predicted temperatures of sylvite dissolution (based on solubility data of D’Ans, 1933; Linke, 1965).

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<th>Wt. % KCl (Halite saturation)</th>
<th>Predicted T (°C)</th>
<th>Observed T (°C)</th>
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<tr>
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<td>Sylvite dissolution</td>
<td>Sylvite dissolution</td>
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<tr>
<td>5</td>
<td>−17</td>
<td>−16.1 – −17.0</td>
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<tr>
<td>11.1</td>
<td>27</td>
<td>24.2 – 28.1</td>
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<td>15</td>
<td>54</td>
<td>53.9 – 54.5</td>
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whereas in others, cooling to as low as −60°C was necessary to nucleate the crystals. Fluid inclusions with sylvite daughter crystals were heated at a rate of 2°C per min. The solubility of sylvite is strongly temperature dependent (D’Ans, 1933; Linke, 1965). As the fluid inclusions are warmed, the sylvite daughter crystals begin to dissolve and the rounding of crystal corners is apparent. The final disappearance temperature of the sylvite was obtained to within 0.2°C by raising the temperature slowly in 0.2°C increments and then cooling rapidly as the final dissolution temperature is approached. By this method, the final dissolution or disappearance temperature of sylvite (Tsylvite) is reached when the sylvite crystals fail to grow larger on cooling.

Halite crystals were grown experimentally at temperatures between 60°C and 90°C in solutions of several compositions in the system NaCl–KCl–H₂O to test the accuracy of the methods described above (table 1). The solutions were at halite saturation and contained 5, 11.1, and 15 wt percent KCl. Halite crystals about 1 mm in size were removed from the solutions, rinsed with alcohol, and dried. They were then placed in the heating/freezing system and cooled to −60°C. At this point sylvite daughter crystals precipitated in fluid inclusions in the halite crystals. The fluid inclusions were slowly warmed, and the final dissolution temperature of sylvite daughter crystals was obtained, as outlined above. The dissolution temperature of sylvite for the 3 sets of experimentally grown halites all fall within 3°C of the temperatures predicted by solubility data (table 1). These results indicate that fluid inclusions in laboratory-grown crystals of halite trap the ambient brines from which the crystals precipitate. Sylvite daughter crystals readily form by cooling fluid inclusion brines that contain 5 wt percent or more KCl. The final dissolution temperature of sylvite daughter crystals is below the temperature at which the halite host precipitated: thus, the dissolution of sylvite faithfully records a minimum temperature of halite crystallization.

OLIGOCENE RHINE GRABEN

Geologic setting—The Oligocene evaporites of the Rhine Graben of France and Germany are an example of a potash deposit that deviates
from the predicted seawater sequence. They contain sylvite and subordinate carnallite but completely lack the MgSO₄-salts (polyhalite, kieserite) characteristic of the seawater sequence (see table 2 for chemical composition of evaporite minerals discussed in text).

The Rhine Graben is a Tertiary rift system 150 km in length and 10 to 25 km wide located along the French and German border (fig. 2: Sittler, 1969). Oligocene evaporites, about 1700 m thick, composed of anhydrite, halite, and mudstones, occur in the subsurface of the southern portion of the graben (fig. 3; Blanc-Valleron and Gannat, 1985). The evaporites are underlain by Eocene, post-rift continental mudstones and conglomerates with lacustrine fossils and local anhydrite (Courtot, Gannat, and Wendling, 1972; Blanc-Valleron and Gannat, 1985). Near Mulhouse, France, (Mulhouse Basin) potash salts occur in the subsurface at depths of 420 to 1100 m. They are virtually all found in two laterally continuous zones in the upper third of the evaporite section (fig. 3). A lower potash interval (Couche Inférieure) up to 5 m thick with sylvite and, in places, carnallite, is separated by about 20 m from an upper zone (Couche Supérieure) up to 2 m thick with sylvite (Courtot, Gannat, and Wendling, 1972).

The stratigraphy, petrography, mineralogy, and geochemistry of the Rhine Graben potash and associated sediments have been studied extensively (Görgey, 1912; Sturmfels, 1943; Maikovsky, 1952; Wagner, 1953; Baar and Kühn, 1962; Braitsch and Herrmann, 1964; Borchert and Muir, 1964; Braitsch, 1966, 1971; Courtot, Gannat, and Wendling, 1972; Kühn and Roth, 1979; Meriaux and Gannat, 1980; Blanc-Valleron and Gannat, 1985). The potash intervals are well bedded and consist of laminated mudstone (with dolomite), anhydrite, halite, and sylvite which in places form repetitive cycles (figs. 3, 4). Based on the extraordinary preservation of layering in these sequences, most workers have interpreted the Rhine Graben potash and associated sediments as primary (Braitsch, 1971). Measurements of the Br in halite show a steady

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<td>polyhalite</td>
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<td>sylvite</td>
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rise in Br below the potash zones, maximum Br in halite within the potash interval, and a drop in Br just above the potash salts (Baar and Kühn, 1962; Braitsch and Herrmann, 1964; Braitsch, 1966; Kühn and Roth, 1979). This is consistent with precipitation of halite from a standing body of brine that has undergone progressive concentration followed by inflow of more dilute waters after precipitation of the potash salts.

The sylvite of the Rhine Graben has been interpreted as a primary mineral formed by the cooling of brines (Sturmfels, 1943; Braitsch, 1971). From Br measurements on sylvite and halite, Braitsch and Herrmann (1964) and Braitsch (1966) hypothesized evaporite precipitation from stratified brines—a bottom brine from which sylvite precipitated and a surface brine from which halite precipitated.

Petrography—The petrographic features of the lower potash zone (Couche Inférieure) from core samples and two mine outcrops (Marie Louise and Theodore) are described here. The sequence is up to 5 m
thick and consists of halite, sylvite, and partings composed of mudstone with dolomite or anhydrite (fig. 3). Three decimeter-thick beds of finely laminated mudstone occur in this interval (Meriaux and Gannat, 1980).

Several types of centimeter to decimeter-thick mineralogical cycles have been recognized in the Couche Inférieure (figs. 4, 5, 6). The most complete sequences begin with a sub-centimeter thick mudstone containing dolomite and with or without anhydrite near the top, followed by halite (± minor anhydrite) and capped by sylvite (± subordinate halite...
and anhydrite). Other sequences observed include anhydrite overlain by halite and capped by sylvite, anhydrite-halite couplets, and halite-sylvite couplets.

In thin section, halite layers show remarkable preservation of depositional textures, fabrics, and primary fluid inclusion banding (fig. 6). Halites commonly exhibit vertically elongated chevron textures with cloudy fluid inclusion bands outlining crystal growth faces. Other halite layers are made of well sorted millimeter-sized cumulates (sunken plates and cubes) or larger, centimeter-sized, randomly-oriented hoppers, with fluid inclusion banding, which were originally skeletal but are now filled with clear halite cement.

The sylvite of the Couche Inférieure occurs in well defined layers which may also contain halite and anhydrite (figs. 5 and 6). In many cases, sylvite layers drape the irregular surfaces of underlying chevron halites (fig. 6A). These sylvite layers thicken and fill in depressions between large halite chevrons and thin over the tops of protruding chevrons. The upper surfaces of sylvite layers are commonly horizontal.

Sylvite crystals commonly form millimeter-sized anhedral mosaics which lack fluid inclusion banding (fig. 6). The color of sylvite crystals varies from pale orange to deep red, due to tiny crystals of incorporated hematite. In some cases, sylvite crystals are flattened and bent around large chevron halite crystals (fig. 6C). Sylvite crystals in a given layer are
Fig. 5. Slabbed hand sample photographs of evaporites from the lower potash interval (Couche Inférieure), Oligocene Rhine Graben of Alsace, France. Scales in centimeters. (A) Halite chevrons (H), clouded with fluid inclusions (white patches), overlain by fine grained, millimeter size crystals of sylvite (S). Note how sylvite layer forms a drape above projecting apices of the underlying chevron halite crystals. (B) Centimeter-thick mineral sequences from bottom to top: halite (H) → sylvite (S); mudstone (black) → halite (H, with cloudy white fluid inclusion banded chevrons) → sylvite (S); mudstone (black) → halite (H).
commonly equigranular (well sorted). It is important to note that halite crystals that occur in sylvite layers are about equal in size to sylvite crystals. The halite crystals may contain well-preserved fluid inclusion banding. Rarely do millimeter-sized cubic crystals of sylvite and halite occur in the same layer.

Fluid inclusions. Fluid inclusions in halites were studied from mine samples (Marie Louise) through the lower part of the Couche Inférieure. The halites with chevron texture or cumulate settle out textures have well preserved fluid inclusion banding. Individual fluid inclusions in bands range in size from less than 1 to about 100 μm on a side with a large majority less than 10 μm. Most inclusions contain a single aqueous phase or an aqueous phase + sylvite daughter crystal at room temperature. However, all inclusions contain a sylvite daughter crystal upon cooling to −60°C. Rarely do inclusions contain birefringent prisms (probably anhydrite) or cryptocrystalline mud, both of which were probably trapped during crystal growth.

Measurements of the final dissolution temperature of sylvite (Tsylvite) were made on 11 samples from 3 stratigraphic intervals, each 10 cm or less in thickness. Tsylvite ranges from 20° to 83°C and averages 63°C from a total of 92 measurements (fig. 7). Within single crystals the range in Tsylvite may be as little as 3° and as much as 56°C.

The average temperatures of sylvite dissolution increase upsection for the two stratigraphic intervals studied in detail (fig. 7). The sequence RG-D, RG-C, RG-B, and RG-A covers 10 cm of section and has average sylvite dissolution temperatures of 54.6°, 60.1°, 62.9°, and 64.2°C from the base to the top. Similarly, the average temperature of dissolution of sylvite daughter crystals for a 5-cm-thick halite layer increase upward: 48.2°C(RG-12), 69.6°C(RG-13), 72.7°C(RG-1), and 71.2°C (RG-2).

Interpretations—Petrographic features of the Rhine Graben evaporites and fluid inclusions in the associated halites confirm earlier interpretations that the potash mineral sylvite is of syndepositional origin (Braitsch, 1966, 1971; Kühn and Roth, 1979). Finely laminated mudstones intercalated with the evaporites are interpreted as perennial lake deposits, because they show no evidence of disruption due to subaerial exposure. Primary subaqueous depositional textures are well preserved in halite layers. These include halite chevrons with competitive growth textures, formed on the floor of the brine body, and halite cumulates (millimeter-sized plates, cubes, and larger, randomly-oriented hoppers) originally crystallized at the air-brine interface (Shearman, 1970; Hardie, Lowenstein, and Spencer, 1985; Lowenstein and Hardie, 1985). The lack of syndepositional dissolution features suggests that the Rhine Graben halites precipitated from a perennial, halite-saturated brine lake.

Sylvite layers are interpreted as primary deposits, because they are interlayered with halites containing unquestionable primary subaqueous textures and because they show no evidence of an origin by replacement. Sylvite crystal layers that drape underlying chevron halites
Fig. 6. Thin section photomicrographs of halite and sylvite from the lower potash zone (Couche inférieure), Mulhouse Basin, Tertiary Rhine Graben. Halite layers (H) are composed of centimeter-size, vertically oriented chevrons that contain fluid inclusion growth-banding (dark gray to black). Sylvite layers (S) contain millimeter-size crystals of sylvite with equigranular mosaic texture. (A) Mineralogical sequence of dolomitic mudstone (black) → halite + minor anhydrite → sylvite + minor halite. Note that sylvite crystals form a drape above projecting crystals of chevron halite; the top of the sylvite layer is nearly flat. Scale bar is 10mm long.
(B) Close-up of contact between halite chevrons and overlying sylvite mosaic. Small cubes of halite (millimeter-size high relief crystals) with primary fluid-inclusion bands (arrows) occur with the sylvite, indicating co-precipitation of halite and sylvite. Scale bar is 2mm long. (C) Chevron halite overlain by sylvite. Crystals of sylvite are flattened and bent around the underlying halite chevrons near the bottom of the sylvite layer. Scale bar is 10 mm long.
strongly suggest deposition of sylvinite by settling out of fine-grained crystals (fig. 6A). Sylvite most commonly forms equigranular mosaics, but in some cases, sylvinite is composed of millimeter-sized cubes. In addition, sylvite layers contain fine-grained, equant cubes of halite with fluid inclusion banding about the same size as the surrounding sylvinite crystals. These halites are identical to modern accumulations (cumulates) of small, rectangular-and square-shaped plates and cubes that originally grew at the brine surface and then sank to form a grain-supported framework (Lowenstein and Hardie, 1985, fig. 11). Based on their crystal size, their association with cumulate halites, and the manner in which they mantle underlying chevron halites, sylvite is interpreted as primary cumulates that precipitated at the brine surface or in the water column and then sank to the brine bottom to form well sorted accumulations. The mosaic textures of sylvinite crystals were probably produced by post-depositional modification of sylvinite crystal boundaries. Sylvinite crystals that are flattened and bent around adjacent halite attest to the ease with which sylvinite may be deformed (fig. 6C).

Fluid inclusions in halite with sylvinite daughter crystals indicate that the halite crystallized from syndepositional surface brines saturated with respect to sylvinite at moderately high temperatures. The sylvinite daughter crystals are found in cumulate halites that probably precipitated at the air-brine interface and in chevron halites that grew at the brine bottom.
Therefore, at times, the entire water column was at or near saturation with respect to sylvite. The temperature of dissolution of sylvite daughter crystals in halite averages 63°C, which we interpret as the minimum temperature of halite precipitation. Temperatures of shallow brines in modern saline lakes may exceed 60° and 70°C (Stewart, 1963). Thus, solar heating of surface brines may account for the majority of the Tsyylvite measurements. Halite precipitated from these warm surface waters. The systematic increase of Tsyylvite upsection for two short stratigraphic intervals indicates a progressive rise in the KCl concentration of the parent brine body contemporaneous with precipitation of halite. The large range in Tsyylvite of up to 56°C in a single halite crystal is difficult to explain. Leakage of fluid inclusions could produce large changes in Tsyylvite, but the inclusions in question contained no vapor when first examined at room temperature, implying that they have not leaked. It is possible that some fluid inclusions may have ‘necked’ or that some inclusions originally trapped a small cube of sylvite plus brine during crystal growth, either of which might produce large ranges in Tsyylvite.

Brine cooling has been proposed as the mechanism by which layers of sylvite crystals accumulated (Sturmfels, 1943; Braitsch, 1971). Our results support this interpretation. Considering that (1) petrographic textures of sylvites, which we interpret as cumulates, most likely precipitated at the brine surface, (2) a warm, perennial brine body existed at or near sylvite saturation, based on fluid inclusions in halite, and (3) the strong dependence of sylvite solubility on temperature between 20° and 100°C compared to other saline minerals, most importantly, halite (Braitsch, 1971), then cooling of the brine body at the air-brine interface, with or without evaporative concentration, would produce supersaturation with respect to sylvite and precipitation of cumulates.

PERMIAN SALADO FORMATION

Geologic setting—The Salado Formation of New Mexico and Texas is a halite-rich, saline giant, with a subsurface extent of about 150,000 km² (fig. 8; Jones, 1972). The Salado Formation is part of the Permian Ochoan Series, a sequence up to 1300 m thick dominated by evaporites and capped by siliciclastic red beds (fig. 9). The Salado evaporites are up to 700 m in thickness and are composed of generally flat-lying beds of halite, muddy halite, anhydrite-polyhalite, dolostone, and mudstone. The abundance of these rock types varies laterally, but overall, halite and muddy halite predominate.

A small portion of the Salado Formation within the Carlsbad Potash District contains potash salts including sylvite, carnallite, langbeinite, and kainite. In this area, the middle of the Salado Formation, the McNutt Zone, contains as many as twelve ore zones with abundant potash salts. The potash salt mineralogy and distribution does not fit what is predicted from the evaporation of seawater (Schaller and Henderson, 1932; Jones, 1960; Adams, 1969, 1970; Lowenstein, 1982: ms; Harville and Fritz, 1986).
In the Carlsbad Potash District, the McNutt Zone consists of two types of meter-scale depositional cycles (Lowenstein, 1982; ms: 1988). Type I cycles begin with mixed siliciclastic and carbonate (magnesite) mudstone, followed by anhydrite-polyhalite with gypsum crystal pseudomorphs, overlain by halite and capped with muddy halite. Type II sequences begin with halite that grades transitionally upsection into muddy halite. Halite and pseudomorphs after gypsum exhibit subaqueous crystal growth fabrics and mechanically-formed sedimentary structures (Lowenstein, 1988). Thus, gypsum and halite are the primary evaporite minerals of the Salado depositional sequences. Each of the basin-center cycles is interpreted to record progressive shallowing (drawdown) and concentration of brine in a marginal marine basin (Lowenstein, 1988).

The Salado evaporites have undergone post-depositional changes which have modified the depositional sequences described above. Anhydrite-polyhalite beds contained pseudomorphs of primary gypsum crystals that have been replaced by anhydrite, polyhalite, halite, or sylvite. Porous beds originally of halite and muddy halite have been transformed into compact crystalline layers, presumably through ce-
Syndepositional origin of potash evaporites

<table>
<thead>
<tr>
<th>Permian Ochoan Series</th>
<th>Guadalupian Series</th>
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Fig. 9. Stratigraphy of Ochoan Series and Guadalupian Series, Permian Basin, southeastern New Mexico and west Texas. Formation names, maximum thicknesses, and major rock types shown. From King (1942, 1948), Newell and others (1953), Jones (1954, 1972, 1973), Ward, Kendall, and Harris (1986).

...mentation by clear halite (Lowenstein and Hardie, 1985; Casas and Lowenstein, 1987). Examples of mineral replacements and “high” temperature salts (langbeinite) led Adams (1970, p. 246) to conclude, “details of the present distribution, geometry, and constitution of the potassium deposits seem, therefore, less related to depositional than to post-depositional processes.” However, no detailed documentation of the timing (syndepositional versus post-burial) of potash mineralization has been advanced.

Petrography—A variety of potash salts, including sylvite, carnallite, langbeinite, kainite, and the associated MgSO₄ salt kieserite occur in many halite and muddy halite beds of the McNutt Zone in the Carlsbad Potash District. These salts are generally distributed throughout the halite and muddy halite of the McNutt Zone in volumes of several percent, but may constitute up to 50 percent of the rock in ore zones. The potash salts are not bedded, do not contain mechanical sedimentary structures, or any features diagnostic of in situ subaqueous crystallization. Furthermore, whereas the potash salts are most common in muddy halite, their overall distribution is independent of rock type and does not follow the stratigraphic boundaries of the Salado depositional cycles (Adams, 1969). These features suggest that the Salado potash is post-
depositional in origin. It remains to be shown whether it formed syndepositionally or upon later burial.

The potash minerals langbeinite, kainite, and associated kieserite occur either as nodules made of microcrystalline aggregates or as euhedral porphyroblasts (see Hardie, Lowenstein, and Spencer, 1985, figs. 14 and 15). Such textures indicate that these sulfate salts formed later than the halite and muddy halite host rock in which they are found, but they do not provide information on the timing, whether syndepositional or post-burial, of crystallization (Hardie, Lowenstein, and Spencer, 1985, p. 24–32).

Sylvite and carnallite occur in all the major rock types of the McNutt Zone. However, sylvite and carnallite are rarely found in the same rock. Either may form a monomineralic potash ore or may coexist with sulfate minerals, most commonly kieserite, langbeinite, kainite, and leonite (fig. 10).

Sylvite and carnallite are most common and volumetrically abundant in muddy halite rock of the McNutt Zone. In thin sections of these rocks, halite commonly occurs as isolated euhedral and subhedral cubes and as subhedral crystalline aggregates (fig. 11). These crystals commonly contain incorporated mud and thin bands of fluid inclusions.

Fig. 10. Slabbed hand sample photograph of muddy halite rock with potash salts from McNutt Potash Zone, Salado Formation (see B-7, fig. 12). Isolated cubes of halite and halite crystal aggregates (dark gray) are surrounded by anhedral crystals of sylvite (light gray) and minor mudstone. Light nodules (arrow) are composed of microcrystalline kainite. Scale divisions in cm.
aligned parallel to crystal faces. Sylvite, carnallite, siliciclastic mud, and small amounts of polyhalite occur between halite crystals. Sylvite and carnallite occur as millimeter to centimeter-sized anhedral crystals. Sylvite crystals are blood-red in color due to included micron size hexagonal plates and rods of hematite. Adams (1969) reports 0.13 to 0.18 percent by weight Fe$^{3+}$ in sylvite from incorporated hematite. Carnallite crystals are purple in color, also due to hematite. Sylvite and carnallite crystals may be internally zoned with dark hematite-rich bands developed at crystal rims and progressively lighter bands, depleted in hematite, in the cores of crystals.

Ore zones in the McNutt Potash Zone are composed of halite beds up to about 1 m thick with up to 50 percent sylvite and carnallite. Thin sections of these ores display poikilitic textures where several halite crystals may be encased in a single sylvite or carnallite crystal (fig. 11).

Fluid inclusions.—In ore zones containing sylvite, primary fluid inclusions in the associated halites contain sylvite daughter crystals (fig. 1). Data on carnallite is limited to one ore zone in which clear halite crystals contain large isolated fluid inclusions with carnallite daughter crystals. In contrast, sylvite and carnallite daughter crystals are not found in halites away from areas of potash mineralization.

Halite samples from three sylvite ore zones found in three different potash mines have been analyzed in detail (fig. 12). Two of the halites consist of chevrons, with vertically aligned crystals that contain well defined primary fluid inclusion banding, which parallels halite crystal faces. In a third sample, clear, randomly oriented cubes of halite contain incorporated mud and thin (<100 μm) bands of fluid inclusions arranged parallel to crystal faces. These are also interpreted as primary fluid inclusions probably trapped during the early diagenetic growth of this displacive halite.

Most commonly, the fluid inclusions contain two phases: aqueous liquid and one cubic daughter crystal of sylvite (fig. 1B). Two types of three phase inclusions occur: (1) aqueous liquid, vapor, and a sylvite daughter crystal; or (2) aqueous liquid, sylvite daughter crystal, and a birefringent, prism-shaped mineral (probably anhydrite or polyhalite). Fluid inclusions may contain rare patches of cryptocrystalline mud in addition to aqueous liquid and a sylvite daughter crystal.

The results of 119 measurements of the dissolution temperature of sylvite in fluid inclusions in halite are shown in figure 13. The temperature of sylvite dissolution ranges from 28° to 150°C and averages 71°C. Within single bands of inclusions in halite crystals, T sylvite varies by as much as 58°C and as little as 10°C.

Interpretations—The halite in muddy halite layers, the major potash host rock, is similar to the early diagenetic halite formed from groundwater brines in the shallow subsurface of modern saline pans and saline mudflats (fig. 14; Lowenstein and Hardie, 1985; Casas and Lowenstein, 1987). At depths of less than 1 m below the surface in these systems, clear halite grows syntactically on halite crystals in porous halite layers and as mud-incorporative displacive cubes within soft muddy
Fig. 11. Thin section photomicrographs of muddy halite rock with sylvite and carnallite from the McNutt Potash Zone, Salado Formation. Clear, randomly oriented, interlocking cubes of halite contain incorporated mud (dark gray to black) and sparse fluid-inclusion bands (arrows). Scale bars are 5mm long. (A) Dark areas between halite cubes are composed of zoned anhedral crystals of sylvite cement and minor mudstone. Sample B-7 (see fig. 12). (B) Dark areas that fill the voids between the halite "framework" cubes are composed of sylvite cement crystals zoned with hematite inclusions.
Fig. 11 (continued) (C) Halite cubes surrounded by anhedral, void-filling carnallite cement (dark gray) and mudstone (black). (D) Large anhedral carnallite cement crystal (dark gray).
Fig. 12. Measured stratigraphic sections of underground mine exposures from the McNutt Potash Zone, Salado Formation. Halites containing sylvite daughter crystals in fluid inclusions were sampled from intervals F-3, T-10, and B-7. Rock types: dotted—laterally continuous polyhalite (2CaSO₄,MgSO₄,K₂SO₄,2H₂O) marker beds (labeled "119," "120"); cross hatched-halite rock; white-muddy halite. Halite rocks with "chevron" structure defined by fluid-inclusion banding (chevron symbol) and "cumulate" textures (small cubes). For more details, see Lowenstein, 1988. Potash salts are shown on right side of columns (S = sylvite, KCl; Ki = kieserite, MgSO₄·H₂O; Ka = kainite, MgSO₄·KCl·11/4H₂O; La = langbeinite, 2MgSO₄·K₂SO₄). Locations of measured sections (numbered at base) are shown in Lowenstein, 1988, figure 1. Stratigraphic positions of measured sections in McNutt Potash Zone are shown in Lowenstein, 1988 figure 4 (F-3, lowermost 10 m of sec. 14; T-10, uppermost 7 m of sec. 2; B-7, 7 to 14 m above base of sec. 16).
interlayers. Based on the identification of displacive halite, mudstone-filled solution pockets, meter-scale, dish-shaped structures that resemble cross sections of buckled salt polygons, and other features, the muddy halite of the Salado has been interpreted as a saline pan and saline mudflat deposit (Lowenstein, 1982, ms, 1988).

The sylvite and carnallite in the Salado Formation occupy areas equivalent in size and shape to the void spaces in modern saline pan halites and are thus interpreted as pore-filling cements (compare figs. 11 and 14). Sylvite and carnallite cements are in sharp contact with framework crystals of halite and show no textures indicating on origin by replacement. Other features supporting a cement interpretation are poikilitic crystals of sylvite or carnallite which enclose several halite framework crystals and color bands in sylvite or carnallite which follow original void boundaries. The large volume of sylvite in some ores is equivalent to the pore volume of cavernous halite crusts of modern saline pans (Saline Valley, Calif.), where porosities of 50 percent or higher are common.

Constraints on the probable timing of sylvite and carnallite cementation have been obtained from study of the profile of halite porosity versus depth from several modern halite deposits (fig. 15). Detailed petrographic work on Quaternary halite rocks from shallow cores in Saline Valley, Searles Lake, and Bristol Dry Lake, California, has shown that major diagenetic modification of porous halite layers occurs during the first few meters of burial. Within the first 30 m of burial, nearly all pore spaces are filled with clear halite cement, producing a rock
Fig. 14. Thin section photomicrographs of halite in a muddy halite layer from just beneath the surface of the modern salt pan of Saline Valley, California. The halite occurs as randomly oriented interlocking cubes with incorporated mud (black) and cloudy patches dense with fluid inclusions (arrows). Primary voids (V) surround halite crystals. These voids are equivalent to the space occupied by sylvite and carnallite cements in the Salado Formation (compare with fig. 11). Aggregates of interlocking small rhombs of glauberite (CaSO₄·Na₂SO₄) and mud (black) are also present. Scale bars are 5 millimeters long.
Fig. 15. Profile of visible porosity versus depth of modern and Quaternary layered halite deposits. Early cementation by clear halite rapidly reduces porosity within the first few meters of burial. Porosity in excess of 10 percent was not observed in layered halites at depths greater than 10m.

indistinguishable from halite and muddy halite in the Salado Formation (Casas, 1988; Casas and Lowenstein, 1987). This general trend of rapid decrease in the porosity of halite rocks with burial seems to hold for many halite deposits (see Sonnenfeld, 1984, p. 296). If such a relation holds for the diagenetic evolution of the Salado halites, then the large volume of sylvite and carnallite in the Salado halites constrains the depth of cementation to the uppermost few meters.

Monomineralic sylvite and carnallite cements, together with the daughter crystals of sylvite in primary fluid inclusions in associated halites, allow for detailed interpretation of the mechanisms of potash mineral crystallization. Sylvite daughter crystals in fluid inclusions in
primary halite crystals establish that the surface brines from which halites precipitated were rich in K+ and saturated with respect to sylvite at moderately high temperatures. The halite crystallized in warm, shallow, surface brines of a saline pan. The large range of Tsylvite within a single fluid inclusion-rich band and the few temperatures of sylvite daughter crystal dissolution above 90°C (fig. 13) may be due to post-entrapment necking of some inclusions or original trapping of a sylvite crystal within fluid inclusions.

The association of sylvite ore zones and sylvite daughter crystals in fluid inclusions in chevron halite and the lack of potash daughter crystals in halites away from areas of potash mineralization indicate that the primary halites and the sylvite cements shared a common, syndepositional parent brine. The halites formed from subaqueous brines, and the sylvite cements formed from shallow groundwaters. We have no independent evidence from fluid inclusions for syndepositional carnallite-saturated brines, because carnallite daughter crystals have only been found in isolated fluid inclusions in clear halite whose timing of entrapment is ambiguous. However, based on petrographic textures, a similar syndepositional origin is suggested for carnallite.

We interpret early diagenetic sylvite and carnallite cements to have formed by cooling of warm brines in the void spaces of halite crystal frameworks. In modern saline pans, flooding is followed by evaporative concentration and precipitation of halite from ponded floodwaters and finally desiccation (Lowenstein and Hardie, 1985). Upon desiccation of the saline pan, surface brines slowly drop below the sediment-air interface. There are significant temperature differences between shallow surface brines and groundwater brines in modern saline pans. For example, in the relatively cool climate of the Qaidam Basin of western China, brine-saturated surface salt crusts along the northern margin of Dabusun Lake were 47.5°C (air temperature of 30°C) during August of 1988 (personal observation). Groundwater brines at depths of 0.6 m were 21°C, and those from depths of 5 m and 8 m were 17°C and 11°C, respectively. Therefore, because of the strong temperature control on sylvite and carnallite solubility in KCl–MgCl₂–NaCl-rich brines over the temperature range of 10° to 100°C (Braitsh, 1971), warm surface brines at sylvite or carnallite saturation would become, when cooled, highly supersaturated with respect to sylvite or carnallite, leading to the growth of potash cements. This mechanism of potash cementation through cooling of groundwater brines explains the irregular distribution of potash salts in the McNutt Zone, their general lack of bedding, and why they crosscut the stratigraphic boundaries of the primary evaporite depositional sequences. Ore zones rich in sylvite or carnallite are interpreted as halite rocks with very large pore volumes prior to the precipitation of potash cements.

DEMONIAN PRAIRIE FORMATION

Geologic setting—The Devonian Prairie Formation (and equivalent units) is a saline giant that occurs in the subsurface below much of
western Canada (fig. 16). The aerial extent is about 425,000 km², with an average thickness of almost 150 m. The dominant saline mineral is halite, which, together with anhydrite and calcite, is commonly arranged in centimeter-thick depositional sequences. The sequences begin with calcite-anhydrite partings of variable thickness overlain by halite (Wardlaw and Schwerdtner, 1966; Brodylo and Spencer, 1987). Halite from the Prairie Formation generally contains well preserved, syndepositional features typical of modern saline pans (Brodylo and Spencer, 1987). Crystalline growth fabrics, mainly vertically elongated chevrons, are found in 50 to 90 percent of the halite from many intervals (Wardlaw and Schwerdtner, 1966; Wardlaw and Watson, 1966; Brodylo and Spencer, 1987). Halite chevrons may be truncated by irregular patches of clear halite. Shearman (1970) and Brodylo and Spencer (1987) interpret the truncations as syndepositional dissolution features and the clear halite as an early diagenetic cement.

Potash salts (sylvite and carnallite) are found only in southern Saskatchewan (fig. 16) where they are limited to the upper portion of the

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Fig. 16. Map showing subsurface extent of Middle Devonian halite deposits in western Canada (close stipple) and the area where potash salts of the Prairie Evaporite (KCl, wide stipple) are located. The Pan Am Telegraph well (PAT) is in east-central Alberta and the Winsal Osler well (WO) is in Saskatchewan.
Fig. 17(A) Core slab of halite-sylvite rock from the Prairie Formation with polygonal mosaic texture. Sylvite (gray, with rims of crystals highlighted by hematite) and clear crystals of halite (dark gray). Scale divisions in centimeters.

(B) Thin section photomicrograph of halite (H)-sylvite (S, dark gray) rock with polygonal-mosaic texture. Dark areas in the centers of halite crystals contain fluid inclusion banding. Fluid inclusions in these bands contain sylvite daughter crystals (see fig. 19A). Sylvite crystal boundaries (black) are rich in hematite. Halite crystals are about 5 mm across.
Prairie Formation (see Meijer Drees, 1986, for a synthesis of the Prairie Formation stratigraphy). Wardlaw (1968) describes three major potash zones, up to 60 m thick, composed of halite + sylvite, halite + carnallite, and interbedded halite. Anhydrite, carbonate, and siliciclastic mudstone, commonly as partings, occur in subordinate amounts (Wardlaw, 1968). The Prairie Formation does not contain any MgSO₄ minerals (polyhalite, kieserite) that are predicted to form by the evaporation of seawater.

The stratigraphic relationships, petrography, and geochemistry (Br and Rb in halite, sylvite, and carnallite) of the Prairie Formation potash zones have been studied by Schwerdtner (1964), Keys and Wright (1966), and Wardlaw (1968). Complex replacement textures involving halite, sylvite, and carnallite are described by Wardlaw (1968). In places, carnallite appears to form a cement between euhedral crystals of halite (Schwerdtner, 1964; Wardlaw, 1968). All studies conclude that the potash zones have undergone pervasive diagenetic alteration.

Petrography—Figure 16 shows the location of the two cores (Pan Am Telegraph, 6-30-84-13W4 and Winsal Osler, 3-28-39-4W3) examined. The Pan Am Telegraph core, described by Brodylo and Spencer (1987), is located in an area with no potash deposits. The Winsal Osler
core was used by Wardlaw and Schwerdtner (1966) to describe the Prairie Formation halites and interpret their origin. The upper portion of this core contains potash salts; data on the geochemistry of carnallite from the Winsal Osler core are reported by Wardlaw (1968). Hand samples and core slabs of halite-sylvite and halite-carnallite rock collected by N. C. Wardlaw from other locations were also studied.

Halite associated with potash salts in the Prairie Formation is atypical, because it generally lacks well defined primary depositional growth textures and fabrics. Halite-sylvite rocks exhibit two characteristic textures, with gradations between the two. Most common are polygonal-mosaic textures, with individual halite and sylvite crystals from several millimeters to a few centimeters in size (fig. 17A). In many samples, sylvite grain boundaries are highlighted by concentrations of blood-red hematite (fig. 17B). Hematite is less abundant, or absent, in
Fig. 19. Fluid inclusions in halite from the Prairie Formation associated with potash salts contain daughter crystals of potassium-bearing minerals. Fluid inclusions in halite away from the potash deposits contain no potash-salt daughter crystals. (A) Most fluid inclusions that outline primary growth bands in halite contain daughter crystals of sylvite (cubic, isotropic crystals—see arrows). Largest inclusion is 20 μm wide.

grain interiors. Some of the halite crystals in the polygonal mosaics contain cloudy, fluid-inclusion-banded cores (fig. 17B). The second and less common texture observed in halite-sylvite rocks is a framework of euhedral and subhedral halite cubes poikilitically enclosed by anhedral crystals of sylvite (fig. 17C). This texture is similar to that found in the halite-sylvite ore zones of the Salado Formation (compare figs. 11 and 17C).

Halite-carnallite rocks in the Prairie Formation display three distinct textures. Most halite-carnallite rocks contain isolated centimeter-size cubes of halite, which are enclosed by poikilitic carnallite crystals (fig. 18A). Halite cubes are clear, but rare halite crystals contain cloudy, fluid inclusion banded cores which outline patches of syndepositional crystal growth textures. The second texture is coarsely crystalline halite-carnallite with equigranular, polygonal-mosaic textures. The third texture, seen in one sample, contains interlayered halite and carnallite with bedding similar in scale to that present in the halite-sylvite rocks of the Rhine Graben (compare fig. 18B with figs. 5 and 6). Halite layers overlie partings of anhydrite and mudstone: halite crystals are generally clear, but chevron halite, outlined by fluid inclusion
Fig. 19 (continued) (B) Carnallite daughter crystal (hexagonal, C) in isolated fluid inclusion from clear halite. Fluid inclusion is 90 \( \mu \)m wide. (C) Chlorocalcite (Cl, partially crossed polars) daughter crystal in isolated fluid inclusion from clear halite. Fluid inclusions are 90 \( \mu \)m wide.

banding, was identified (fig. 18C). Carnallite occurs as anhedral crystals between framework crystals of halite within the halite layers (fig. 18C). Carnallite layers are composed of anhedral carnallite crystals and subordinate euhedral to subhedral cubes of halite (fig. 18B).

**Fluid inclusions**—Fluid inclusions in halite from the Prairie Formation contain an aqueous phase and may also contain daughter crystals of sylvite, carnallite, or, in one example, chlorocalcite (CaCl\(_2\)·KCl) (fig. 19). Sylvite daughter crystals are present in fluid inclusions from primary fluid-inclusion-banded halite. Fluid inclusions in bands in primary chevron halite from the one sample of layered halite-carnallite may contain carnallite daughter crystals but sylvite daughter crystals are far more common. Sylvite and carnallite daughter crystals are present in isolated fluid inclusions from clear crystals of halite; all three daughter
minerals occur in clear halite cement which surrounds fluid inclusion-banded chevron halite.

Brodlyo and Spencer (1987) examined fluid inclusions in halite from the Pan Am Telegraph core from depths between 630 and 690 m. Daughter crystals are not present at room temperature in any fluid inclusions, nor do any of the above daughter minerals nucleate on cooling. No potash salts occur in this core.

The lower portion of the Winsal Osler core (945–1010 m) consists of chevron halite, clear halite, and carbonate-anhydrite partings (Wardlaw and Schwerdtner, 1966). Small quantities of potash salts (mainly cinnabar) first occur in some halite beds above 945 m depth, and larger amounts occur above 930 m (top of core is at 900 m). Fluid inclusions in halite from below depths of 950 m in the Winsal Osler core do not contain daughter crystals at room temperature nor do any of the above daughter minerals nucleate on cooling. Fluid inclusions that outline chevron fabrics in halite at 945 m do not contain daughter crystals at room temperature, but sylvite crystals nucleate on cooling. The temperatures of dissolution of the sylvite range from 5°C to 13.4°C (fig. 20). The data were obtained from two centimeter-scale depositional sequences separated by an anhydrite rich parting. The sylvite dissolution temperatures average 5.9°C at the base of the first sequence and increase to 10.3°C at the top of the same sequence. The average sylvite dissolution temperature at the base of the overlying sequence is 7.6°C and increases to 13°C at the top.

Most fluid inclusions within primary fluid inclusion bands in halite from 915 m in the Winsal Osler core contain sylvite daughter crystals at room temperature. The range of sylvite dissolution temperatures is from 8.4°C to 58°C (fig. 20). The three fluid inclusions with sylvite dissolution temperatures between 8°C and 9°C are from the base of a 7.5 cm thick depositional sequence. The fluid inclusions with sylvite dissolution temperatures between 23°C and 32°C are from near the top of the same sequence. Other depositional sequences from 915 m depth in the Winsal Osler core do not show any systematic stratigraphic variation in the sylvite dissolution temperatures which average 57.5°C. The sample with chlorocalcrite daughter crystals in clear halite cement is also from this interval. Two of these inclusions were heated, and the chlorocalcrite dissolution temperatures were 60°C.

Fluid inclusions in halite crystals from other cores through the Prairie potash zones were also examined. Halite-sylvite rocks and halite-cinnabar rocks contain halite crystals with cloudy, fluid inclusion-rich cores (fig. 17B). Fluid inclusions from the cores of cloudy halite crystals contain sylvite daughter crystals, most of which dissolve between 55°C and 61°C (fig. 20). Carnallite daughter crystals found in fluid inclusions outlining primary chevron textures in the sample of bedded halite-cinnabarite dissolve between 57°C and 80°C. Sylvite daughter crystals in fluid inclusions from the same bands dissolve between 74°C and 79°C (fig. 20).
Fig. 20. Histogram of the temperature of dissolution of sylvite daughter crystals in fluid inclusions in halite from the Winal Osler well at 915 and 945 m; sylvite daughter crystal dissolution temperatures from fluid inclusions in the cloudy centers of halite crystals associated with potash salts from other cores (such as shown in fig. 17B); and sylvite and carnallite daughter crystal dissolution temperatures from fluid inclusions in fluid inclusion banded halite from bedded halite-carnallite.

Carnallite daughter crystals occur mainly in isolated fluid inclusions in clear halite from halite-carnallite rocks. Most of these carnallite daughter crystals dissolve between 50° and 80°C, approximately the same temperature range as the dissolution of sylvite and carnallite daughter crystals in fluid inclusions outlining primary growth bands. Some inclusions are almost completely filled with carnallite, indicating a trapped solid rather than a daughter crystal.

Interpretations—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. In contrast, no sylvite daughter crystals have been observed in fluid inclusions outlining primary growth textures from chevron halites away from the potash deposits. This establishes that potash salts occur in stratigraphic intervals where syndepositional surface brines contained high concentrations of K+. 
The lower 65 m of halite from the Winsal Osler core, with no sylvite daughter crystals, were deposited from surface brines low in K+. The concentration of K+, as indicated by the presence of sylvite daughter crystals, increases upsection as the potash deposits are approached (fig. 20, 945 m). The higher temperatures of sylvite daughter crystal dissolution at depths of 915 m compared to 945 m indicates a progressive rise in the K+ of surface brines for the entire potash zone in the Winsal Osler core. The systematic increase of Tsylvite upsection for three centimeter-thick halite sequences reflects smaller scale increases in the K+ concentration of the parent brine body contemporaneous with precipitation of halite.

Halite-sylvite rocks in which sylvite poikilitically encloses an open framework of euhedral to subhedral halite cubes (fig. 17C) are similar in texture to the sylvite-cemented halites observed in the Salado Formation. They are interpreted to have formed by the same mechanism: syndepositional cementation of a halite crystal framework by sylvite. As in the Salado Formation, fluid inclusions in primary, fluid inclusion-banded halite contain sylvite daughter crystals that dissolve at moderately high temperatures, which demonstrates the existence of warm, syndepositional brines capable of precipitating sylvite without further brine concentration. The sylvite cement in the Prairie is interpreted to have formed by cooling of parent surface brines as they sank into the shallow subsurface (see interpretation of potash cements from the Salado Formation).

Halite-sylvite rocks with polygonal-mosaic textures preserve no petrographic evidence on the origin and timing of potash mineralization. We, however, also interpret the halite-sylvite polygonal mosaics as original frameworks of halite cemented syndepositionally by sylvite for the following reasons: (1) Fluid inclusion growth bands occur in some halites from the halite-sylvite mosaics. Fluid inclusions in these bands contain sylvite daughter crystals with the same range of moderately high Tsylvite as seen in rocks with poikilotopic sylvite cementing a halite crystal framework. (2) A complete gradation of textures—from anhedral polygonal mosaics to euhedral cubes of halite poikilitically surrounded by sylvite—exists in the halite-sylvite rocks of the Prairie evaporite. The present halite-sylvite polygonal mosaic textures thus may represent halite rock, cemented early by sylvite and then later recrystallized (Hardie, Lowenstein, and Spencer, 1985).

We interpret the halite-carnallite rocks of the Prairie Formation as syndepositional in origin. However, as outlined below, sylvite daughter crystals in fluid inclusions from primary growth-banded halite in halite-carnallite rocks make this interpretation problematic.

Bedded halite-carnallite, with fluid-inclusion banded chevrons (figs. 18B and C) may have formed from a standing brine body undergoing progressive evaporation and changes in temperature (see interpretation of bedded halite-sylvite from the Rhine Graben). Considering that carnallite is less soluble at low temperatures, carnallite layers may have
precipitated following cooling of warm Mg-K-rich surface brines. This interpretation is speculative because no primary textures are preserved in carnallite layers in the bedded halite-carnallite.

Coarse poikilotopic crystals of carnallite enclosing a framework of halite cubes are interpreted as cements (see interpretation of Salado Formation potash cements). The large volume of carnallite in some samples and comparison with porosity profiles of modern and Quaternary halite suggest the carnallite formed during very shallow burial (fig. 15).

Fluid inclusions from primary, fluid inclusion-banded halite in halite-carnallite rocks contain sylvite daughter crystals which indicate that surface brines were rich in K and at or near sylvite saturation. However, the Mg content of these brines, based on the dissolution temperatures of hydrohalite (NaCl·2H₂O) during warming of frozen inclusions, appears to be far below that expected for carnallite saturation. The brines in fluid inclusions in halite from halite-carnallite rocks, which presumably were syndepositional surface waters, are rich in K, but their Mg concentration is much too low for direct precipitation of carnallite. There is a general lack of carnallite daughter crystals in fluid inclusions from primary growth bands in halites from halite-carnallite rocks. We therefore cannot rule out the following alternative interpretation for the origin of halite-carnallite rocks: sylvite, rather than carnallite was first precipitated from syndepositional brines. The sylvite was replaced by carnallite, either syndepositionally or following burial, as a result of interaction with Mg-rich brines. We have seen no petrographic evidence for carnallite replacement of sylvite in samples of halite-carnallite.

One final point is that isolated fluid inclusions in clear halite crystals associated with carnallite may contain carnallite daughter crystals. The carnallite daughter crystals dissolve over the same temperature range as the sylvite daughter crystals from primary fluid inclusion bands. The uncertainty here is that these inclusions and the clear halites in which they occur may have formed syndepositionally or during burial.

DISCUSSION AND CONCLUSIONS

In three major ancient potash evaporites studied, petrographic textures and fluid inclusions in associated halites document that the potash mineral sylvite is syndepositional in origin. The sylvite may form a subaqueous deposit, as in the Rhine Graben evaporites, or a void-filling cement, as in the Salado and Prairie Formations. Textural evidence also suggests a syndepositional cement origin for carnallite in the Salado and Prairie Formations. The moderately high temperatures of dissolution of sylvite daughter crystals from fluid inclusions in primary subaqueous halites in all three deposits indicates precipitation of halite from warm surface brines. Cooling of these brines at or just below the surface is a major mechanism by which to achieve supersaturation with respect to sylvite.
Published accounts of petrographic features from other important ancient potash deposits also carry the earmarks of a syndepositional origin. The Upper Eocene Pyrenean Potash Basin of Spain contains layers of halite, sylvite, and carnallite with cumulate textures that are virtually identical to those described here from the Rhine Graben (Rosell Ortiz and Orti Cabo, 1982; Orti Cabo, Pueyo Mur, and Rosell Ortiz, 1985). A strong case may be made that these are also subaqueous potash deposits precipitated from a perennial brine body. The Cretaceous Ihours Member of the Muribeca Formation of coastal Brazil contains spectacular subaqueous carnallite “chevrons” interlayered with halite (Wardlaw, 1972a, b; Wardlaw and Nicholls, 1972) as well as halite cumulates enclosed by probable sylvite cements (personal observation). The Boulby Potash and Upper Potash of the third and fourth cycle of the Permian English Zechstein Formation (EZ3 and EZ4) contain halite-sylvite-mud layers that are similar to the sylvite-cemented halites of the Salado Formation (Stewart, 1951a, b; Armstrong and others, 1951; Smith, 1973; Smith and Crosby, 1979). The textural features discussed above lead us to conclude that the sylvite and carnallite of many of the world’s best studied potash deposits may have formed syndepositionally. This is contrary to commonly accepted beliefs, especially for sylvite. Since sylvite is not predicted to form from evaporated seawater at 25°C except under metastable equilibrium conditions (Braithsch, 1971; Valyashko, 1972; Hardie, 1984), most workers have interpreted the sylvite as a diagenetic mineral formed by the incongruent dissolution of carnallite (an important marine evaporite mineral) via the reaction:

$$\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O} \rightarrow \text{KCl}_{(s)} + \text{Mg}^{+2}_{(aq)} + 2\text{Cl}^-_{(aq)} + 6\text{H}_2\text{O}_{(l)}$$

carnallite sylvite

According to Braithsch (1971, p. 120), “The incongruent alteration of carnallite is probably the most important process in the alteration of potash salts.” Sylvite interpreted to have formed from alteration 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 the Gabon Basin, West Africa (Wardlaw, 1972a, b; Wardlaw and Nicholls, 1972; Szatmari, Carvalho, and Simoes, 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).

Direct evidence of sylvite formed from the alteration of primary carnallite is difficult to find because the original carnallite is removed
from the rock. Trace elements in sylvite such as Br (Adams, 1970; Wardlaw and Nicholls, 1972; Hite and Japakasetr, 1979) fall below values expected of primary sylvite precipitated from modern seawater, which has been used in support of a secondary origin. But this could also be used as evidence that the sylvites formed from non-marine waters with a low Br content (Holser, 1979; Hardie, 1984). More convincing evidence that sylvite formed at the expense of carnallite is the lateral change in stratigraphic thickness between sylvite and carnallite-bearing halites in the Middle Devonian Prairie evaporites of Canada (Wardlaw, 1968). Yet in the Prairie Formation, Wardlaw (1968) presented petrographic evidence that some of the carnallite has formed at the expense of sylvite. For all those potash evaporites cited above where the evidence for the incongruent alteration of carnallite to sylvite is lacking or ambiguous, this carnallite alteration process should be considered as one alternative. The evidence presented in this paper for the formation of syndepositional sylvite casts doubt on these previous interpretations.

The sylvite in ancient evaporites lies at the root of the controversy over the origin of potash evaporites and the sources and evolution of evaporite parent waters. If, as suggested here, the sylvite is an early formed syndepositional mineral, then depositional models calling upon the equilibrium evaporation of seawater are probably not valid, and alternative models must be tested, including: (1) mixed marine and non-marine parent waters, (2) non-marine parent waters, and (3) syndepositional recycling of marine and non-marine source waters.

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