[AMERICAN JOURNAL OF SCIENCE, VOL. 290, JANUARY, 1990, P. 43–106]

THE ROLES OF RIFTING AND HYDROTHERMAL $CaCl_2$ BRINES IN THE ORIGIN OF POTASH EVAPORITES: AN HYPOTHESIS

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ABSTRACT. Ancient potash evaporites fall into two groups: (1) an $MgSO_4$-rich group with mineral assemblages predicted to form from evaporative concentration of seawater with the composition of today's oceans, and (2) an $MgSO_4$-poor group with mineral assemblages that cannot be derived from the evaporation of modern seawater. This latter group, characterized by a halite–sylvite–carnallite ± tachyhydrite ± bischofite paragenesis, comprises the most abundant of ancient potash deposits, and their origin remains a major unsolved problem.

This paper offers an hypothesis for the origin of those $MgSO_4$-poor potash evaporites that accumulated in extensional fault block basins. Modern active rift and transtensional strike-slip basins are notable for their hydrologic closure and their arid climates regardless of latitude (orographic deserts). These features, essential to evaporite formation, make high relief extensional basins ideal sites for accumulation of thick saline deposits. But, in addition, it is now well documented that modern active rift and strike-slip systems, both oceanic and continental, are zones of upwelling hydrothermal $CaCl_2$ brines rich in Na, K, and Ca but poor in Mg and SO_4. Where these convecting subsurface brines, driven upward by density instabilities of thermal origin or by topographic gradients, leak to the surface in closed basins, they may mix with surface waters to produce $CaCl_2$ lakewaters. These $CaCl_2$ lakewaters will produce, on evaporative concentration, $MgSO_4$-poor non-marine evaporites, for example, as occur in the Danakil Depression (Ethiopia) and the Qaidam basin (China). Based on these and other modern examples that demonstrate a direct connection between $MgSO_4$-poor salt deposits, rifting, and hydrothermal brines, it is postulated that ancient $MgSO_4$-poor potash evaporites that accumulated in extensional fault basins owe their particular chemical signature to upwelling $CaCl_2$ brines.

Criteria for the recognition of this type of evaporite are: (1) accumulation in a rift or transtensional strike-slip basin, (2) primary mineralogy of the $MgSO_4$-poor type, that is halite-sylvite-carnallite ± tachyhydrite ± bischofite ± anhydrite/gypsum ± rinneite ± borates, (3) fluid inclusions with $CaCl_2$ brine compositions, (4) high concentrations of Fe, Mn, Pb, Zn, Cu, Ba, and other trace elements in the primary salts, (5) interbedded volcanics, (6) contemporaneous Pb–Zn–Cu mineralization in the basin, (7) zeolite, greenschist, or amphibolite facies hydrothermal metamorphism of parts of the coeval basin sediments. Based on these criteria a number of well-known ancient potash deposits qualify as hydrothermal brine-sourced evaporites, for example, the tachyhydrite-rich potash evaporites of Cretaceous age in Brazil, Gabon, and Thailand; the Carboniferous of the Paradox basin and the Canadian Maritimes; the Oligocene of the Rhine Graben; the

Triassic of the Moroccan Meseta; and the Silurian of the Michigan basin.

The proposed mechanism for the origin of $MgSO_4$-poor potash evaporites has significant implications for the evolution of $CaCl_2$-rich basinal brines (saline formation waters, oil field brines) and their relation to thermal and tectonic events, and for the genetic connection between evaporites, hydrothermal metamorphism, and hydrothermal ore deposits (and possibly, hydrocarbon migration) and their relations to thermal and tectonic events.

INTRODUCTION: THE PROBLEM OF $MgSO_4$-POOR POTASH EVAPORITES

Based on their major ion chemistry and mineralogy, ancient potash evaporites found throughout the Phanerozoic record fall into two distinct groups, an $MgSO_4$-rich group and an $MgSO_4$-poor group (tables 1 and 2).

Potash deposits rich in $MgSO_4$ (table 1) are composed mainly of various combinations of gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), halite (NaCl), polyhalite ($2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$), kieserite ($MgSO_4 \cdot H_2O$), kainite ($MgSO_4 \cdot KCl \cdot 11/4\ H_2O$), carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), and bischofite ($MgCl_2 \cdot 6H_2O$). Parageneses involving these minerals are predicted to form from seawater with the composition of today's oceans (Harvie and others, 1980; Hardie, 1984). Figure 1 illustrates the brine composition pathways and mineral changes expected as modern seawater evaporates at 25°C and 1 atm under conditions of perfect equilibrium without fractionation. Clearly, $MgSO_4$ is a dominant component of seawater bitterns and the co-existing potash-stage mineral assemblages. Marine potash evaporites, then, should be characterized by $MgSO_4$-bearing minerals.

Potash deposits free of, or poor in, $MgSO_4$ (table 2) typically consist of some combination of halite, carnallite, and sylvite (KCl) in the absence of (or with mere traces of) $MgSO_4$ salts. Gypsum and anhydrite commonly are present in very minor amounts or may be absent completely. Several quite unusual potash deposits of this group are not only free of $MgSO_4$-bearing minerals but carry substantial amounts of the very soluble $CaCl_2$ mineral tachyhydrite ($CaCl_2 \cdot MgCl_2 \cdot 12H_2O$) as well as bischofite, for example, the Cretaceous of Brazil, Gabon, and Thailand (table 2). In distinct contrast to the $MgSO_4$-rich group of potash deposits, *$MgSO_4$-poor potash deposits cannot be derived by evaporation of seawater with the composition of modern ocean waters* or any similar sulfate-enriched composition (fig. 1; see also Hardie, 1984).

Ancient potash deposits free of, or poor in, $MgSO_4$ are found throughout the Phanerozoic and constitute the majority of the potash deposits of the record (compare tables 1 and 2; see also the tables in the comprehensive compilation of data on Paleozoic evaporites by Zharkov, 1981). Not only are $MgSO_4$-rich potash deposits far less abundant than the $MgSO_4$-poor types, but they are confined to the Permian, the Miocene, and the Quaternary (table 1), a temporal distribution that has yet to be satisfactorily explained.

TABLE 1

Ancient potash deposits rich in magnesium sulfate

LOCATION	FORMATION	AGE	VOLUME OF POTASH DEPOSIT	NOTABLE FEATURES
Dnieper-Donets Depression, USSR	Kramatorsk Fm.	Early Permian (Sakmarian)	7.35 km^3	laminae carrying halite, polyhalite, kieserite, carnallite; beds of sylvinite - carnallite also occur (Zharkov, 1984)
Cis-Ural, Volga-Ural, and Caspian basins, USSR	Iren Fm. (and equivalents in 10 basins)	Early Permian (Kungurian)	15,000 km^3	polyhalite is most common of magnesium sulfate minerals but kieserite also found. However, in most basins carnallite - sylvite-halite beds ± bischofite predominate (Zharkov, 1984)
Delaware basin, New Mexico and Texas	Salado Fm.	Late Permian (Tatarian)	500 km^3	polyhalite is most common magnesium sulfate salt but kieserite and langbeinite also occur. Main potash minerals are sylvite and carnallite (Jones, 1972)
N.W. European basin	Zechstein 1,2,3,4	Late Permian (Kazanian to Tatarian)	2000 km^3	at Stassfurt the Zechstein 2 sequence involving anhydrite, halite, polyhalite, kieserite, and carnallite follows that predicted quantitatively for evaporation of modern seawater (Harvie and others, 1980)
Iran	Lower Fars Fm.	Early Miocene	(?)	thick salt with minor polyhalite (Stocklin, 1968)
Mediterranean Sea		Late Miocene (Messinian)	(?)	polyhalite + kainite + halite encountered beneath the floor of the Mediterranean by DSDP (Kuehn and Hsu, 1978)
Sicily	Solfifera Series	Late Miocene (Messinian)	~50 km^3	predominantly kainite but carnallite, kieserite, bischofite also present in some areas (Decima and Wezel, 1973)
Danakil Depression, Ethiopia	Houston Fm.	Pleistocene (< 1 my)	>40 km^3	basal kainite + halite member (4-14m) passes upward into kainite + carnallite + kieserite + polyhalite + halite (6-26m). Upper member is sylvite + halite + anhydrite (up to 12m). (Holwerda and Hutchinson, 1968)

The origin of $MgSO_4$-poor potash-rich salt deposits stands as one of the major unsolved problems in the field of evaporitology. Several solutions to this problem have been offered in the past, and all of them have sought to explain $MgSO_4$-poor potash deposits either as "unusual" marine evaporites or as altered marine evaporites. For example, Borchert has called on burial alteration of normal marine evaporites by groundwaters (Borchert, 1977) and has also proposed an explanation that involves bacterial reduction of sulfate ions in seawater (for example, Borchert and Muir, 1964; see also Sonnenfeld, 1984). Mixing of seawater and bicarbonate-rich river water in marine evaporitic environments has been invoked by the German school ("altered seawater" model, see Braitsch, 1971, p. 168–173) and by the Russian school ("metamorphosis of brine" concept, see Valyashko, 1972a, p. 295–296).

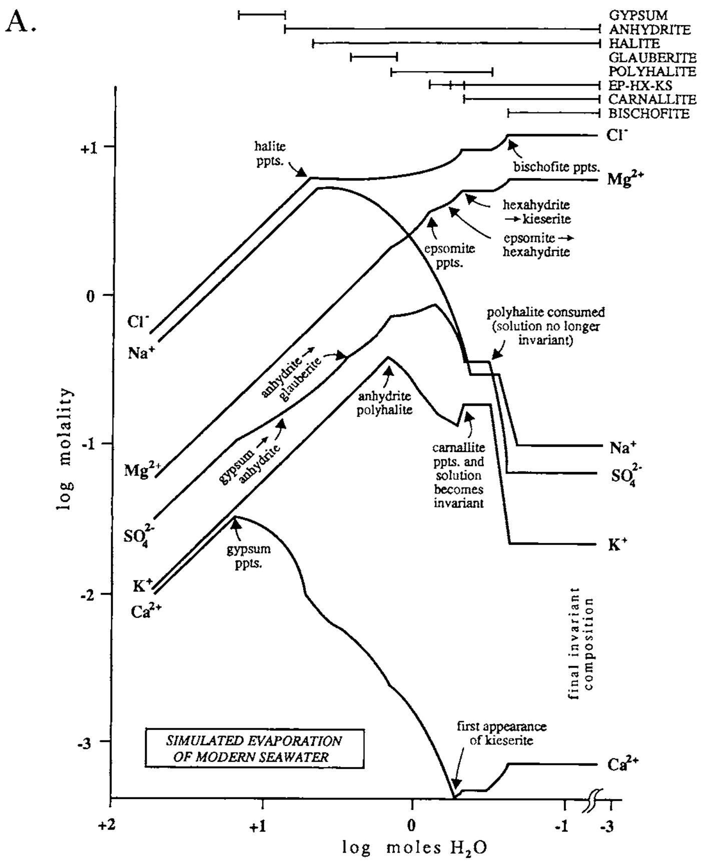

Fig. 1. Evaporative concentration of modern seawater simulated using the computer program of Harvie and Weare (1980). (A) Progressive changes in major ion concentrations in the brine as evaporation and mineral precipitation and resorption proceed.

And, finally, an explanation commonly called on involves contemporaneous dolomitization of co-existing marine carbonates by seawater brines in a marine evaporite environment (Shearman, 1966; Holland, 1978, p. 205).

A quite different explanation for the origin of the source waters of at least some of the $MgSO_4$-poor potash evaporites in the geologic record, particularly those deposited in rift and strike-slip basins, was suggested by Hardie (1978). This explanation calls on upwelling $CaCl_2$ hydrothermal brines as the determinant source waters for $MgSO_4$-poor potash deposits. Hydrothermal brines, rich in $CaCl_2$ and poor in SO_4, are known from a number of modern active continental rift and strike-slip basins where they are driven upward by free (thermal)

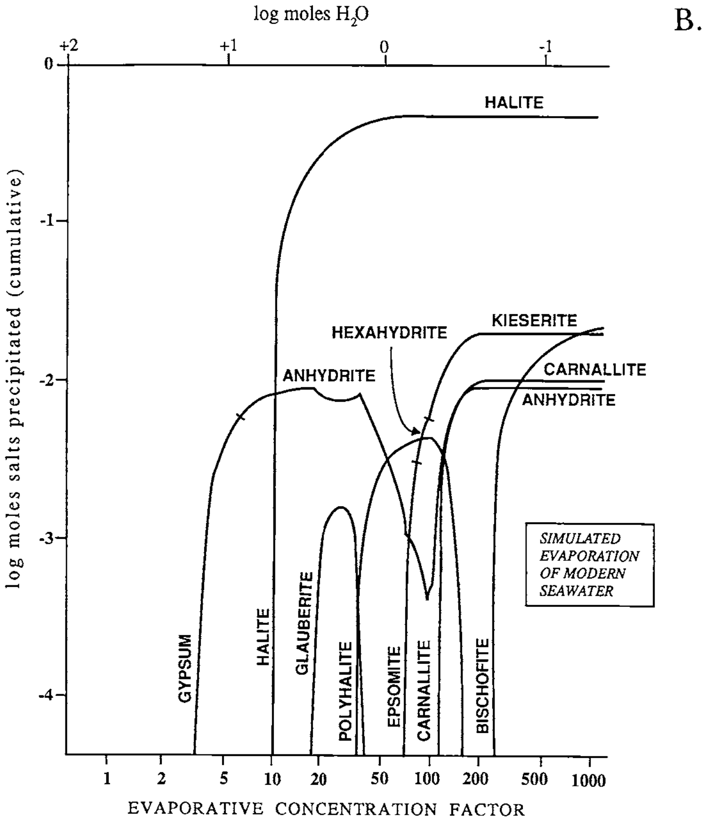

Fig. 1 (continued) (B) Cumulative masses of minerals precipitated and resorbed as evaporation proceeds (initial mass of seawater contained 1 kg of H_2O).

convection over thermal anomalies or by forced (gravitational) convection related to topographic gradients. Such rift and strike-slip zone hydrothermal brines, because of the special combination of their unusual chemical composition and their closed basin hydrologic setting, make ideal source waters for $CaCl_2$-rich $MgSO_4$-poor potash evaporites (Hardie, 1978; see also Hardie, 1984). The present paper documents in detail the case for this connection between sulfate-poor potash deposits, continental rifting, and hydrothermal brines.

During the review process it was brought to the author's attention that N.M. Dzhinoridze of the Institute of Halurgy in Leningrad has suggested a hydrothermal origin for salt deposits involving heated waters of magmatic origin, a process he has termed "exhalatory-sedimentary halogenesis" or "exhalation-sedimentary salification" (for example, Dzhinoridze, 1987). Dzhinoridze (1987) pointed to the time-

TABLE 2

Ancient potash deposits poor in magnesium sulfate

LOCATION	FORMATION	AGE	VOLUME OF POTASH DEPOSIT	NOTABLE FEATURES
East Siberia, USSR	Usolye Fm.	Early Cambrian	15 km^3 (Zharkov, 1981)	KCl type, see Zharkov (1981, table 3)
	Angara Fm.	Early Cambrian	25 km^3 (Zharkov, 1981)	halite + carnallite + sylvite (Zharkov,1984)
Michigan basin	Salina Group	Mid. to Late Silurian (Wen. - Prid.)	1000 km^3 (Matthews and Egleson, 1974)	sylvite + halite (some Ca borates); primary halite chevrons in sylvite beds (Nurmi and Friedman, 1977)
Tuva basin, USSR	Ikhedushiihgol Fm.	M. Devonian (U.Eif. - L. Giv.)	area 1000 km^2 but volume unknown (Zharkov, 1981)	halite + sylvite + rinneite (Zharkov, 1984)
Morsovo basin, USSR	Morsovo Salt Member	M. Devonian (Eifelian)	0.02 km^3 (Zharkov, 1981)	see Zharkov (1984)
Pripyat Depression, USSR	Lower and Upper Salt units	Late Devonian (Fras. - Famm.)	potash of Upper Salt ~6000 km^3 (Zharkov, 1984)	cycles of carbonate+siliciclastic+anhydrite --> halite --> potash (sylvite+carnallite); some interbeds of volcanics (Zharkov, 1984)
West Canadian basin	Prairie Evaporite	M. Devonian (Givetian)	3000 km^3 (Holter, 1972)	three potash members of halite +sylvite+ carnallite (Holter, 1969, 1972)
Canadian Maritimes	Windsor Group	E. Mississippian (Tournasian)	30 km^3 (Zharkov, 1981)	halite+sylvite+carnallite+rinneite+borates (Anderle, Crosby, and Waugh, 1979)
Paradox basin, Colo.- Utah	Paradox Fm. (Hermosa Gp.)	M. Pennsylvanian (Desmoinesian)	450 km^3 (Zharkov, 1981)	eleven cycles of black shale ->anhydrite ->halite ->potash (Petersen and Hite, 1969)
Eagle basin, Colorado	Eagle Valley Evaporite	M. to Late Penn. (Des.- E. Virg.)	0.1 km^3 (Zharkov, 1981)	two thin potash beds (sylvite+carnallite) encountered in drillholes (Zharkov, 1984)

space relationship of "salification with rift-formation and orogeny" and drew particular attention to the evidence for hydrothermal mineralization of the deposits underlying many ancient halite deposits. Thus, he argued for the origin of halitic evaporite deposits as the result of "discharge of thermal springs . . . from below . . . the basin" which introduces ". . . plutonic heat and matter, stratifies it under deep-water conditions, and leads to the complete removal of the sulfate ion from the waters of the lower stratum of the basin." Dzhinoridze (1987) derives the hydrothermal chloride waters directly from "crystallizing magmas" formed during rifting and orogeny. He notes that "30 times more chlorine transfers into the fluid phase than its residual content in the silicate fusion" during the process of "differentiation between mantle magma and granitic magma". Dzhinoridze (1987), then, sees most

TABLE 2
(continued)

LOCATION	FORMATION	AGE	VOLUME OF POTASH DEPOSIT	NOTABLE FEATURES
Amazon basin	Nova Olinda Fm.	L. Carboniferous to E. Permian	area ~5000 km^2 thickness unknown (Szatmari, Carvalho, and Simoes,1979, fig. 7)	sylvite cap to uppermost of seven halite cycles (Szatmari, Carvalho, and Simoes, 1979)
Supai basin, Arizona	Supai Fm. (Upper)	Early Permian (Leonardian = Art.)	0.1 km^3 (Zharkov, 1981)	sylvinite in the 3rd of 4 salt zones (Peirce and Gerrard, 1966)
Solikamsk basin (Cis-Ural trough), USSR	Berezniki Fm.	Early Permian (Kungurian)	119 km^3 (Zharkov, 1981)	potash member is 7 to 40 m thick. Thin (cms) interbeds of halite and sylvinite; red carnallite in some beds of the upper potash horizon (Zharkov, 1984)
English Zechstein basin	Teesside Group (= Leine Series)	Late Permian (E. Tatarian)	Boulby Potash covers >30,000 km^2 (Smith and Crosby, 1979, fig.2)	sylvinite reaches >30 m beneath the North Sea (Smith and Crosby, 1979)
	Staintondale Group (= Aller Series)	Late Permian (L. Tatarian)	Upper Potash covers >30,000 km^2 (Smith and Crosby, 1979, fig.3)	sylvinite reaches >50 m beneath the North Sea (Smith and Crosby, 1979)
Moroccan Meseta basins		Late Triassic (Car.- Norian) to perhaps Early Liassic	(?)	Doukkala, Berrichid, Khemisset, and Meknes basins carry sylvite, carnallite, bischofite, and rinneite. Interbedded basalt flows. (Salvan, 1972; Tortochaux, 1968; van Houten, 1977)
Northern Sahara Salt basin, Algeria	Trias a evaporites	Late Triassic (Car.-Norian)	(?)	sylvinite (Merabet and Popov, 1972)
Sergipe-Alagoas basin, Brazil	Ibura Member, Muribeca Fm.	E. Cretaceous (Aptian)	50 to 200 km^3 of carnallite (Borchert, 1977)	cycles of halite → halite + carnallite; thick tachyhydrite at tops of some cycles (Wardlaw, 1972)
Gabon basin, W. Africa		E. Cretaceous (Aptian)	(?)	highly deformed but mainly carnallite (de Ruiter, 1979)

ancient salt deposits in rift (and other tectonic) basins: (1) as derived from hot magmatic (juvenile) waters rather than from seawater or other surface waters, (2) as the result of cooling rather than evaporative concentration. Shakhnovskiy (1987) of the Institute of Geology in Moscow has presented an idea similar to that of Dzhinoridze, arguing that the close association between volcanic rocks and halite deposits in rift systems such as the Devonian Pripyat-Dnieper basin points to co-genesis. He calls on magmatic waters derived from the mantle as source waters for the thick halites of rift and other large evaporite

TABLE 2
(continued)

LOCATION	FORMATION	AGE	VOLUME OF POTASH DEPOSIT	NOTABLE FEATURES
Congo basin, W.Africa		E. Cretaceous (Aptian)	~5x10^{6}km^{3} of potash bearing evaporites (de Ruiter, 1979, figs. 11 and 12)	~500 m of carnallite and sylvite ± bischofite including one 155 m unit of tachyhydrite (Belmonte, Hirtz, and Wenger, 1965)
Khorat plateau, Thailand	Maha Sarakham Fm.	L. Cretaceous	>1.5x10^{6}km^{3} potash may cover 30,000km^{2}	carnallite (avg 40-50m) with some sylvite; major volumes of tachyhydrite (Hite and Japakasetr, 1979)
Catalan basin, Spain		Late Eocene to Early Oligocene	>80 km^{3}	carnallite (30-50m) and sylvinite (8-10m) in a 200 to 240 m salt unit (Rios, 1968)
Navarra basin, Spain		Late Eocene to Early Oligocene	(?)	carnallite (12-14m) and sylvinite interbedded with halite and salt clays; potash zone located between "old salt" (4-6m) and "new salt" (15-120m thick) (Rios, 1968)
Rhine Graben	Zone Salifere	Early Oligocene (Sannoisian)	~22 km^{3}	thin interbeds of chevron halite and sylvinite (minor carnallite) (Courtot, Gannet, and Wendling,1972; Meriaux and Gannat, 1980)
Dead Sea basin	Sedom Fm.	Late Pliocene to E. Pleistocene	minor	minor amounts of sylvite, carnallite, and calcium chloride salts in thick halite deposit (>2 km) (Zak, 1974)
Danakil Depression, Ethiopia	Sylvite Member, Houston Fm.	Pleistocene	>35 km^{3} of sylvinite	basal member is magnesium sulfate-rich (mainly kainite) but upper member is sylvinite (up to 36 m thick) (Holwerda and Hutchinson, 1968)
Qaidam basin, China		Holocene	>60 km^{3}	70 m of halite underlie the 6000 km^{2} modern salt pan; upper 10 m contains carnallite (Lowenstein and Spencer, personal commun., 1987)

basins. Apollonov (1987) has argued vigorously against any such "endogenic" sources for salt deposits in general and against Shakhnovskiy's evidence in particular.

It is hoped that the present paper, which approaches the possible connection between waters of hydrothermal origin and rift-basin evaporites with a perspective different from that of Dzhinoridze, Shakhnovskiy, or Apollonov, will add fuel to the ongoing debate in Russia as well as stimulate new debate among western geologists and geochemists on the origin of the source-waters for evaporites.

EVAPORITES AND RIFTING

Rift and Strike-Slip Basins as Favored Sites for Evaporite Accumulation

Evaporite deposits require for their formation: (1) an arid climate (evaporation > inflow) and (2) hydrologic closure of the depositional basin (outflow < inflow). The high relief basins produced by continental rifting and transtensional strike-slip faulting are ideal in providing both of these requirements, as exemplified by the many modern rift and strike-slip basins that contain saline lakes (the African rift basins, the Dead Sea trough, the Basin and Range province of the western United States, et cetera). Topographically, both rift (Freund, 1965; Baker, Mohr, and Williams, 1972; Veevers, 1981) and strike-slip (Reading, 1980; Ballance and Reading, 1980) systems are characterized by uplifted mountains flanking a string of elongated downdropped valleys (tens of kilometers wide, tens to hundreds of kilometers long) which are effectively closed sedimentary basins. In rift-systems (symmetrical rifts, half graben, aulocogens) closure is due to master fault discontinuities and oblique horsts uplifted along cross-faults. In strike-slip systems isolated *en echelon* basins (pull-apart basins, wedged and elliptical basins) are produced by curving, anastomosing faults, by side stepping of faults, and by transpressive upfolded arches oblique to the master faults (Reading, 1980). In both systems, the enclosing upfaulted mountains not only produce hydrologically closed basins but may also act as rainfall-snowfall traps and barriers, so that the valley floors become local *rain-shadow deserts independent of latitude,* as the abundance of modern evaporite basins beyond the horse-latitudes demonstrates (see Eugster and Hardie, 1978, fig. 3; Drewry, Ramsey, and Smith, 1974, fig. 1).

For accumulation of substantial thicknesses of evaporites there are two additional requirements. First, the closed arid basin must be either a deep receptacle before evaporite accumulation or must actively subside during evaporite accumulation. Rift and strike-slip basins meet either of these space needs perfectly in that they are sites of rapid and substantial subsidence and uplift (for example, vertical movement on the strike-slip Alpine Fault, New Zealand, is up to 10m/1000 yrs, Adams, 1981). This leads to high relief basins (kilometer-scale) with floors that downdrop to accommodate great thicknesses (kilometer-scale, as in the Dead Sea basin) of rapidly deposited sediment. For example, sedimentation rate of Quaternary lacustrine sediment in the Danakil Depression is 1.5m/1000 yrs (Tiercelin and Faure, 1978). The second additional requirement is that inflow of solutes into the basin must be substantial, greater than the rate of supply of sand and mud to the basin center. Inflow waters may be seawater or non-marine waters (Hardie, 1984). If seawater is to be the primary inflow water, then the evaporating basin must be a coastal depression with the floor below sealevel and with a constricted, very shallow inlet channel or a "leaky" sill of some kind. These basic hydrologic restrictions on the accumulation of marine evaporites were outlined many years ago in the classic "barred basin" model (see particularly the writings of Ochsenius, 1888, 1893, et cetera). Such a hydrologic system of necessity must be fundamentally enslaved to sealevel position. As Woolnough (1937, p. 1125) observed "if it were not for (the) *maintained* connection with the sea, the history of such a basin would be short." In this regard, then, and despite the constraints of basin closure and climate, *the formation of marine evaporites is ultimately controlled by sealevel.* No more striking a case can be found than the present day absence of major marine evaporite depocenters. The rising Holocene sea has overrun all the existing major basins that are potential marine evaporite basins, that is, those large restricted arms of the ocean with arid climates such as the Red Sea, the Persian Gulf, and the Mediterranean Sea. It will take a significant drop in relative sealevel due to global eustasy or tectonic uplift of the restricting sills to initiate salt deposition in these major basins (>100 m for the Red Sea and Persian Gulf, considerably more for the Mediterranean Sea). It is, of course, just this scenario that Hsü (1972) invoked to explain the Miocene "saline giant" discovered by drilling beneath the floor of the Mediterranean Sea. Clark and Tallbacha (1980) and Smith (1981) have used a similar argument for the Permian Zechstein evaporites, as has Lowenstein (1988) for the Permian cyclic evaporites of the Salado Formation.

For substantial accumulation of evaporites in non-marine basins the fundamental constraint of the position of sealevel obviously does not apply. All that is needed, in addition to appropriate volume, closure, and aridity of the basin, is an adequate inflow of water with dissolved solutes. Contrary to the prevailing and long-held view that non-marine evaporites are mainly sodium carbonate or sodium sulfate deposits found in small terrestrial basins, most Quaternary continental saline basins are dominated by NaCl-rich brines, and many contain thick halite deposits (Hardie, 1984, p. 194–197 and figs. 1 and 2; see also Hardie and Eugster, 1970; Eugster and Hardie, 1978). The source waters for these non-marine evaporite basins are of meteoric, diagenetic, volcanogenic, or hydrothermal origin (Hardie, 1984). Especially significant is that in many active continental rift and strike-slip basins a large, continuous inflow of such source waters is common. In particular, deep circulating groundwaters may be driven upward along fault and fracture zones by magmatic heat sources in the axis of the extensional trough or by gravity from the uplifted mountains. Examples of tectonically active closed basins with active upward circulation of saline $CaCl_2$ groundwaters are the Dead Sea, the Salton Sea, and the Danakil Depression. This characteristic of rift and strike-slip basins is central to the thesis of the present paper and is treated below.

In summary, continental rift and strike-slip basins are particularly favored settings for the deposition and accumulation of evaporites, because the flanking uplifted mountains not only provide hydrologic closure but also can turn the basins into orographic deserts *at any latitude.* In tectonically active basins thermal anomalies along the axis of extension are a powerful driving force for substantial groundwater convection which can surface in fault-line springs to feed the development of basin-center evaporites. All these characteristics make it unnecessary to restrict the formation of major salt deposits to the evaporation of seawater in coastal basins in the subtropical zones of global high pressure.

TABLE 3

Ancient salt deposits in extensional fault basins

LOCATION	FORMATION (THICKNESS)	AGE	AREA UNDERLAIN BY SALT	BASIN TYPE	NOTABLE FEATURES
Amadeus basin, Australia	Bitter Springs Fm. (1100 m)	Late Precambrian	83,000 km^2	(?)	oldest drilled salt; occurs in lower 400m Gillen member (McNaughton and others, 1968; Wells, 1980)
Canning Basin, W. Australia (Fitzroy Graben and Kidson subbasin)	Carribuddy Fm. (1700 m)	Early Devonian	207,000 km^2	Fitzroy Graben is strike-slip (Smith, 1968)	unconformably overlies Ordovician, overlain by Early Devonian red beds and aeolianites or an unconformity. Halite (low Br.) is red-brown due to iron oxide, barite present.
Tuva basin, USSR	Ikhedushiingol Fm. (600 - 900 m)	M. Devonian (L. Eif. - E. Giv.)	10,000 km^2	(?)	overlain and underlain by red beds; sylvite interbeds; rinneite is common (Zharkov, 1984)
West Canadian basin, Alberta	Lower Elk Point Fm., (300 m)	M. Devonian (Eifelian)	140,000 km^2	(?)	mud - halite interbeds; halite has very low Br (Holter, 1969; Holser, Wardlaw, and Watson, 1972)
Adavale basin, Queensland, Australia	Etonvale Fm., (Boree Salt Member, 900 m)	M. Devonian	8000 km^2	(?)	sylvite present in halite beds; coarse red beds below (with volcanics) and above (Wells, 1980; Zharkov, 1984)
Pripyat Depression, USSR	Lower Salt (200 m - 1000 m) Upper Salt (1500 m)	Late Devonian (Fras. - Fam.)	Lower Salt 20,000 km^2 Upper Salt 26,000 km^2	rift	8 cycles each capped by bedded sylvinite characterize Upper Salt. Volcanics in the unit between the Lower and Upper Salts. Eastern part of the basin is almost exclusively volcanics (Zharkov, 1984).
Dnieper - Donets Depression, USSR	unnamed (> 2000 m ?)	Late Devonian	> 40,000 km^2	rift	mainly salt domes but drilling has demonstrated thick salt interbedded with marls, anhydrite, siliciclastics, and volcanics (Zharkov, 1984).
Bonaparte Gulf, Australia	unnamed (190+ m)	pre-Late Devonian	26,000 km^2	strike-slip (Smith, 1968)	extensive salt domes (Wells, 1980; Zharkov, 1984).
Canadian Maritimes	Albert Fm. (1600 m) of Horton Group	Early Miss. (Tournaisian)	?	strike-slip (Zeigler, 1978, fig. 7)	non-marine Hiram Brook Member (70-488 m) is composed of halite, anhydrite, and glauberite. Gautreau member is also halitic. Overlain by coarse red beds. (Gussow, 1953; Hamilton, 1961)

Ancient Evaporites Deposited in Extensional Fault Basins

Many ancient halite evaporites appear to have accumulated in rift and strike-slip fault basins or in interior basins that were initiated as extensional fault basins (table 3). In this context, the most significant development in the field of evaporites in recent years has been the discovery of thick halite deposits of Mesozoic age in rift basins beneath

TABLE 3
(continued)

LOCATION	FORMATION (THICKNESS)	AGE	AREA UNDERLAIN BY SALT	BASIN TYPE	NOTABLE FEATURES
Canadian Maritimes	Cassidy Fm. (>1000 m) of Windsor Group	M. Miss. (E. Visean)	55,000 km^2	strike-slip (Zeigler, 1978, fig. 7)	potash member (18-45 m) is sylvinite ± carnallite, rinneite, and borates. Minor polyhalite occurs at Pugwash (Zharkov, 1984)
Paradox basin, Utah-Colorado	Paradox Fm. (>1200 m, probably 2000 m)	M. Penn. (Desmoinesian)	28,000 km^2	strike-slip (Stevenson and Baars, 1986)	29 saline cycles, 11 of which contain potash salts (mainly sylvite and carnallite but minor polyhalite). Minor rinneite, kieserite, and borates also occur (Hite, 1968; Petersen and Hite, 1969)
Amazon basin	Nova Olinda Fm. (1200 m)	Late Carb. - Early Perm.	100,000 km^2	rift	7 saline cycles, one of which (#7) contains potash (sylvinite)(Szatmari, Carvalho, and Simoes, 1979)
N.W. European basin	Upper Rotliegende (1000 - 1500 m)	Early Permian (Saxonian)	> 80,000 km^2	strike-slip / rift (Ziegler, 1978; Ziegler, 1975, fig. 17)	thick salt pan halite deposit (up to 900 m) in a non-marine red bed setting (Glennie, 1972)
Chu-Sarysu basin, USSR	Zhidelisai and Kinger Fms. (1000 m)	Early Permian (Art. - Kun.)	10,000 km^2	(?)	salt with gypsum, anhydrite, and glauberite interbedded with red beds (Zharkov, 1984)
Dnieper-Donets Depression, USSR	Nikitova (250 m) and Slavyansk (600 m) Fms.	Early Permian (Sakmarian)	60,000 km^2	rift	thin alternations of salt, anhydrite, siliciclastics and carbonates (Zharkov, 1984)
	Kramatorsk Fm. (600 m)	Early Permian (Sakmarian)	10,000 km^2	rift	mainly halite but several potash zones (sylvite , carnallite), some of which carry polyhalite, kieserite, and langbeinite (Zharkov, 1984)
N.W. European basin	Zechstein Z1=10-400m Z2=50-1200m Z3=40-300m Z4=20-200m	Late Permian	Z1=250,000 km^2 Z2=431,250 km^2 Z3=413,500 km^2 Z4=270,000 km^2	strike-slip / rift	Zechstein 2 is the classic Mg sulfate potash evaporite
	Upper Buntsandstein (Rot) (100 m)	Early Triassic (Scythian)	120,000 km^2	strike-slip / rift (Ziegler, 1978; Ziegler,1975, fig. 17)	salt in red beds (Richter-Bernburg, 1972)

the continental shelves and slopes of the Atlantic Ocean (Belmonte, Hirtz, and Wenger, 1965; Ayme, 1965; Schneider and Johnson, 1970; McIver, 1972; Pautot and others, 1973; Leyden and others 1976, 1978; among others). These discoveries, together with the very thick Miocene salts found in the Red Sea rift (Heybroek, 1965; Frazier, 1970; Ahmed, 1972; Lowell and Genik, 1972; Coleman, 1974; Mulder, Lehner, and

TABLE 3
(continued)

LOCATION	FORMATION (THICKNESS)	AGE	AREA UNDERLAIN BY SALT	BASIN TYPE	NOTABLE FEATURES
N.W. European basin	Middle Muschelkalk (100 m)	M. Triassic (Anis. - Lad.)	two basins 60,000 km² 40,000 km²	strike-slip / rift (Ziegler, 1978; Ziegler, 1975)	overlies marine carbonates in Germany (Richter-Bernburg, 1972)
Eastern North Atlantic (North Sea, Britain, France, Portugal, Spain)	Keuper (3000 m) [salt in the North Sea is ~200 m thick, Brennand, 1975]	Late Triassic (Carn. - Nor.)	salt occurs in many places over a wide area 500,000 km² (Ziegler, 1978, fig.11)	strike-slip / rift (Ziegler, 1978; Ziegler, 1975, fig.17)	red beds with salt in extensional basins that mark the break up of Pangea in N.W. Europe (Ziegler, 1978; Rona, 1981)
Moroccan Meseta	Doukkala basin (salt ~ 500 m)	Late Triassic (Carnian to Norian or Early Liassic)	11,250 km²	strike-slip / rift (van Houten, 1977, fig. 4)	non-marine red beds (up to 2000m) and basaltic lava flows with local thick salt. Potash (sylvite, carnallite, rinneite) at Doukkala, Berrichid, Khemisset, and Meknes (Salvan, 1972; Tortochaux, 1968; van Houten, 1977)
	Berrichid basin (salt ~ 500 m)		3200 km²		
	Khemisset-Meknes (Boufekrane)-Rharb Dahar n'Sour basin (salt 500-1400+m)		40,000 km²		
Essaouira basin, Morocco	Argiles d'Argana (salt 800+m)	Late Triassic (Car. - Nor.)	85,000 km²	strike-slip / rift (van Houten, 1977)	non-marine red beds (5000m) with salt and basaltic lava flows (van Houten, 1977; Evans, 1978)
Aaiun basin, Morocco and Spanish Sahara	(?) (1070 m)	Late Triassic (Car. - Nor.)	45,000 km²	strike-slip / rift (van Houten, 1977)	salt beneath the continental shelf (Uchupi and others, 1976; van Houten, 1977)
Saharan Atlas salt basin, Algeria	Formation Salifere (250-570 m)	Late Triassic (Car. - Nor.)	60,000 km² (van Houten, 1977, fig. 1) to 140,000 km² (Merabet and Popov, 1972)	strike-slip / rift	salt interbedded with basalt flows and gypsiferous shales (Merabet and Popov, 1972)
Northern Sahara salt basin, Algeria	Trias a evaporites (or Salina d'Ouargla) (2030 m)	Late Triassic (Car. - Nor.)	>250,000 km² (Demaison, 1965) >360,000 km² (Merabet and Popov, 1972, fig. 1)	strike-slip / rift	salt interbedded with anhydrite and saline mudstones. Some potash (sylvinite). Upper part of the section is anhydritic (100-900 m). Marine carbonates to the east in Tunisia (Demaison, 1965; Merabet and Popov, 1972)

Allen, 1974), led to the recognition that evaporites are one of the characteristic sediments of the early rifting stage of continental breakup and subsequent development of oceans by sea floor spreading (Belmonte, Hirtz, and Wenger, 1965; Allard and Hurst, 1969; Schneider and Johnson, 1970; Hallam, 1971; Wardlaw and Nicholls, 1972; Kins-

TABLE 3
(continued)

LOCATION	FORMATION (THICKNESS)	AGE	AREA UNDERLAIN BY SALT	BASIN TYPE	NOTABLE FEATURES
Senegal basin, offshore Senegal and Mauritania	identified by massive salt domes only	Triassic to Liassic (?)	>5000 km^2	rift	see Ayme (1965), Evans (1978)
Grand Banks and Scotian Shelf, offshore Newfoundland and Nova Scotia	Argo Fm. (~1800 m)	Late Triassic-Early Jurassic	>40,000 km^2	rift	see van Houten (1977), Jansa, Bujak, and Williams, (1980)
Mandawa basin, coastal Tanzania	Pindiro Series (3200 m, of which about 2500 m is salt)	Late Triassic-Early Jurassic	>60,000 km^2 (perhaps larger, see Kent, 1965, fig. 6)	rift	halite, red shales and arkoses pass upward into a thick sequence of halite with some anhydrite and carbonates. Overlain conformably by Bajocian gypsiferous shales (Kent, 1965)
Gulf of Mexico	Louann Fm. (4000 m)	M. Jurassic (Callovian)	>800,000 km^2 (Antoine and others, 1974, fig.1; Salvador, 1987, fig.13)	rift	see Kirkland and Gerhard (1971), Salvador (1987)
	Buckner Fm. (100 - 800 m)	Late Jurassic (Kimm.)	<1000 km^2(?)		localized halite in an anhydrite deposit (Lowenstein, 1987)
Central Eurasian platform, USSR	Black Sea area (1500 m salt)	Late Jurassic (Kimm.- Tithon.)	~75,000 km^2	rifts (perhaps related to strike-slip faulting)	salt in a number of "grabens, linear depressions and isometric basins" with thick (2-3 km) sediment fills (Beznosov and others, 1978)
	Caspian Sea to Pamirs area (500 m salt)		several basins within an area of 500,000 km^2 or greater		
North Sea, Lower Saxony basin, N.W. Germany	200 m salt	Late Jurassic (Tithonian)	5000 km^2 (Richter-Bernburg, 1972)	strike-slip (Ziegler, 1978, p. 613)	salt is associated with anhydrite and carbonates (Richter-Bernburg, 1972). Minor volcanic centers at the N.W. edge of the basin (Ziegler, 1978)
Sergipe-Alagoas basin, coastal Brazil	Muribeca Fm. (Ibura Member, 450 m salt)	Early Cretaceous (Aptian)	>3000 km^2	rift	thick potash deposit (carnallite with sylvite) containing a significant volume of tachyhydrite (Wardlaw, 1972; Asmus and Ponte, 1974)

man, 1974, 1975; Burke, 1975; Evans, 1978; Rona, 1981; among others).

In the sedimentary wedges that make up the passive margins of the Atlantic Ocean, Late Triassic to Mid-Cretaceous salt deposits occur in downfaulted troughs (Rona, 1981) at or near the stratigraphic boundary

TABLE 3
(continued)

LOCATION	FORMATION (THICKNESS)	AGE	AREA UNDERLAIN BY SALT	BASIN TYPE	NOTABLE FEATURES
Espirito Santo basin, coastal and offshore Brazil	salt domes offshore (unknown thickness)	Early Cretaceous (Aptian)	>12,500 km^2	rift	see Asmus and Ponte (1974)
Santos basin, offshore Brazil	salt domes offshore (thickness unknown)	Early Cretaceous (Aptian)	(?)	rift	see Asmus and Ponte (1974)
Gabon basin, coastal W. Africa	salt beds (>300 m) between Cocobeach and Madiela Fms.	Early Cretaceous (Aptian)	>40,000 km^2 (Belmonte, Hirtz and Wenger,1965; Brink,1974)	rift	potash deposit, mainly carnallite (Franks and Nairn, 1974; Brink,1974; de Ruiter, 1979)
Congo basin, coastal W. Africa	salt beds (900 m) between Chela Series and Mavuma Beds	Early Cretaceous (Aptian)	>6000 km^2 (Belmonte, Hirtz and Wenger,1965)	rift	potash deposit (carnallite, sylvite) with thick unit of tachyhydrite and bischofite (Belmonte,Hirtz, and Wenger,1965; Franks and Nairn,1974)
Cuanza basin, coastal Angola	"Sel Massif" (600 m)	Early Cretaceous (Aptian)	>6000 km^2 (Franks and Nairn,1974, fig. 6)	rift	"Sel Massif" (Brognan and Verrier, 1966) is overlain by a cyclic halite-anhydrite-carbonate sequence
Khorat plateau, Thailand	Maha Sarakham Fm. (salt >610 m)	Late Cretaceous	57,000 km^2	strike-slip	major potash deposit (carnallite with some thick sylvite beds); significant volume of tachyhydrite. Overlain and underlain by continental red beds (Hite and Japakasetr, 1979; Ridd, 1978)
Northern Sahara, Algeria	Bechar basin (salt 685 m)	Late Cretaceous (Senonian)	>20,000 km^2	rift (?)	see Merabet and Popov (1972)
	Oued Mya basin (salt 180 m)		100,000 km^2		
Bresse basin, France	(?) (salt 1400 m)	Late Eocene to Early Oligocene	950 km^2	rift	3 formations of salt: lower is 90% halite; middle is 50% halite with interlayered clay beds and carbonate beds; upper is 90% halite. 1 formation of calcium sulfates. (Curial, 1986; Moretto, 1986)

between basal continental rift sediments and the overlying marine sediments (Evans, 1978, fig. 4). Thus, in the context of global tectonics and the Wilson Cycle the development of halite evaporites with thicknesses measured in hundreds to thousands of meters is taken to mark the initial inflow of seawater along the narrow rift axis of the incipient ocean basins. However, in the context of the details of the origin of the salts

TABLE 3
(continued)

LOCATION	FORMATION (THICKNESS)	AGE	AREA UNDERLAIN BY SALT	BASIN TYPE	NOTABLE FEATURES
Valence basin, France	Lower Salt Series (salt 520 m) Upper Salt Series (salt 150 m)	Late Eocene to Early Oligocene	760 km^2	rift	upper series contains glauberite (Dumas, 1988)
Rhine Graben	Zones Saliferes (1700 m)	Late Eocene to Early Oligocene (Sannoisian)	2200 km^2	rift	3 zones of salt and mud (475, 350, 400 m) separated by mudstones. Potash beds (sylvite, carnallite) in the upper zone (Courtet,Gannat, and Wendling, 1972; Meriaux and Gannat,1980)
Gulf of Suez	Evaporite Group (3400 m)	M. Miocene	4000 km^2 (?)	rift	salt confined to the deeper parts of the graben (Heybroek, 1965)
Red Sea	In the southern Red Sea salt (up to 5000m) is equivalent to Habab Fm. (Lowell and Genik, 1972, fig. 5)	M. Miocene	> 300,000 km^2 (?)	rift	>3 km continuous salt penetrated by drills (Lowell and Genik, 1972; see also Heybroek, 1965)
Rhine Graben	>1000 m salt	Miocene	2000 km^2	rift	see Richter-Bernburg (1972)
Virgin Valley, Nevada	Muddy Creek Fm. (> 500 m salt)	Pliocene	"salt probably underlies hundreds of square miles" (Mannion, 1963, p.174)	strike-slip	salt with glauberite and minor anhydrite in non-marine basins. Upper 700 m of the formation carries gypsum and basalt flows (Mannion, 1963)
Avawatz Mtns., California	30 to 200 m salt	Early to M. Pliocene	(?)	strike-slip	salt with red shale overlain by 200 to 300 m of gypsum in a non-marine basin (ver Planck, 1958)

themselves, the situation is far more complex. Belmonte, Hirtz, and Wenger (1965), who first outlined the connection between the Cretaceous salt basins of the Brazilian and west African coasts and the "new born Atlantic Ocean," recognized the hydrologic difficulties of accumulating these evaporites without their being overrun by "full marine conditions." Evans (1978, p. 225) noted that the "abrupt transition from continental sediments to evaporites might be interrupted by brackish-water sediments or by a zone of interbedded evaporites and continental sediments. These modifications would represent the competition between marine and non-marine environments at the edge of the encroaching sea." However, salt deposits could form from the very earliest stages of continental rifting before the entry of the sea, as several thick non-marine halite deposits in Quaternary fault basins

TABLE 3
(continued)

LOCATION	FORMATION (THICKNESS)	AGE	AREA UNDERLAIN BY SALT	BASIN TYPE	NOTABLE FEATURES
Dead Sea basin	Sedom Fm. >2000 m (probably 6 km based on gravity data)	Late Pliocene to Early Pleistocene	2500 km^2 (Zak and Bentor, 1972, fig. 6)	strike-slip	mainly halite with interbedded shales carrying anhydrite and dolomite. Minor sylvite, carnallite and "$CaCl_2$ salts". Mudcracks; bird and animal tracks; fish, plant and insect fossils (Zak, 1974; Neev and Emery, 1967)
	Amora Fm. >500 m (25-30% salt) perhaps >2 km in graben center	Pleistocene	~1000 km^2 (Zak and Bentor, 1972, fig. 7)		laminated organic shales, carbonates gypsum-anhydrite, and salt. Minor dispersed "$CaCl_2$ and $MgCl_2$ salts". Rare plant remains. Paleoenvironment = lacustrine. (Zak, 1974; Neev and Emery, 1967)
	Lisan Fm. 40 m (minor halite)	Late Pleistocene (>12,000 yr.)	(?)		laminated chalk and gypsum with minor halite. Traces of "$MgCl_2$, $CaCl_2$ and KCl salts in distinct laminae" (Zak, 1974). Paleoenvironment = inland lake.
Danakil Depression, Ethiopia	>1000 m salt	Pleistocene (< 1 my)	(?)	rift	thick halite with two potash zones. Upper potash is 5 to 50m thick with basal kainite member, a middle carnallite-kieserite member, and an upper sylvite-anhydrite member. Basalts are intercalated with evaporites in the east. (Holwerda and Hutchinson,1968).

demonstrate (Hardie, 1984, fig. 2), and could continue to accumulate after a "proto-ocean" rift had widened by plate divergence, particularly in isolated "failed arms" oblique to the axis of divergence. In this regard the genesis of ancient evaporites, which accumulated in proto-ocean rifts and associated aulacogens, needs careful analysis, even where such deposits rest on a "breakup unconformity" and are overlain by normal marine sediments that record the full influx of the sea and the flooding of the subsiding margins of the diverging continents. And it is here that the "unusual marine evaporites" (Wardlaw, 1972) of Aptian age in the Sergipe (Brazil) and Gabon-Congo (west Africa) basins are of particular significance.

The Sergipe and Gabon-Congo salt basins on opposite coasts of the south Atlantic Ocean have a similar stratigraphy (fig. 2), common faunas (Belmonte, Hirtz, and Wenger, 1965, p. 72–73), and the same unusual type of evaporites (fig. 3), and in reconstructions of Pangea they fit side-by-side across the line of juncture (fig. 2; see also Belmonte, Hirtz, and Wenger, 1965, fig. 12; Allard and Hurst, 1969, fig. 10; Evans, 1978,

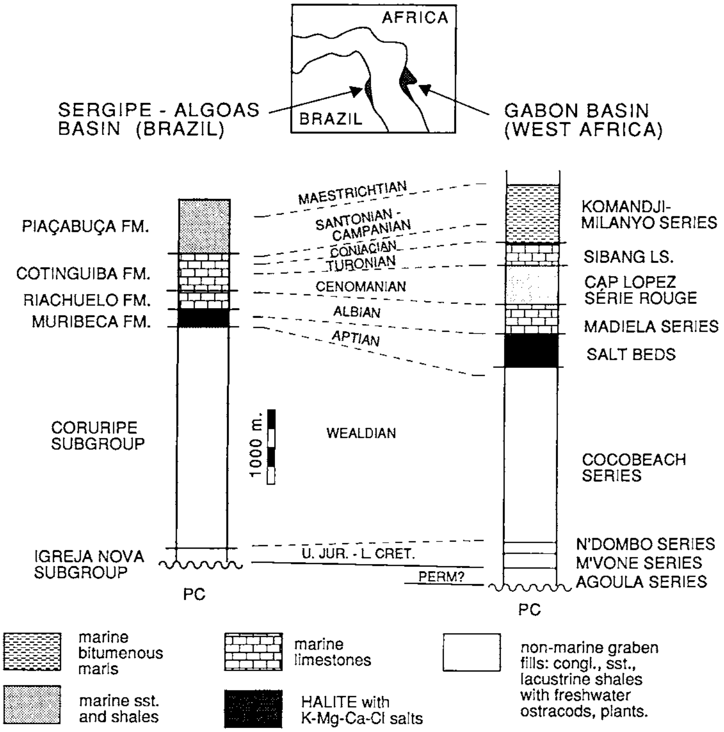

Fig. 2. Comparison of the stratigraphies of the Sergipe-Alagoas basin (Brazil) and the Gabon-Congo basin (west Africa). Data of Asmus and Ponte (1973) and Franks and Nairn (1973).

fig. 1). What is most remarkable is the mineralogical composition of the evaporites. In the Sergipe basin the evaporite sequence (Ibura member of the Muribeca Formation, up to 800 m thick, Meister and Aurich, 1972) is an $MgSO_4$-free potash deposit made up of cycles composed of halite, carnallite, and sylvite. Most significantly, several of these cycles carry thick units (many tens of meters) of the very unusual, very soluble $CaCl_2$ mineral *tachyhydrite* ($CaCl_2 \cdot MgCl_2 \cdot 12H_2O$) (Wardlaw, 1972; Wardlaw and Nicholls, 1972; Borchert, 1977). The tachyhydrite-bearing section in the Taquari basin is shown in figure 3 (from Wardlaw, 1972, fig. 4; see Borchert, 1977, fig. 3, for a more detailed section). A similar cyclic potash deposit, free of $MgSO_4$ and carrying thick tachyhydrite units, is found in the Congo basin (fig. 3) (see Belmonte, Hirtz, and Wenger, 1965; de Ruiter, 1979). Such $CaCl_2$-rich salt deposits without $MgSO_4$ or $CaSO_4$ minerals cannot be derived from evaporation of seawater with the composition of the present-day oceans (fig. 1; see also Hardie, 1984), a geochemical dilemma acknowledged by Wardlaw (1972), Franks and Nairn (1973), and Borchert (1977). Yet these

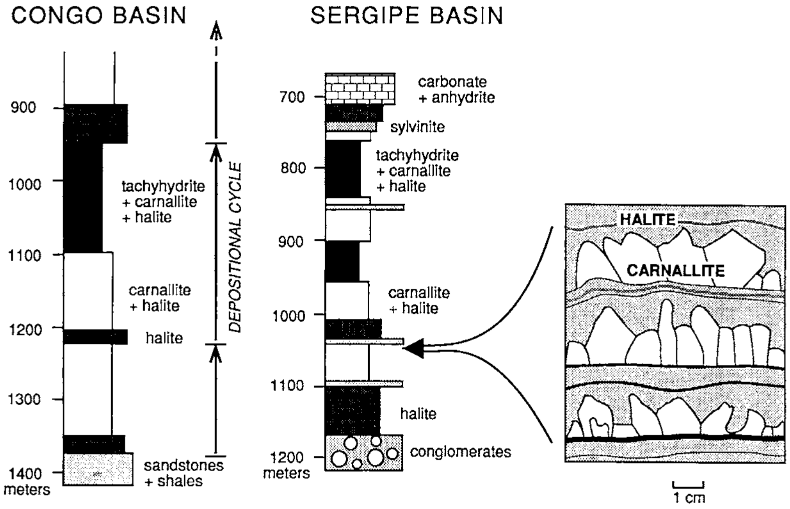

Fig. 3. Evaporite depositional cycles of the Sergipe and Congo basins (from data of Belmonte, Hirtz, and Wenger, 1965, fig. 4; Wardlaw, 1972, figs. 4 and 7). On the right is shown the primary layering and bottom-growth features of the Sergipe halite-carnallite subfacies in the Sergipe basin (after Wardlaw, 1972, fig. 7).

deposits are clearly primary precipitates "little altered since they grew from the Cretaceous brines" (Wardlaw, 1972, p. 163), a conclusion fully supported by textural evidence (Wardlaw, 1972, fig. 7; Szatmari, Carvalho, and Simoes, 1979, fig. 12). Preconcentration basins farther down the ever widening rift and closer to the newly ingressing ocean have been suggested as an answer (Belmonte, Hirtz, and Wenger, 1965; Wardlaw and Nicholls, 1972; Kinsman, 1975), although not without some measure of doubt (Franks and Nairn, 1973, p. 328; Evans, 1978, p. 231–232). But fractional crystallization of seawater in a series of preconcentration basins cannot lead to a $CaCl_2$ brine (Hardie, 1984, see especially table 7), as is clearly demonstrated during fractionation in commercial salt operations (Herrmann and others, 1973). A more radical explanation is needed. The search for such an explanation for these unusual tachyhydrite-bearing evaporites and the more usual, but still problematical, $MgSO_4$-poor potash evaporites without tachyhydrite found in ancient rifts and other extensional fault basins is the concern of the remainder of this paper.

RIFTING AND HYDROTHERMAL BRINES

It is now well documented that the axial zones of tectonically active rift and strike-slip systems, both oceanic and continental, are sites of subsurface convective circulation of hot brines over thermal anomalies, for example, the Salton Sea (California) and the Guyamas Basin (Gulf of California), the Red Sea, and the Mid-Ocean Ridge hydrothermal fields of Reykjanes (Iceland), TAG (Atlantic Ocean), the East Pacific Rise, and Galapagos (Pacific Ocean).

In the M.O.R. rift zones the deep circulating brines are seawater altered significantly by interaction with oceanic basalts at zeolite, greenschist, and amphibolite facies temperatures (for recent summaries, see Holland, 1978, p. 190–200; Thompson, 1983). In the reaction:

$$\text{basalt} + \text{seawater} \rightarrow \text{spilitic greenstone} + \text{hydrothermal brine},$$

normal seawater becomes enriched in Ca and K but depleted in Mg and SO_4 (table 4) and thus is converted to a $CaCl_2$-brine, that is, a brine in which at least part of the Ca is balanced by Cl as defined by $mCa^{2+} > mSO_4^{2-} + \frac{1}{2}mHCO_3^- + mCO_3^{2-}$ (Hardie, 1983). Of considerable interest to ore geologists is the fact that these hydrothermal brines also show enrichment in heavy metals, such as Fe, Mn, Cu, Pb, Zn, et cetera, compared to normal seawater; in some cases so much so that sulfide minerals are precipitating around active vents, such as the "black smokers" of the East Pacific Rise (Speiss and others, 1980; MacDonald and others, 1980; Thompson, 1983, fig. 47.10). In those active systems

TABLE 4

Chemical compositions of M.O.R. hydrothermal brines

	1	2	3	4	5	6
	REYKJANES, ICELAND HOLE #8 ppm	REYKJANES, ICELAND HOT SPRING ppm	GALAPAGOS RIDGE mg/l	E. PACIFIC RISE N21° (NGS vent) mg/l	RED SEA, ATLANTIS II DEEP ppm	MODERN SEAWATER 35 °/oo ppm
SiO_2	636	544	21.9	1172	28	1
Ca	1500	2260	1611	835	5150	411
Mg	16	123	0	52	764	1293
Na	9610	14,325	11,196	11,724	92,600	10,762
K	1348	1670	731	1009	1800	399
HCO_3	1926 **	5			185	142
SO_4	31	206	214	0	840	2709
Cl	19,260	29,100	21,095	20,527	156,030	19,353
Fe	0.5	0.192		49	81	< 0.003
Mn	2.0		63	55	82	< 0.002
Pb				0.04	0.6	< 0.00003
Zn				2.5	5.4	< 0.005
Ba			6	>2		< 0.03
TOTAL	32,400	52,160	36,232	35,700	257,600	35,000
pH	6.1	6.2		3.8		8.3-7.6
TEMP	277°C	99°C	350°C	273°C	56°C	2°-30°C
DEPTH	1750 m	surface	submarine vent	submarine vent	submarine vent	
ΔCa*		+110.38			+236.47	-38.22

Sources of data : 1, 2 - Björnsson, Arnorsson, and Tomasson (1972); 3 - Edmond and others (1979), Thompson (1983); 4 - von Damm and others (1985); 5 - Brewer and Spencer (1969); 6 - Riley and Chester (1971).

** Reported as carbon dioxide

* $\Delta Ca = mCa^{2+} - mSO_4^{2-} - mCO_3^{2-} - 1/2\, mHCO_3^-$ and is a measure of whether the water is a $CaCl_2$ water (+ value) or not (- value).

where oceanic hydrothermal brines have been sampled (Iceland and the seafloor vents of the East Pacific Rise and the Galapagos Ridge), there is little increase in salinity or chlorinity over that of normal seawater (table 4). However, fluid inclusions in quartz veins in M.O.R. metagabbros show that these brines can become very saline (up to 58 wt percentage NaCl equivalent) due to phase separation that occurred during either subsurface boiling or condensation (Vanko, 1988).

In the young spreading center of the Red Sea, where oceanic crust underlies only the very narrow axial rift zone (4–30 km wide), hydrothermal brines, enriched in $CaCl_2$ and with a chlorinity 8x that of seawater (table 4), are actively venting at temperatures of 56° to 60°C on to the seafloor (Degens and Ross, 1969; Ross, 1972). These subsea brines are exceedingly rich in heavy metals (table 4), which are precipitating as sulfides and oxides to produce stratiform Pb–Zn–Fe ores that cover the floor of isolated "deeps" into which the brines are upwelling, for example the Atlantis II Deep (Hackett and Bischoff, 1973). Although the origin of these Red Sea hydrothermal brines remains uncertain (Manheim, 1974), interactions between hot seawater and the underlying Miocene evaporites (White, 1968) and rift axis basalts (see the He data of Lupton, Weiss, and Craig, 1977) appear to have been important. Whatever their origin, these hot $CaCl_2$ brines, now venting into the Red Sea rift axis at a rate that would fill the Red Sea basin in less than 10 my (based on the data of Ross, 1972), appear to have been active in the present deeps for the past 13,000 yrs (Hackett and Bischoff, 1973). But it is also clear from the Pb-Zn, Mn, and Cu mineralization of Middle Miocene age along transform faults at the margins of the Red Sea in Egypt and Saudi Arabia (Bonatti and others, 1972, fig. 8; Mitchell and Garson, 1976, fig. 39) that hydrothermal brines were circulating during the early opening of the Red Sea rift, perhaps before, or even as, thick Middle-Upper Miocene evaporites (Lowell and Genik, 1972) were deposited in the new rift.

In modern continental rift and strike-slip systems, hot $CaCl_2$ brines are known from several closed arid basins. Active hydrothermal circulation of very hot $CaCl_2$ brines in the subsurface has been documented by drilling in the Salton trough (California) and Cerro Prieto (Mexico) and is testified to by hot brine springs at the surface in the Lake Tiberis area of the Dead Sea-Jordan rift, in the Danakil Depression (Ethiopia), and along the Wasatch fault bordering Great Salt Lake, Utah (table 5).

With regard to the origin of $CaCl_2$ brines in continental basins, the well documented hydrothermal system in the Salton Sea trough (California) is an invaluable case study (Doe, Hedge, and White, 1966; Helgeson, 1968; Muffler and White, 1969; Elders and others, 1972). The Salton trough lies at the north end of the Gulf of California, which is an active transtensile strike-slip depression made of a series of pull-apart basins produced by dextral motion along transform faults (Crowell, 1974; Kelts, 1981). The Salton trough is filled with 6 km of Pliocene to Recent non-marine shales, sandstones, and conglomerates

TABLE 5

Chemical compositions of hydrothermal brines in some modern continental rift and strike-slip basins (in ppm)

	1	2	3	4	5	6	7
	SALTON TROUGH, CALIF.	CERRO PRIETO, MEXICO	TIBERIAS HOT SPRING, DEAD SEA	UTAH HOT SPRING, GREAT SALT LAKE	STINKING HOT SPRING, GREAT SALT LAKE	HOT SPRINGS, LAKE GUILIETTI, DANAKIL, ETHIOPIA	
SiO_2	400	106	23	38	48		
Ca	28,000	370	3930	1140	946	500	6400
Mg	54	23	825	70	297	30	190
Na	50,400	4580	6910	7030	12,600	1,000	13,750
K	17,500	679	77	904	571	70	660
HCO_3	500	66	366	192	324		
SO_4	5	250	891	189	111	20	620
Cl	155,000	8170	19,200	13,300	21,600	2350	35,900
Br	120		1.4	8.2	15		
HS	16		28		60		
Fe	2290		7.8	0.4			
Mn	1400			1.9			
Pb	102						
Zn	540						
Ba					4.1		
TOTAL	258,000	14,300	32,300	22,800	36,500	3970	57,520
pH	5.2	5.9	7.3	6.7			
TEMP	300°C	82°C	61.9°C	57°C	48°C	40-50°C	
DEPTH	1500 m	surface	surface	surface	surface	surface	surface
ΔCa*	+1385.03	+12.18	+171.56	+49.80	+39.58	+24.53	+306.45

Sources of data: 1 - Muffler and White (1969); 2 - White,Hem, and Waring (1963, table 18); 3 - White, Hem, and Waring (1963,table 16); 4, 5 - Whitehead and Feth (1961), see also White, Hem, and Waring (1963, tables 15 & 16); 6, 7 - Martini (1969), Bonatti and others (1972).

* $\Delta Ca = mCa^{2+} - mSO_4{}^{2-} - mCO_3{}^{2-} - 1/2\ mHCO_3{}^{-}$ and is a measure of whether the water is a $CaCl_2$ water (+ value) or not (- value).

(Muffler and Doe, 1968) and rhyolite extrusives (Muffler and White, 1969). Today, the axis of the trough is occupied by a 50 km long saline lake, the Salton Sea, which is surrounded by alluvial fans. This axial zone is also a zone of abnormally high heat flow, which has produced the Salton Sea geothermal field characterized by hot subsurface brines (300°C at 1.5 km depth) that have been explored for geothermal energy. These brines are saline chloride brines very rich in Ca, K, and the heavy metals Fe, Mn, Pb, and Zn, poor in Mg, and almost devoid of SO_4 (table 5). Drilling has shown that under an impermeable cap of 800 to 900 m of muddy sediment, a considerable volume of sandy sediments saturated by these brines has been hydrothermally altered to greenschist facies metamorphic rocks. The original sediments, composed of quartz + K-feldspar + plagioclase + smectite + illite + kaolinite + dolomite + calcite, have been converted to the mineral assemblage quartz + albite + chlorite + epidote + K-feldspar ± anhydrite, pyrite, chalcopyrite, sphene, hematite, and K-mica (Muffler and White, 1969). The conversion reaction, sediment + groundwater → "greenschist" + $CaCl_2$ brine, involves net exchange of Ca + K for Na + Mg, expressed in the rocks as albitization–chloritization–epidotization of the sediments and in the resulting hydrothermal waters as high concentrations of calcium and potassium but very low magnesium. The hyrothermal reaction responsible for generating the $CaCl_2$ brines of the Salton trough is, despite the different starting materials, analogous to the albitization–chloritization–epidotization of basalt that converts seawater to a $CaCl_2$ hydrothermal brine in M.O.R. rift zones (see above). The presence of anhydrite as a "sporadic mineral throughout the well" (Muffler and White, 1969, p. 168) suggests that the large amount of Ca released into the brine by the albitization reaction has combined with the SO_4 in the groundwater to form anhydrite. This, in turn, resulted in the brine being swept free of SO_4 while the concentration of Ca increased antipathetically in the manner outlined by Hardie (1983, p. 211) for the M.O.R. hydrothermal brines of Iceland (see also discussion of chemical divides in Hardie and Eugster, 1970; Drever, 1982; Hardie, 1987). Massive reduction of sulfate to sulfides is not required to explain the removal of sulfate.

On the basis of the isotopic composition of the Salton trough hot brines, White (1968, p. 313–316) has argued for meteoric waters from the nearby mountain ranges as the primary source waters (see also Craig, 1966). These groundwaters are presumed to circulate deep down into the Salton trough sedimentary pile where they dissolve buried evaporites before entering the geothermal zone (White, 1968, p. 313). Helgeson (1968) also called on meteoric waters as the source waters, but he suggested that the high salinity of the Salton hydrothermal brines was the result of subsurface boiling (see White, Muffler, and Truesdell, 1971; Ridge, 1974; Cathles, 1977; Sondergeld and Turcotte, 1979, for a discussion of boiling of hydrothermal waters). Despite the uncertainty about the process by which the Salton hot brines became saline, it is important to recognize that the Salton trough water-rock reaction as documented by Muffler and White (1969) demonstrates unequivocally that hydrothermal brines, rich in Ca and K and depleted in Mg and SO_4, can be generated by interaction of meteoric groundwaters with typical siliciclastic sediments over thermal anomalies in tectonically active continental basins. In attempting to explain the enigmatic $CaCl_2$ brines found in other closed basins where thermal anomalies exist today or may have existed in the past, this mechanism deserves serious consideration. Muffler and White (1969, p. 177) expressed the view that "mineral transformations similar to those observed in the Salton Trough should be taking place in other basins," but they acknowledged that such transformations may not be easily recognized because "many of the (altered) rocks of the Salton Sea geothermal field itself are not readily distinguished from ordinary sedimentary rocks." Perhaps many ancient hydrothermal systems of the Salton trough-type that generated $CaCl_2$ brines while they were thermally active may have gone unrecognized for this reason.

AN HYPOTHESIS FOR THE ORIGIN OF SULFATE-POOR POTASH DEPOSITS

The significance of hydrothermal $CaCl_2$ brine "factories" in rift and strike-slip zones to the problem of the origin of $MgSO_4$-poor potash evaporites is that these "factories" occur precisely in those tectonic basin settings most favorable to the deposition and accumulation of evaporites. In active tensional basins, then, it is possible that subsurface $CaCl_2$ hydrothermal brines might escape through appropriate conduits to the surface where they can contribute their unusual combination of solutes to the lake waters or seawater evaporating on the floor of the basin (Hardie, 1978). It is this connection that constitutes the essence of the explanation for the origin of sulfate-poor potash evaporites offered in this paper.

Clues from the Holocene

Modern arid closed basins are characterized by inflow waters that display a wide range of compositions derived from a variety of sources (Jones, 1966; Jones and VanDenburgh, 1966; Hardie and Eugster, 1970; Eugster and Hardie, 1978; Hardie, 1984). In any one basin the final lake or playa brine is a blend of waters from different sources, and this is true also for modern marine sabkhas (Patterson and Kinsman, 1977; Pierre, Ortlieb, and Person, 1984; Hardie, 1984, 1987). Some of these modern closed basins are notable for their saline lakes or salt pans in which the evaporating brines are $CaCl_2$-rich, for example, Bristol Dry Lake and Cadiz Lake (California), the Dead Sea, the Danakil Depression (Ethiopia), Lake Assal (Afar-Issas, Africa), Ushtagan Lake (Kazakhstan, Russia), and the Qaidam basin (China) (see brine analyses in table 6). In many of these basins it can be demonstrated that the main sources of the $CaCl_2$ component of the surface brines are upwelling subsurface $CaCl_2$ hydrothermal brines or basinal brines (saline formation waters) as is outlined in the following brief descriptions of several modern, active saline lake systems, characterized by $CaCl_2$ brines.

Bristol Dry Lake and Cadiz Lake.—Just north of the Salton Sea in southern California are the Bristol Dry Lake and Cadiz Lake basins floored by halite saline pans (Handford, 1982; Lowenstein and Hardie, 1985) in which $CaCl_2$ brines are evaporating. The chemical signature of these brines is very similar to that of the Salton trough and M.O.R. hydrothermal brines, that is, they are very rich in $CaCl_2$, very poor in SO_4 and Mg, but with sufficient K to put them in the sylvite field (table 6 and fig. 4). Thus, it is most likely that the principal sources of solutes for these continental evaporite systems are Salton trough-type hydrothermal groundwaters.

The Dead Sea.—The Dead Sea is a well-known example of a modern saline lake characterized by $CaCl_2$-rich brines (table 7) in a narrow fault-bounded basin. It has no direct connection to the sea, and its brines result from evaporative concentration of non-marine inflow waters from a number of sources, in particular, perennial rivers (the Jordan and Arnon Rivers), ephemeral floodwater channeled in wadis, and dilute

TABLE 6

Chemical compositions of some modern $CaCl_2$ saline lake brines

	1	2	3	4	5	6	7	8	9	10
	BRISTOL DRY LAKE, CALIF.	CADIZ LAKE, CALIF.	USHTAGAN LAKE, U.S.S.R.	NAMIB DESERT, S.W.AFRICA	DALLOL SALT PAN, DANAKIL	L.GUILIETTI DANAKIL, ETHIOPIA	LAKE ASSAL, AFARS-ISSAS, N.E. AFRICA			
							open lake, N.E. area	open lake, N.W. area	salt pan, N.E. edge	salt pan, N.W. edge
	ppm	ppm	ppm	ppm	ppm	mg/l	mg/l	mg/l	mg/l	mg/l
SiO_2				46						
Ca	43300	4504	39,673	27,500	23,290	15,400	8310	9200	8950	8980
Mg	1070	412	11,336	15,900	16,570	910	6760	1446	4480	10,500
Na	57,400	22,603	45,867	75,200	46,020	44,400	50,300	26,300	40,200	80,000
K	3300	1038	1343	8000	8860	2770	3100	2220	2420	3970
HCO_3			690	340			52	34		
SO_4	210	280	797	568	0	1150	860	190	1000	860
Cl	173,000	44,764	173,794	200,000	168,560	94,200	113,600	67,450	110,050	169,925
TOTAL	279,000	73,600	273,500	350,000	263,300	158,830	182,982+	106,840+	167,100+	274,235+
pH							6.2	6.1	6.2	6.4
TEMP			21.5°C		"ambient"					
DEPTH	surface	surface	surface		surface	surface	surface	surface	surface	surface

<u>Sources of data</u>: 1, 2 - ver Planck (1958); 3 - Posohov (1949); 4 - Cagle and Cruft (1970); 5 - Holwerda and Hutchinson (1968); 6 - Martini (1969), Bonatti and others, (1972); 7, 8, 9,10 - Valette (1975)

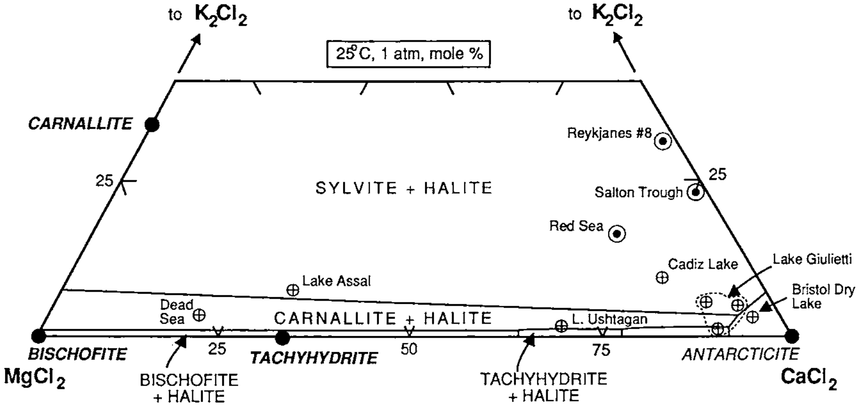

Fig. 4. Phase relations in the system $CaCl_2$–$MgCl_2$–KCl–NaCl–H_2O at halite saturation, 25 °C, and 1 atm total pressure (based on data of D'Ans, 1933, p. 190). Composition of modern saline lake brines and M.O.R. hydrothermal brines are plotted as per the legend on the diagram.

and saline springs (Bentor, 1961; Mazor, 1962). Most of the water that sustains the Dead Sea as a deep (400 m) perennial lake is supplied by the Jordan River (75 percent), but the bulk of the solutes in the lake brines are added by saline springs (70 percent) that upwell around and beneath the lake (Bentor, 1961; Mazor, 1962). These saline springs, for example,

TABLE 7

Chemical compositions of waters of the Dead Sea (mg / l)

	1	2	3	4	5	6
	Upper Layer DEAD SEA (1959)	Lower Layer DEAD SEA (1959)	Mt. SDOM SPRINGS	SDOM I WELL	ZOHAR SPRINGS	JORDAN R. near the mouth (annual avg)
SiO_2	12	< 10				
Ca	16,380	17,180	48,010	82,865	2986	129
Mg	36,150	42,430	45,650	19,765	6323	95
Na	38,510	39,700	14,390	20,515	8115	224
K	6500	7590	14,720	28,730	787	32
HCO_3	230	220		trace	91	181
SO_4	580	420	58	108	752	97
Cl	196,940	219,250	255,530	265,150	36,660	762
Br	4600	5270	3060	2985	810	9
TOTAL	299,890	332,060	381,418	420,118	56,524	1529
pH	6.4	6.2				
TEMP	19 - 35°C	21.7°C				
DEPTH	0 - 40 m	100 - 400 m	surface	several 100 m	surface	surface
ΔCa *	+801.52	+844.94	+2394.5	+4132.74	+131.86	+1.45

Sources of data : 1, 2, 6 - Neev and Emery (1964); 3, 4 - Bentor (1969); 5 - Bentor (1961).

* $\Delta Ca = mCa^{2+} - mSO_4{}^{2-} - mCO_3{}^{2-} - 1/2\ mHCO_3{}^{-}$ and is a measure of whether the water is a $CaCl_2$ water (+ value) or not (- value).

TABLE 8

Chemical compositions of waters of the Lake Tiberias area, northern Dead Sea graben (mg / l)

	1 JORDAN R. 20 Km north of the lake	2 JORDAN R. outlet of the lake	3 LAKE TIBERIAS	4 TIBERIAS HOT SPRINGS	5 TIBERIAS HOT SPRINGS	6 FULIYA SPRINGS	7 TANNUR SPRINGS	8 TABHA SPRINGS
SiO_2				23				
Ca	65	50	63	3930	3501	151	364	223
Mg	16	31	6	825	584		105	49
Na	11	153	131	6910	6915	496	978	523
K			7	77	295	12.5	27	5
HCO_3	207	109		366	162	143	240	127
SO_4	46	48	34.5	891	734	128	173	93
Cl	19	318	283	19,200	18,016	1042	2231	1210
Br			2.35	1.4	246	7.1	20.5	11.8
TOTAL	350	730	507	32,300	30,453	1977	4139	2242
TEMP				61.9°C				
DEPTH	surface	surface	surface	surface	surface	surface	surface	surface
ΔCa *	-1.11	-0.29		+171.59	+156.76	+2.54	+10.63	+7.10

Sources of data : 1, 2 - Mazor (1962); 3, 5, 6, 7, 8 - Bentor (1961); 4 - White, Hem, and Waring (1963).

* $\Delta Ca = mCa^{2+} - mSO_4{}^{2-} - mCO_3{}^{2-} - 1/2\ mHCO_3{}^{-}$ and is a measure of whether the water is a $CaCl_2$ water (+ value) or not (- value).

Zohar and Sdom springs (table 7), are $CaCl_2$ brines, and it is their calcium-rich sulfate-poor chemical signature that is inherited by the present evaporating lake brines. However, even the Jordan River itself derives much of its water and dissolved solutes from $CaCl_2$ spring waters. These include *hot* springs that discharge into Lake Tiberias (the Sea of Galilee) through which the Jordan passes some 100 km north of the Dead Sea. Here, in a region noted for volcanic activity in sub-Recent times, the Tiberias Hot Springs and the Fuliya, Tabha, and Tannur Springs (table 8) rise through Tertiary and Pleistocene basalts. These $CaCl_2$ spring waters turn the Sea of Galilee and the outflowing Jordan river into NaCl waters in which Ca essentially balances HCO_3 + SO_4 (table 8). Thus, the Dead Sea basin stands as a clear-cut case of a

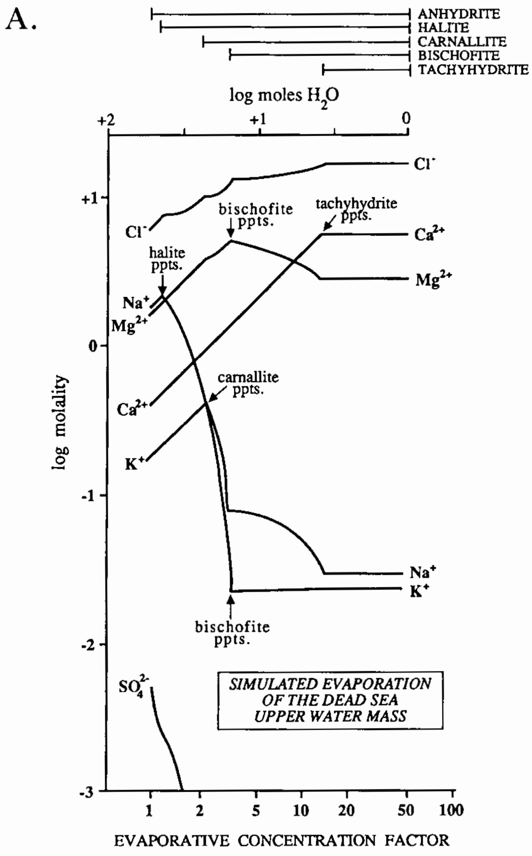

Fig. 5. Evaporative concentration of the Dead Sea brine (Upper Water Mass, Neev and Emery, 1967, table 6) simulated using the computer program of Harvie and Weare (1980). (A) Changes in major ion concentrations in the brine.

non-marine evaporite depositional site where the evaporating brines are $CaCl_2$-rich and SO_4-poor because the inflow-waters are $CaCl_2$-rich and SO_4-poor. The Dead Sea has been co-precipitating aragonite and gypsum for a considerable period from the Upper Water Mass (Neev and Emery, 1967) while the Lower Water Mass has remained at or near halite saturation (Lerman, 1967). But recently the inflow from the Jordan River has decreased (a man-made condition), and if this continues then evaporative concentration will lead to drawdown and precipitation of halite → halite + carnallite → halite + carnallite + bischofite → halite + carnallite + bischofite + tachyhydrite (fig. 5; see also, Lerman, 1967, fig. 3). In other words, a primary $MgSO_4$-free potash deposit of *non-marine origin* will be formed in a narrow fault-bounded basin fed by $CaCl_2$-rich source waters. The question that remains is the origin of the $CaCl_2$ signature of these source waters. Both Mazor (1962) and Bentor (1969) have called on recycling of fossil brines stored in groundwater reservoirs. Drilling has revealed the existence of

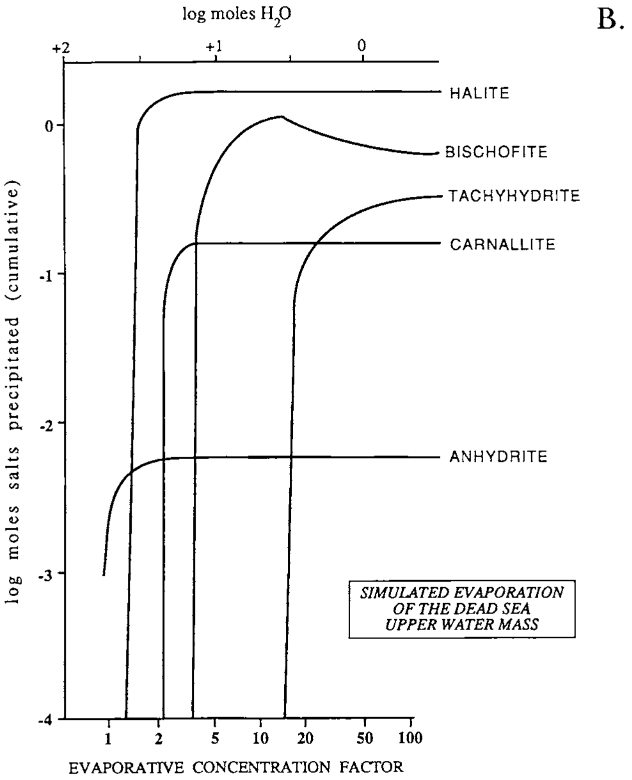

Fig. 5 (continued) (B) Cumulative masses of minerals precipitated (initial brine contained 1 kg of H_2O).

very saline brines, rich in $CaCl_2$ and poor in $MgSO_4$, at depths of 1000 to 3000 m in Lower Cambrian to Lower Cretaceous rocks throughout the Dead Sea region (Bentor, 1969). Bentor (1969) suggested that these subsurface $CaCl_2$ brines "represent Early Paleozoic evaporation brines, which have later been modified by ultrafiltration" and which flowed in the subsurface from the highlands into the downdropped bedrock and sediment fill of the Dead Sea rift as the axial trough subsided in post-Cretaceous times. He further suggested that these transported fossil brines then leaked into the "various Plio-Pleistocene Rift Valley lakes, such as Sodom, Gomorrah, and Lisan Lakes which preceded the present Dead Sea" (Bentor, 1969, p. 103). There they evaporated to produce the >3.6 km of salt carrying minor sylvite, carnallite, and $CaCl_2$ salts (Zak, 1974) that underly the Dead Sea rift axis (Neev and Emery, 1967; Zak and Bentor, 1972; Zak, 1974). In turn, these Plio-Pleistocene evaporite brines, exceedingly rich in $CaCl_2$ (see table 7, Sdom I well), are now seeping into the rift as very saline $CaCl_2$ brine spings that supply the bulk of the solutes to the present day Dead Sea lake. In this regard, Bentor (1961) reported that when the Sdom I well penetrated the halite beds beneath impermeable shales at a depth of a few hundred meters, the fluid pressure was enough to cause very saline $CaCl_2$ brines (over 400,000 mg/l) saturated with respect to halite + sylvite (Lerman, 1967, table 8) to rise up the drillhole to the surface. Although not discussed by Bentor (1969), hydrothermal circulation of groundwater must have played a significant role in the hydrologic history of the Dead Sea-Jordan rift to judge by the masses of Tertiary to Pleistocene basalts at the northern end of the rift (see Bentor, 1961, fig. 1; Barbieri, Santacroce, and Varet, 1982, fig. 8). The hot springs in this area that are discharging into Lake Tiberias today are testimony to the ongoing geothermal groundwater activity in the rift. These springs, with chlorinities at or below that of seawater, are $CaCl_2$ waters (table 8) with high Ca/Na ratios that suggest an origin by a hydrothermal albitization mechanism in the manner of the Salton trough sediment-groundwater interaction or M.O.R. basalt-seawater interaction. It is possible, indeed likely, that such hydrothermal activity was more copious in the earlier history of the rift than it is today and produced the $CaCl_2$ inflow waters from which the buried evaporites and their interstitial brines originally were formed. In any event, it is manifest that the Dead Sea basin has been a site for the accumulation of non-marine $CaCl_2$ brines and the very thick salt deposits formed from them, for a considerable part of its history as a subsiding strike-slip basin.

Danakil Depression.—Intense hydrothermal activity related to magmatism characterizes the axial zone of the Afar rift in Ethiopia (Holwerda and Hutchinson, 1968; Marinelli, 1971; Bonatti and others, 1972) at the triple junction of the East African, Red Sea, and Carlsberg rifts. Hot springs rich in $CaCl_2$ supply and maintain brine pools and saline lakes in the Danakil Depression within the Afar triangle (table 6). Lake Giulietti (70 km^2 in area, >100 m in depth), the largest of the saline lakes, is located within the active volcanic field of the northern Danakil (Erta'Ale range, Barbieri and others, 1970, figs. 1–3). Both the inflowing hot spring waters (40°–50°C) (table 5) and the brines of the lake itself are rich in $CaCl_2$ and poor in $MgSO_4$ (table 6, see also Martini, 1969), and extensive evaporative concentration of the saline lake must lead eventually to deposition of an $MgSO_4$-poor potash evaporite composed of halite, sylvite, carnallite, and $CaCl_2$ minerals (fig. 4). The inflow waters have the high Ca/Na and very low Mg and SO_4 signatures of M.O.R. and Salton trough hydrothermal waters, although, like the brines of Bristol Dry Lake and Cadiz Lake, they are relatively low in K (fig. 4). Thick Pleistocene evaporites underline the northern part of the Danakil Depression, but these evaporites, except for the upper sylvite zone, are $MgSO_4$ rich (Holwerda and Hutchinson, 1968), and thus the Lake Giulietti waters cannot have derived their $CaCl_2$-rich $MgSO_4$-poor composition through dissolution of these buried Pleistocene deposits. Interaction between hot groundwaters and the volcanic bedrock seems to be the most likely origin. Nonetheless, at the northern end of the Danakil Depression in the Dallol salt pan, upwelling springs rich in $MgCl_2$ and KCl in addition to $CaCl_2$ (table 6; see also Holwerda and Hutchinson, 1968, p. 130–132) point strongly to dissolution of the underlying potash evaporites (which, in places, outcrop in surrounding uplands) or to recycling of the original brines of these evaporites. One hot brine spring, the Black Mountain spring, discharges at 130°C almost pure $MgCl_2$ brine (2 percent KCl, 1 percent NaCl), which, on evaporation, precipitates sylvite and carnallite. During World War I the large quantities of these KCl minerals that had been deposited from this flowing brine spring were a major source of potash for the Allied Powers (Holwerda and Hutchinson, 1968, p. 126). Other hot brine springs in this geothermally active region around the Dallol salt pan are rich in $FeCl_2$ (Marinelli, 1971), sulfur, and manganese (Holwerda and Hutchinson, 1968, p. 130–132), which clearly indicates significant interaction of hot groundwaters with the volcanic bedrock. Another agency for adding solutes to the Dallol salt pan is flash flooding, which produces alternating layers of halite and mud (Holwerda and Hutchinson, 1968, p. 129) characteristic features of all ephemeral salt pans (Lowenstein and Hardie, 1985). In the Dallol region of the Afar rift, then, a complex mix of inflow waters which includes hydrothermal brines is yielding a modern non-marine salt deposit that carries sylvite and carnallite in the absence of $MgSO_4$ salts.

Lake Assal.—Lake Assal is a small $CaCl_2$ saline lake in the French Territory of Afars-Issas between Ethiopia and Somaliland. It lies in the active graben that extends from the Gulf of Tadjoura into the Afar triangle. The lake is 54 km^2 in area with a maximum depth of 21 m and is bordered to the northeast by a 60 km^2 salt flat covered with a thick halite-gypsum crust (Valette, 1975, fig. 3). Subaqueous "banks" of large gypsum crystals occur within the open lake. Lake Assal is fed by numerous hot springs (40°–80°C) located around the perimeter of the lake. Lake waters and groundwaters in the immediate vicinity of these hot springs are concentrated $CaCl_2$ brines low in sulfate and bicarbonate (table 6). Along the southeast shore, closest to the Gulf of Tadjoura (the Goubet el Kharab is only 10 km away), the waters of Lake Assal carry the highest sulfate and bicarbonate concentrations and the lowest calcium, measured by Valette (1975), table 1). Seawater from the Goubet el Kharab apparently moves in the subsurface through the bedrock and into Lake Assal (Langguth and Pouchan, 1976, fig. 5). In transit the deeper circulating seawater becomes heated and presumably reacts with the basaltic bedrock before surfacing around the lake edge as hot $CaCl_2$ brine springs like those of the Mid Ocean Ridge hydrothermal systems. Mixing of the $CaCl_2$-bearing hot spring waters with cooler less altered seawater springs, together with evaporative concentration has led to massive precipitation and bottom growth of gypsum and has produced the high salinity and $CaCl_2$-enriched composition of the brines of the present open lake (table 6).

Qaidam Basin.—A continental basin where $MgSO_4$-free potash evaporites are forming today, and which is almost as remote from the sea as it is possible to get, is the huge (150,000 km^2) Qaidam (or Chaidam) basin that stands in the interior highlands of China at an elevation of 2000 to 3000 m above sealevel. This extensional basin was downdropped between the Kunlun and Altyn Tagh strike-slip faults (Molnar, Tapponnier, and Chen, 1981, fig. 1). The floor of this arid interior basin is covered by a 6000 km^2 salt pan which carries Holocene potash deposits composed of halite and carnallite (Valyashko, 1972b; Yuan, Chenguy, and Keqin, 1983; Chen Kezao and Bowler, 1986). The origin of these important potash deposits is presently under study by T. K. Lowenstein and R. J. Spencer and their preliminary work indicates upwelling $CaCl_2$ brines (saline formation waters) as a major source of solutes (personal commun.). Thus, Qaidam, a remote interior basin, contains a modern, *non-marine potash deposit* free of $MgSO_4$ salts in a tectonic basin which rivals or exceeds the size of those in which many ancient potash evaporites in the geologic record were deposited.

In summary, the direct connection between upwelling $CaCl_2$ brines that discharge at the surface within arid closed basins and the formation of $MgSO_4$-poor potash evaporites can be documented in modern, active rift and strike-slip systems. These Holocene examples provide the basis for a working hypothesis for the origin of ancient $MgSO_4$-poor potash evaporites.

A Working Hypothesis

It is proposed as a working hypothesis that ancient $MgSO_4$-poor potash evaporites deposited in continental rift or strike-slip basins owe their non-marine chemical signature to $CaCl_2$ inflow waters of hydrothermal origin (fig. 6). Included in this category of waters are $CaCl_2$ basinal brines (saline formation waters, oil field brines) which have been

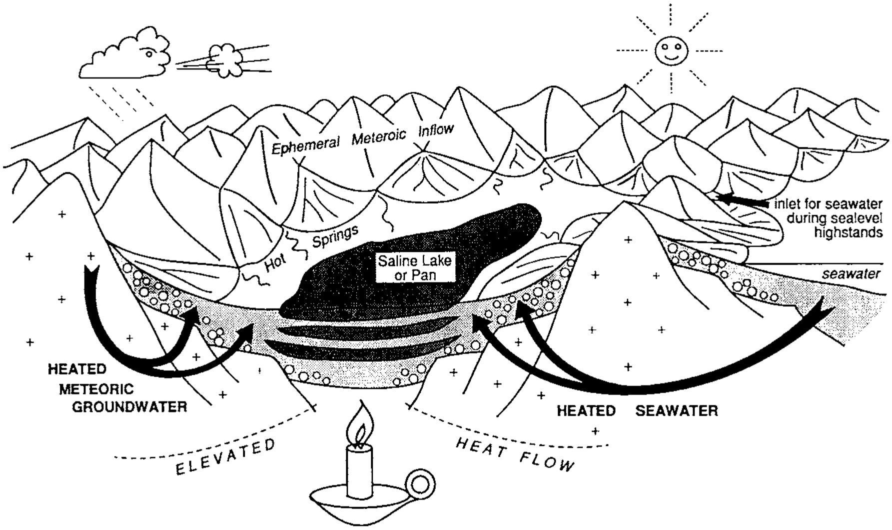

Fig. 6. Cartoon illustrating the hypothesis of the hydrothermal brine origin of $MgSO_4$-poor potash evaporites proposed in this paper.

recirculated by free (thermal) or forced (gravitational) convection (see below).

The fault basin that served as the evaporite depocenter could have been remote from the sea and thus have been entirely non-marine (as is the present day Qaidam basin). Or it could have been a marginal marine basin which on occasions was flooded with seawater (as happened in the Danakil Depression during the Pleistocene) or into which seawater leaked more or less continually (no modern examples have been described). But in all cases it is postulated that upwelling hydrothermal $CaCl_2$ brines or cooler basinal $CaCl_2$ brines mixing with surfaces waters were responsible for the $MgSO_4$-poor composition of the resulting potash evaporites.

Discussion of Some Particular Aspects of the Hypothesis

1. A subsurface brine is considered to be a *hydrothermal brine* when it is at a temperature significantly higher than that expected from a purely conductive thermal regime. Such hydrothermal brines are generated by upward fluid circulation driven by either free or forced convection (Freeze and Cherry, 1979) and hence are highly effective not only as mass transfer agents for dissolved solutes but also as thermal catalysts for chemical reaction of these solutes with the host bedrock. It is this hydrothermal process that produces the $CaCl_2$ signature of hydrothermal brines, as discussed earlier. *Basinal brines* (formation waters, oil field

brines), on the other hand, are in equilibrium with the conductive thermal field of the basin and typically are static or moving only sluggishly (Freeze and Cherry, 1979). Such basinal brines can be advected upward by forced convection due to changes in topographic gradients (Garven, 1985) or by fluid density-instabilities due to changes in the local thermal regime (free convection) (see Elder, 1967). In both cases the rising basinal brines become active hydrothermal brines.

In extensional fault basins the most dramatic trigger for hydrothermal circulation is magmatic intrusion beneath the basin. These intrusions provide the energy to heat the existing groundwaters, to drive the convection cells, and to promote the hydrothermal reactions with the bedrock (Stefánsson and Björnsson, 1982; Morgan, 1982). Such hydrothermal activity, because of its effectiveness as a heat transfer mechanism, will rapidly cool down the pluton heat source (Cathles, 1977; Norton and Knight, 1977) and so generally will have a relatively short lifespan of 10^4 to 10^5 yrs (Stefánsson and Björnsson, 1982). However, continental rift systems are notable for the episodic nature of their magmatism and faulting which recur over an extended period that covers tens of millions of years (Mohr, 1982). Thus, hydrothermal activity almost certainly will also be episodic but operative over a substantial part of the long history of an active continental rift basin. As a consequence, evaporite deposits influenced by hydrothermal inflow waters may punctuate a substantial part of the thick stratigraphic record of a continental rift. But $CaCl_2$ brines may also be circulated during periods when thermal activity is at its lowest ebb. At these times the subsurface hydrothermal brines will have cooled to ambient subsurface temperature and become basinal brines (formation waters) moving only sluggishly below the active meteoric groundwater zone. However, if faulting or load-induced subsidence alters the groundwater topography sufficiently, then these $CaCl_2$ formation waters may be driven to the surface by gravity (forced convection), as appears to be happening today in the Dead Sea trough.

2. In the present hypothesis there are several different pathways by which the parent brines for $MgSO_4$- poor potash deposits could have evolved. These are summarized in figure 7. Some of the steps in these pathways need explanation. The critical step in all the pathways is the *calcium-enrichment* that is a consequence of bedrock-groundwater interaction at zeolite, greenschist, or amphibolite facies temperatures. It is the essential geochemical aspect of the evolution of $CaCl_2$ waters. Subsurface $CaCl_2$ brines may have originated as marine groundwaters (Hardie, 1983), as meteoric groundwaters that dissolved buried evaporites (Land and Presbindowski, 1982), or as the residual brines of evaporites (Carpenter, 1978; Spencer, 1987), but whatever their original state it is postulated that their $CaCl_2$ chemical character was imparted as a result of interaction with bedrock at elevated temperatures, that is, they are all of hydrothermal origin. If the bedrock is basaltic, then albitization of plagioclase releases large amounts of Ca^{2+},

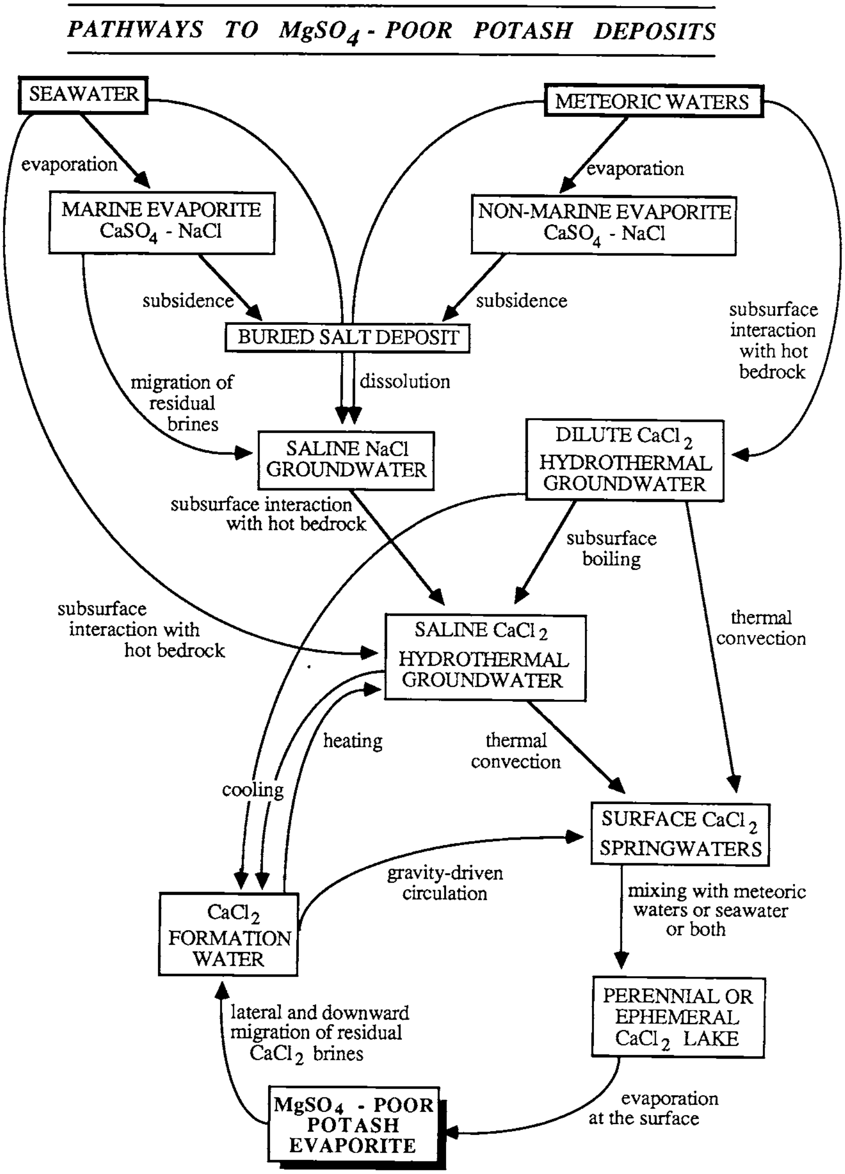

Fig. 7. Postulated hydrological-chemical pathways in the genesis of $MgSO_4$-poor potash evaporites.

which in turn combines with SO_4^{2-} to precipitate anhydrite and with HCO_3^- to precipitate calcite in the subsurface in fractures or intergranular pores as cements (Hardie, 1983). Clearly, if enough calcium is released by albitization then the resulting water will not only become Ca-rich but, most significantly, will be swept almost free of sulfate and bicarbonate, leaving Cl as the dominant anion. In this way even meteoric waters initially richer in sulfate and bicarbonate than in chloride could evolve in the subsurface into chloride waters. Seawater, although a chloride water, must go through the same $Na \rightleftharpoons Ca$ interactions if it is to be converted to a $CaCl_2$ brine (Hardie, 1983). So, too, must subsurface NaCl brines that are residual brines of marine evaporites (Carpenter, 1978; Spencer, 1987) or are the result of dissolution of buried anhydrite-halite deposits (Land and Presbindowski, 1982). In the latter case, simple dissolution of anhydrite (or gypsum) and halite by meteoric waters or seawater cannot produce a $CaCl_2$ brine because these minerals dissolve congruently (that is, Ca^{2+} and SO_4^{2-} are added in *equal* molar proportions, and likewise for Na^+ and Cl^-). Similar Ca-enrichment with similar consequences will follow from interactions between hot groundwater and siliciclastic sediments, as the modern Salton trough system demonstrates (see above). If the arkoses carry plagioclase, then, as for basalts, albitization will be a primary source of calcium. But calcium will also be released by chloritization of calcium smectites in red siltstones and shales. When carbonate sediments are present then dolomitization, if it can proceed, will release Ca^{2+} to the groundwaters. At the elevated temperatures of the hydrothermal regime the kinetic factors are favorable for dolomitization (Hardie, 1987), and high Ca/Mg ratios can be generated in the reacting hot groundwaters.

Seawater, with its relatively high potassium concentration compared to most meteoric waters, is generally assumed to be the only viable source for potash evaporites. But potassium concentration in modern hydrothermal brines can be extremely high (tables 4 and 5), and much higher proportions of potash minerals to other salts are possible from evaporation of such hydrothermal inflow waters than from seawater. The source of K^+ for the hydrothermal waters is the reacting bedrock. In basalt-hot seawater interaction beneath mid-ocean ridges, almost all the potassium in the basalt is released to the fluid phase (Thompson, 1983; Hardie, 1983), an exchange duplicated in hydrothermal experiments (Thompson, 1983). Basalts and other volcanics of continental extensional basins are even higher in K_2O than M.O.R. basalts (Barbieri, Santacroce, and Varet, 1982), and so hydrothermal waters that have reacted with volcanics in continental rifts and strike-slip systems can be relatively rich in potassium. But high concentrations of K^+ can also result from hydrothermal reactions involving the siliciclastic sediments of extensional basins. Potassium feldspar in arkoses can contribute K^+ to the fluid by direct dissolution at elevated temperatures (Mahon, 1967) or perhaps by alteration to sericite. Considerable amounts of potassium can be released by smectites and illites in red siltstones and shales when they are hydrothermally altered to chlorite.

Sodium and magnesium concentrations in the fluid are also strongly influenced by the hydrothermal interactions. Albitization takes Na^+ and chloritization takes Mg^{2+} from the fluid, so that the resulting hydrothermal waters can have considerably higher values of the ratio (Ca + K)/(Na + Mg) than that of seawater, a characteristic that in combination with the low SO_4^{2-} concentrations favors the precipitation of sylvite (KCl) before carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) from such brines evaporating at the surface at sedimentary temperatures. In addition, such a chemical signature also favors the precipitation of tachyhydrite ($CaCl_2 \cdot MgCl_2 \cdot 12H_2O$) before bishofite ($MgCl_2 \cdot 6H_2O$) in the final stages of evaporative concentration. In contrast, hydrothermal brines rich in $MgCl_2$ (for example analysis 5, table 6) must have originated as late stage bitterns of primary evaporites or, perhaps, were formed by dissolution of buried carnallite-bearing evaporites (fig. 7).

3. Surface expression of the magmatism that powers the hydrothermal systems in extensional basins is basaltic volcanism (Sengor and Burke, 1978; Barbieri, Santacroce, and Varet, 1982; Williams, 1982; Martin and Piwinskii, 1972; many papers in Ramberg and Neumann, 1977; et cetera), although in some strike-slip basins volcanism may be completely absent (Mitchell and Reading, 1986). The range of lava compositions varies widely, with "low volcanicity" rifts being characterized by basic lavas with high K/Na + K ratios while "high volcanicity" rifts show a biomodal distribution of basic and acidic lavas (Barbieri, Santacroce, and Varet, 1982). Ancient potash evaporites formed from brines with a hydrothermal component, then, are most likely to be found in rift and strike-slip basins that carry such volcanics or volcaniclastics.

4. A special manifestation of hydrothermal circulation of $CaCl_2$ brines in rift and strike-slip basins is Pb, Zn, Cu, Fe, Mn, and barite mineralization in fault-related fractures and in permeable rift sediments (Mitchell and Garson, 1976; Sawkins, 1982), or, most spectacularly, as stratiform ores where hydrothermal brines vent directly through the floor of the rift into standing water, as in the Red Sea (Degens and Ross, 1969). A more subtle expression of the latter phenomenon is the high Pb concentration in the bottom sediments of modern Lake Kivi in the East African rift (Degens and Kulbicki, 1973). In the scenario envisaged for the hydrothermal brine origin of $MgSO_4$-poor evaporites, some form of this base metal mineralization might be expected to occur within the sedimentary fill or in the faulted margins of the rift or strike-slip basin where the evaporites accumulated (as in the Danakil Depression, Bonatti and others, 1972). A less obvious indication of the contribution of heavy metal-bearing hydrothermal waters to the brines from which $MgSO_4$-poor potash deposits precipitated might be seen in higher than average concentrations of Pb, Zn, Cu, Fe, Mn, et cetera, in the saline

minerals themselves, as, for example, the 10,300 ppm Fe, 150 ppm Mn, 14 ppm Cu, and 5.2 ppm Pb values exhibited by the anhydrite of the Pennsylvanian Paradox basin evaporites (Stewart, 1963, table 23; Dean, 1978, table 5.3).

5. The extent to which upwelling $CaCl_2$ brines can influence the composition of the lake (or lagoon) brines from which the salts will ultimately precipitate depends, of course, on the flux of upwelling $CaCl_2$ brine relative to the fluxes of other inflow waters. To produce potash evaporites free of $MgSO_4$ salts by mixing of inflow waters, upwelling $CaCl_2$ brine must be added to the overall inflow system in sufficient proportion to bring mCa^{2+} above $mSO_4^{2-} + 1/2mHCO_3^- + mCO_3^{2-}$. For example, if the ambient surface water is normal seawater, then only 3 parts of Salton trough hydrothermal brine would be needed to convert 100 parts of seawater into a $CaCl_2$ brine (see fig. 8). On evaporative concentration gypsum precipitation would quantitatively remove sulfate (fig. 9B), and the resulting salt deposit would be characterized by various assemblages involving halite, sylvite, carnallite, and bischofite. If the contribution of Salton trough-type hydrothermal brine was raised to only 5 parts per 100 parts of seawater, then the $CaCl_2$ mineral *tachyhy-*

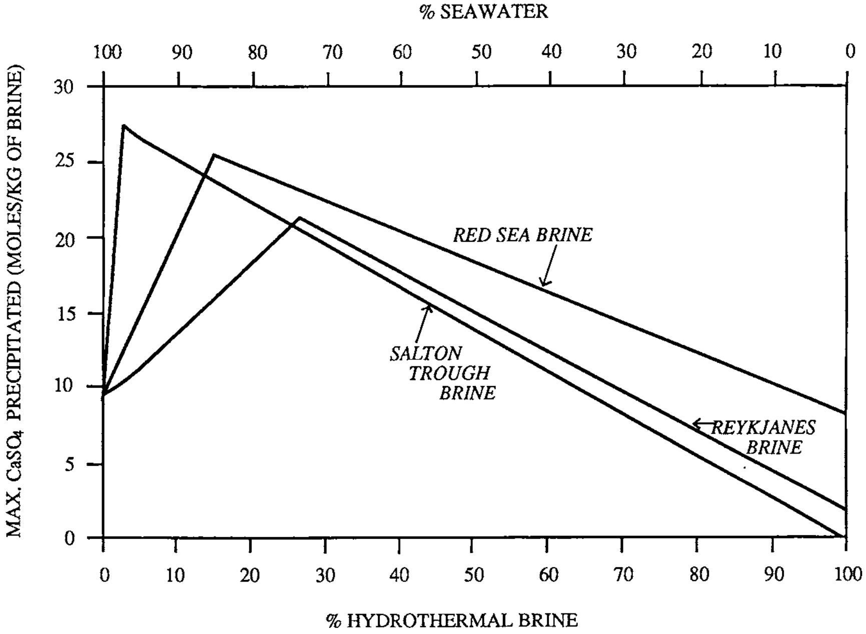

Fig. 8. Calculated curves showing the *maximum* amount of $CaSO_4$ that can be precipitated from mixtures of modern seawater and some $CaCl_2$ hydrothermal brines of modern rift and strike-slip systems.

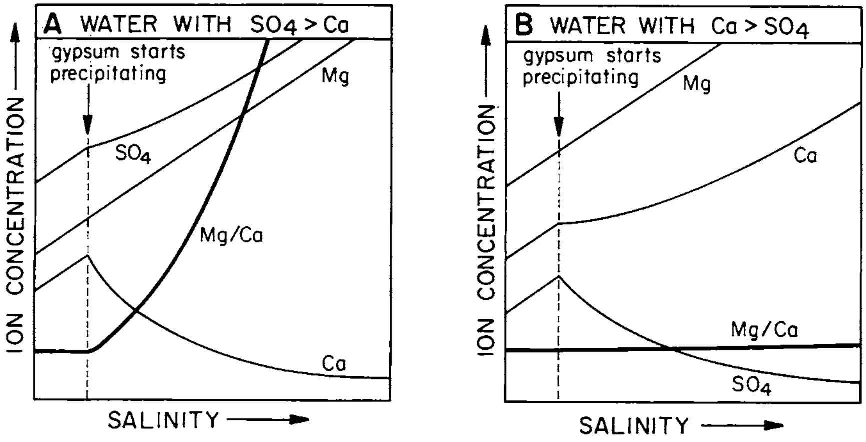

Fig. 9. Hypothetical chemical trends of Ca, Mg, SO_4 concentrations and Mg/Ca ratio as chloride brines are progressively evaporated into the gypsum field. (A) For a water with $SO_4 > Ca$, gypsum precipitation leads to a progressive increase in SO_4/Ca ratio and hence a steep rise in Mg/Ca ratio, as predicted quantitatively for seawater evaporation (Hardie, 1984, fig. 3B). (B) For a water with $Ca > SO_4$, such as a calcium chloride brine, gypsum precipitation leads to a progressive increase in Ca/SO_4 ratio (Hardie and Eugster, 1970), and hence there is little change in Mg/Ca ratio. From Hardie (1987).

drite would be a primary precipitate along with halite, sylvite, and carnallite. This latter suite, high-lighted by tachyhydrite, is exactly that of the Cretaceous potash deposits of the Sergipe and Gabon-Congo rift basins (see above) as well as the Thailand basin. But because closed basins can, and do, have a variety of inflow waters, a host of mixes involving upwelling $CaCl_2$ hydrothermal brines is possible. In continental basins not connected in any way with the sea, mixing will be restricted entirely to non-marine waters, but as long as the final blend is a $CaCl_2$ water the final salt deposit will be composed of some combination of halite, sylvite, carnallite, bischofite, tachyhydrite, and antarcticite (or other $CaCl_2$ hydrate) in the system $NaCl\text{-}KCl\text{-}MgCl_2\text{-}CaCl_2\text{-}H_2O$ (fig. 4). Gypsum (or anhydrite) and carbonates may precipitate depending on the initial amounts of sulfate and bicarbonate ions in the brine before evaporative concentration.

6. The temporal and spatial distribution of saline minerals deposited in any evaporite basin depends to a significant degree on the physical conditions that existed during evaporative concentration. Of particular consequence is whether the system was perennial or ephemeral during evaporite deposition. An ephemeral system starts out as a temporary, shallow brine body that shrinks in diameter as the brine concentrates by evaporation before ultimately drying up to become a saline pan (see Lowenstein and Hardie, 1985, for a discussion of the saline pan cycle). In such shallow ephemeral systems both the brine compositions and the distribution of minerals are profoundly influenced

by: (1) syndepositional recycling of the most soluble phases (Hardie, 1984), (2) lateral migration of precipitation sites as the surface brine volume dwindles during the temporary saline lake stage, (3) fractional crystallization of inflowing groundwaters in the subsurface during dry saline pan conditions (Hardie, 1968), and (4) diagenetic modification of earlier deposited salts by late stage bitterns in the shallow subsurface during the desiccation stage (precipitation of cements, alteration or replacement of primary precipitates, polygonal disruption of cemented crusts, et cetera, see Lowenstein and Hardie, 1985).

It is necessary, therefore, to look at the possible role that saline pan conditions may play in determining the composition of the late stage potash facies. Consider a marginal marine basin in an arid climate being cut off temporarily from the sea by a eustatic sealevel drop or by tectonic movements, and then undergoing evaporative drawdown profound enough to reach very shallow perennial saline lake pan conditions. At drawdown rates of 1 to 2 m/yr, as is occurring today in Walker Lake (Nevada) and Mono Lake (California) due to man-made diversions of the inflow streams, it would not take long to achieve such conditions even in basins that originally contained 1 or 2 km of water. The result would be the transformation of a deepwater marine basin into a shallow non-marine saline pan fed by non-marine inflow waters. If these non-marine inflow waters were dominated by upwelling hydrothermal or basinal brines of $CaCl_2$ composition, then the residual seawater bitterns soon would be altered to $MgSO_4$-poor brines, as discussed earlier. In this way the basal saline facies of the evaporite deposit would be *marine* (carbonates → sulfates → halite), but the potash cap would be *non-marine.* Many potash-bearing evaporite cycles throughout the geologic record could be most satisfactorily accounted for by this hybrid basin model, even some of the Permian and Neogene-Quaternary $MgSO_4$-rich potash deposits that carry terminal KCl zones poor in $MgSO_4$ salts (for example, cycles 1, 3, and 4 of the Zechstein, the Permian Salado Formation, and Pleistocene of the Danakil Depression). An analogous hydrologic history for completely non-marine arid basins would result in a depositional cycle of deep water saline lake evaporites (bituminous carbonate → laminated gypsum/anhydrite → cumulate halite) capped by saline pan halite carrying $MgSO_4$-poor potash salts, a fate that could easily befall the Dead Sea basin if the present drawdown trend continues over the next several hundred years.

With this depositional model, then, arid basins that pass through cycles of filling and desiccation (driven by climatic cycles for non-marine basins and by eustatic or tectonic cycles for marginal marine basins) will see the influence of any small but steady groundwater flux of upwelling $CaCl_2$ brine wax and wane in concert with the cycles. During the deep water stages the influence will be minimal, but during the saline pan stage this small flux of $CaCl_2$ brine may become the dominant source of solutes from which $MgSO_4$-poor potash salts would be precipitated to register the termination of the filling-disiccation cycle.

The deep water phase of such an evaporite cycle could be prolonged well into the stage of potash deposition, if the principal inflow source (seawater or river water) continued to supply the basin at a rate that nearly balanced losses by evaporation. If the basin had no surface outlet that would allow brine to escape as underflow, then a deep perennial brine could progressively increase in salinity beyond halite and into the bittern stage with only a moderate decrease in brine depth. Hardie, Smoot, and Eugster (1978) have discussed the general features of this model, and Harvie and others (1980) have applied it to the thick Zechstein 2 cycle that matches so closely the equilibrium sequence expected on evaporation of modern seawater. It is likely that for a huge *perennial* brine body in a marginal marine basin (a "small ocean" basin), such as that evisioned for the Zechstein 2, its sheer size would protect against significant metamorphosis by minor fluxes of upwelling $CaCl_2$ groundwater. The resulting evaporite would be a normal marine one with a potash mineral succession and abundance in accord (or nearly so) with predictions for a seawater parent brine (Hardie, 1984, table 7). It may well be that only under such stable deep water conditions is it possible to generate and preserve a mineral paragenesis that quantitatively reflects the composition of ancient seawater. Shallow perennial and ephemeral marine evaporite environments are so prone to recycling of salts and contamination by non-marine waters that their mineral successions and abundances will not be accurate records of the chemical compositions of the ancient seas that contributed to their genesis. Herein may lie the reason for the considerable differences between the $MgSO_4$-bearing potash facies of the Zechstein 2 (deep) and the Salado Formation (shallow), both of which were deposited primarily from Upper Permian seawater (compare Harvie and others, 1980; Lowenstein, ms and 1988).

Thus, the potash evaporite problem and the role of hydrothermal brines cannot be considered without taking into account the influence of sedimentation conditions on the nature of potash deposits.

The basic elements of the hypothesis presented here for the origin of $MgSO_4$-poor potash deposits are deeply rooted in modern examples of hydrothermal brine "factories" and $CaCl_2$ saline lakes in active rift and strike-slip basins. Extensional tectonic settings in which these elements could have co-existed have occurred throughout geologic time, and so the prospect should be high that at least some of the $MgSO_4$-poor potash evaporites in the geologic record were the products of hydrothermal inflow waters. This question is pursued next.

APPLICATION OF THE HYPOTHESIS TO THE ROCK RECORD

Criteria for Identifying Hydrothermally-Sourced Potash Evaporites

Based on the information and discussions in all the foregoing sections, the following set of features would characterize ancient potash evaporites deposited from brines influenced by hydrothermal source waters:

1. *Tectonic setting.*—The depositional site of the evaporites will be within a rift or strike-slip basin. Continental interior basins sited over earlier rifts should not be ruled out.

2. *Mineralogical and chemical characteristics.*—The potash deposits will be free (or nearly so) of $MgSO_4$ salts typical of normal marine evaporites, that is, polyhalite ($2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$), kieserite ($MgSO_4 \cdot H_2O$), or other magnesium sulfate hydrates, kainite ($MgSO_4 \cdot KCl \cdot 11/4H_2O$), langbeinite ($2MgSO_4 \cdot K_2SO_4$), or other magnesium potassium sulfate double-salts, will be absent (or in trace amounts). Gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) may also be absent, as also may be true for calcite and dolomite. Instead, the characteristic mineral assemblages will involve *halite* (NaCl), *sylvite* (KCl), *carnallite* ($MgCl_2 \cdot KCl \cdot 6H_2O$), and in some cases, *bischofite* ($MgCl_2 \cdot 6H_2O$). Where upwelling $CaCl_2$ brines have been the predominant suppliers of solutes, the unusual but very diagnostic mineral *tachyhydrite* ($CaCl_2 \cdot MgCl_2 \cdot 12H_2O$) and, perhaps, other $CaCl_2$ hydrates (such as antarcticite) will be added to the above assemblage. Unusual amounts of *rinneite* ($FeCl_3 \cdot NaCl \cdot 3KCl$) and sodium calcium *borates* may also signal a hydrothermal source (see Barker and Barker, 1985, for a discussion of the hydrothermal source of boron in inflow waters in evaporite basins). Particularly important would be to find these minerals in primary beds or laminae with their primary depositional bottom growth textures still delicately preserved (Hardie, Lowenstein, and Spencer, 1983). This would demonstrate conclusively that the primary, undersaturated inflow waters were $MgSO_4$-poor and would rule out any post-depositional alteration mechanism as the cause of the lack of sulfate. In addition, where the procedure is feasible, chemical analyses of fluid inclusions in those minerals with preserved primary depositional fabrics (chevron and cornet halite, see Hardie, Lowenstein, and Spencer, 1983; Lowenstein and Hardie, 1985) should reveal the $CaCl_2$-rich composition of the primary brines. For halite evaporites that did not reach the potash deposition stage, fluid inclusion analysis may be the only certain way to discover whether the source brines were $CaCl_2$-rich or not. Other geochemical clues to a hydrothermal origin for the source waters would be higher than average concentrations of the heavy metals Pb, Zn, Cu, Fe, Mn, et cetera as trace elements in the evaporite minerals. These metals may occur in the form of finely and very sparsely dispersed minerals (hematite, galena, et cetera), as dissolved species in the brines trapped in fluid inclusions, or in cation sites in the saline minerals. The latter form is more likely to occur in the Ca and Mg salts, such as anhydrite, carnallite, and tachyhydrite, because of the valency requirements of ionic substitution.

3. *Associated features.*—Other features that point to the likelihood of hydrothermal activity in the evaporite depositional basin are: (A) volcanics interbedded with the rift sediments or, in certain cases, even

with the evaporites themselves, (B) plutons underlying or intruding the rift-sediments (these may be deep-seated and not easily detected, as in some modern extensional basins, see Sanford and Einarsson, 1982), (C) at least parts of the siliciclastic sediment and volcanic fill of the basin will be altered by zeolite and greenschist facies hydrothermal metamorphism, but, as discussed earlier, this may not be easy to detect (anhydrite and ferroan calcite cements containing fluid inclusions with high filling temperatures may be strong clues here), and (D) Pb–Zn–Cu–Fe–Mn–Ba hydrothermal deposits in fractures in the bedrock at the rift margins or underlying the rift, as veins and pods within the permeable rift sediments themselves, or, in unusual cases, as stratiform ores in the basin center sedimentary sequence that carries the evaporites, particularly basal bituminous shales or marls of a perennial lake facies.

Some Illustrative Examples

As noted earlier, there are numerous ancient salt deposits that meet the criterion of accumulation in extensional fault basins (table 3). Halite deposits that did not reach the stage of potash accumulation but that nevertheless precipitated from brines with a $CaCl_2$ inflow water component may be difficult to recognize. For these halite deposits indirect clues would be the presence of interbedded volcanics [for example, Devonian of the Dnieper-Donets Depression (Zharkov, 1984); Upper Triassic of the Sahara Atlas basin in Algeria (Merabet and Popov, 1972); Paleogene of the Zagros basin (Stöcklin, 1968)] and coeval Pb–Zn–Cu–Fe–Mn–Ba deposits in the basin [for example Mississippian of the Canadian Maritimes (Swinden and Strong, 1976); Miocene of the Red Sea (Mitchell and Garson, 1976); Cretaceous of the Cuanza basin in Angola (Caïa, 1976; van Eden, 1979)]. More substantive clues might be found in fluid inclusions in primary halite crystals (Salina Formation of the Michigan basin, see below) or in trace metal concentrations in associated gypsum or anhydrite.

Potash-bearing salt deposits carry in their primary mineralogy the most direct evidence of whether they formed from a $CaCl_2$ parent brine or not (criterion #2 above). Among these deposits the possibilities are narrowed to those potash evaporites free, or nearly so, of $MgSO_4$ minerals (table 2). Of special interest because they carry more than one line of evidence pointing to upwelling $CaCl_2$ brines as possible source waters are the potash deposits of the Cretaceous of Brazil, west Africa, and Thailand, the Oligocene of the Rhine Graben, the Carboniferous of the Paradox and Canadian Maritimes basins, the Late Triassic of the Moroccan Meseta basins, and the Silurian of the Michigan basin.

The brief discussions of these deposits given below are not comprehensive. They do not cover all the available literature, nor do they in every case present existing or alternative views of the origin of the deposits. Instead, these short discussions are intended simply to show, using the criteria listed above, what kinds of features in these deposits make them *candidates* for consideration as potash evaporites formed from upwelling $CaCl_2$ brines. A wide variety of deposits is included to illustrate the range of associated features compatible with the hypothesis. Only further study of these, and similar, deposits using multiple working hypotheses can ultimately resolve the problem of the origin(s) of $MgSO_4$-poor potash evaporites.

1. *Cretaceous of Brazil and West Africa.*—Without doubt the most compelling cases for primary deposition from nonmarine $CaCl_2$ source waters are the Aptian evaporites of the Sergipe-Alagoas and Gabon-Congo basins (fig. 2). These deposits, as illustrated in figure 3, are characterized by thick cycles of halite (100 percent) → halite (35–90 percent) + carnallite (10–65 percent) → halite (0–50 percent) + carnallite (0–40 percent) + tachyhydrite (5–100 percent) (the proportions are for the Sergipe deposit, Wardlaw, 1972, fig. 8). Most significant to the understanding of the genesis of these deposits is the textural evidence presented by Wardlaw (1972, p. 163) for *primary precipitation* of the salts (see fig. 3, which reproduces Wardlaw's textural relationships between halite and carnallite; see also Szatmari, Carvalho, and Simoes, 1979, fig. 12). On the basis of this evidence any origin for these $MgSO_4$-free deposits involving post-depositional alteration can be ruled out (for example, the explanation of Borchert, 1977). Thus, each cyclic sequence must record progressive evaporative concentration of *primary $CaCl_2$-brines* in the mode of the present-day Dead Sea (see fig. 5). Based on the minerals, their succession (tachyhydrite before bischofite), and their proportions, these Cretaceous brines must have been richer in Ca and poorer in Mg than the modern Dead Sea brines (compare with fig. 5, which predicts that the Dead Sea will precipitate bischofite before tachyhydrite due to initial high Mg/Ca ratio). Wardlaw (1972) recognized the need for a non-marine $CaCl_2$ inflow component to explain the primary mineralogy of the Sergipe (and Gabon-Congo) evaporites, but he nevertheless considered these deposits to be basically of marine origin. He suggested that $CaCl_2$ formation waters were discharged into a restricted marine basin where they mixed with evaporating seawater. Two difficulties arise with this idea: (1) the upfaulted highlands surrounding the Sergipe-Alagoas and Gabon-Congo basins during Cretaceous times were primarily Precambrian crystalline basement rocks (see cross sections and maps in Asmus and Ponte, 1973; Meister and Aurich, 1972; Wardlaw, 1972; de Ruiter, 1979), and (2) evaporative concentration of mixtures of seawater and $CaCl_2$ brines leads to precipitation of significant proportions of $CaSO_4$ minerals, with the largest values yielded by seawater-dominated mixtures (see fig. 8). Wardlaw (1972) did not address the problem of the source of the formation waters, but he did suggest that the absence of $CaCO_3$ and $CaSO_4$ minerals from the Sergipe potash deposits might be the result of preconcentration of seawater in other more seaward basins before this concentrated seawater flowed into the Sergipe potash depocenters (see also Wardlaw and Nicholls, 1972).

An alternative and simpler explanation for these unusual tachyhydrite-bearing potash deposits of the Sergipe-Alagoas and Gabon-Congo basins is that they are *non-marine evaporites* formed primarily from $CaCl_2$ inflow waters of hydrothermal origin, as depicted in the working hypothesis for $MgSO_4$-poor potash deposits of rift basins presented above. It is suggested that the $CaCl_2$ chemical signature of the upwelling hydrothermal waters in these closed basins was derived by interaction between the rift sediments or basement bedrock and hot meteoric groundwaters or deeply circulated seawater (if a subsurface connection between the isolated potash basins and the proto-Atlantic ocean existed in Aptian times, as depicted in fig. 6). To produce the mineral sequences found in the Sergipe-Alagoas and Gabon-Congo basins, the upwelling hydrothermal waters would need to have had: (1) a Ca/Mg mole ratio higher than that of the present Dead Sea (see above) but less than that of Bristol Dry Lake (see fig. 4), (2) K/(Ca + Mg) mole ratio less than that of the Reykjanes, Red Sea, or Salton Sea hydrothermal brines (see fig. 4), and (3) little or no SO_4, as is typical of modern $CaCl_2$ hydrothermal brines in active extensional fault basins.

With the mechanism outlined above, the source areas for the upwelling $CaCl_2$ waters should be recognizable as zones of albitization-chloritization-epidotization in the rift sediments or the basement bedrock, while the flow paths to the surface might be marked by heavy metal mineralization. In the Sergipe-Alagoas and Gabon-Congo basins hydrothermal alteration of basin sediments or basement bedrock has not, to the author's knowledge, been reported. It is not clear whether such alteration is simply not present or whether it has been overlooked (see discussion of this latter possibility given earlier). On the other hand, evidence for hydrothermal mineralization during Lower Cretaceous times is widespread in the South Atlantic rift basins. Along the faulted eastern border of the Gabon basin at Kroussou, Pb deposits occur in Lower Cretaceous sandstones as pore cements and vein fillings of galena and pyrite with minor sphalerite, barite, smithsonite, and chalcopyrite (Caïa, 1976). Pb (with Cu) deposits of Lower Cretaceous age are also found in the Araripe basin to the northwest of the Sergipe-Alagoas basin in Brazil (van Eden, 1979), in the Benue Trough, Nigeria (Mitchell and Garson, 1976; Laznicka, 1976), and in the Amazon rift (Mitchell and Garson, 1976). In the Angola coastal basins Zn deposits (with minor Pb and asphaltic hydrocarbons) are found near Loeto in Lower Aptian gypsiferous carbonates and siliciclastics, while Cu deposits are widespread in Upper Cuvo sediments laterally equivalent to the Aptian Sel Massif evaporites (table 3) in the Cuanza basin (van Eden, 1979; Caïa, 1976). In the Mossamedes basin of Angola barite and "manganiferous limestone" beds occur with gypsum beds of Aptian age (Franks and Nairn, 1973, p. 343 and fig. 7).

Further strong support for heavy metal enriched source waters for the Sergipe-Alagoas and Gabon-Congo potash deposits comes from the elevated heavy metal concentrations in the evaporite minerals themselves. Wardlaw and Nicholls (1972, table 5) determined the concentrations of a number of trace elements in the halite, carnallite, and tachyhydrite of the Sergipe, Gabon, Congo, and Angola basins. Zn was found to be considerably higher (4.9–7.5 ppm) in the halite of these Aptian deposits than the range for halite deposits of the world (<0.01–1.47 ppm), while Ba was slightly higher (2.8–3.6 ppm versus 0.9–2.7 ppm for the world range). The carnallites were abnormally high in Zn (6.2–7.8 ppm compared to the 0.22–1.47 ppm world range), Cu (3.6–4.0 ppm compared to 0.64–3.12 ppm), and Mn (0.6–0.7 ppm compared to <0.01–0.23 ppm). In the tachyhydrites Pb (7.5–24 ppm) and Cu (1.5–6.1 ppm) were "anomalously enriched . . . compared with sea water. . . ." (Wardlaw and Nicholls, 1972, p. 53). These authors estimated that the tachyhydrites contained 3300 to 44,000 times as much Pb as modern seawater.

All in all, there exists compelling evidence that the principal source waters for the Aptian tachyhydrite-bearing potash evaporites of the Sergipe-Alagoas and Gabon-Congo basins were heavy metal-enriched $CaCl_2$ hydrothermal brines driven upward into a closed continental rift basin by either thermal or gravity circulation. There is no evidence for, and considerable evidence against, marine conditions during deposition of these saline deposits. Not only does the composition of the deposits speak for a non-marine system but so does the absence of marine fossils in the interbedded, adjacent, and underlying non-saline facies (see, for example, de Ruiter, 1979, fig. 5). The lack of alkaline earth carbonates and calcium sulfate minerals in the potash deposits indicates that there was no mixing with seawater before, or during, evaporative concentration of the $CaCl_2$ brines (see fig. 8). In the Gabon basin west of the Lambarene horst a minor incursion of the sea during uppermost Upper Cocobeach times (fig. 2) is recorded by forams and an ammonite (Brink, 1974; Franks and Nairn, 1973), but non-marine conditions that had prevailed since pre-Cocobeach time (Upper Jurassic to Middle Aptian) returned (the Gamba Formation, de Ruiter, 1979, fig. 5) prior to deposition of the potash evaporites. Undoubtedly the proto-Atlantic Ocean was not far from the evaporite basins during Upper Aptian times so that seawater circulating in the subsurface of the horst-block barriers could have been the parent waters that were hydrothermally altered to produce the upwelling $CaCl_2$ brines from which the evaporites formed (as per fig. 6), such as is occurring today in the $CaCl_2$-rich system of Lake Assal in Northeast Africa (as described earlier). Widespread normal marine conditions were not established in the Sergipe-Alagoas and Gabon-Congo basins until the Albian (fig. 2). These Albian marine deposits and not the Aptian evaporites are the true markers of the massive Cretaceous marine transgression of these particular regions of the South Atlantic passive margins.

2. *Cretaceous of Thailand.*—The Maha Sarakham Formation of Cretaceous age in the Khorat Plateau of Thailand and Laos is a non-marine red bed sequence with three interbedded salt units (Hite and Japakasetr, 1979). The thick lower salt unit (up to 450 m) is capped

by a potash deposit (up to 95 m thick) which covers an area of about 30,000 km^2. This potash deposit consists mainly of carnallite and halite but locally sylvite can be abundant. What is unusual about this deposit is: (1) the presence of significant volumes of *tachyhydrite,* which occurs in layers up to 16 m thick and which may make up as much as 30 percent of the potash deposit; (2) the absence of $MgSO_4$, $CaSO_4$ (only traces of anhydrite occur in the insoluble residues), and carbonate minerals; and (3) the abundance of the borate mineral boracite (up to 8.5 percent by wt). Hite and Japakasetr (1979) interpreted these evaporites as the result of marine incursions from the Tethys Sea into the non-marine basin along "a marine accessway . . . somewhere to the west . . . several thousand kilometers in length." To explain the paucity of carbonates and calcium sulfates in the potash deposit they called on pre-concentration basins "somewhere near the marine connection to the evaporite basin." The deposition of large volumes of tachyhydrite from seawater they believed to be due to the "strong concentrative system" created by the "lengthy marine connection." They did not give any details of the chemical processes involved in converting seawater to a $CaCl_2$ brine, but they did note that the similarities in mineralogy among the Khorat, Brazil, and Gabon-Congo tachyhydrite-rich potash deposits "might suggest that the chemistry of the Cretaceous ocean was somehow different from that of the modern ocean." However, they finally concluded that it was more likely that the "duplication was simply the result of similar circulation systems." An entirely different explanation is offered here. The hydrothermal brine hypothesis given above for the Brazilian and West African tachyhydrite deposits would also provide a satisfactory solution to the problem of the origin of the Khorat tachyhydrite deposit. An intrabasinal source of upwelling $CaCl_2$ hydrothermal brine or formation waters would resolve many of the dilemmas raised by Hite and Japakasetr's (1979) adherence to a marine origin for these $CaCl_2$-rich $MgSO_4$-free evaporites interbedded with non-marine red beds in a continental basin far distant from the Cretaceous sea.

3. *Oligocene of the Rhine Graben.*—The very thick (1.7 km) Early Oligocene halite deposit of the Rhine Graben includes two very thin, but economically important, zones of potash (Couche inferieure 3.9 m, and Couche superieure 1.6 m) that underlie an area of 400 km^2 in the Mulhouse (France) subbasin. The significance of these thin potash units in the context of the present discussion lies in the textural evidence they provide for primary precipitation of an $MgSO_4$-free potash deposit (see Lowenstein and Spencer, 1990, for an important study of primary sylvite in the Rhine graben and other potash deposits). Both potash units consist of a succession of thin, parallel-sided beds (average thickness about 8 cm), each of which is a couplet composed of gray-colored halite overlain by red-colored sylvite. In freshly mined cuts the mine walls look as though they are covered by horizontally striped wallpaper. Several intercalated beds (12–27 cm thick) of finely laminated bituminous shale carrying some dolomite and anhydrite are internal stratigraphic mark-

ers that allow the halite-sylvite beds to be traced over the entire mining area. With T. K. Lowenstein, the present author has examined in mine exposures and in cores the halite-sylvite couplets from the Mulhouse mining area, and the following descriptions are taken from this work (Lowenstein and Hardie, unpublished data). An individual bed has a sharp base that separates the basal halite member from the sylvite cap of the underlying bed. In some cases this bedding surface is marked by a bituminous parting. The bottommost halite consists of an aggregate of small euhedral hopper crystals with a cumulate texture (Hardie, Lowenstein, and Spencer, 1983) that passes up into large but delicate chevrons and cornets that record primary bottom growth of halite (Shearman, 1970; Hardie, Lowenstein, and Spencer, 1983; Lowenstein and Hardie, 1985). Large clusters of this chevron-cornet halite swell upward to make a very hummocky boundary with the overlying sylvite. The sylvite member of the couplet consists of a granular aggregate of small clear cubes of halite and rounded grains of red sylvite (with some euhedral sylvite hoppers) that fill in the swales between the hummocky clusters of the underlying halite crystal framework. Typically this upper sylvite member is sufficiently thick to bury the highest protuberances of the underlying halite crystal clusters so that the upper boundary of each couplet is essentially flat. Notably absent are dissolutional pipes and intercrystalline cavities typical of salt pan deposits (see Lowenstein and Hardie, 1985), although in some couplets the halite chevrons and cornets, where they are overlain by the sylvite cap, show minor dissolutional truncations. Thus, the couplets appear to record unaltered settle-out and bottom growth features of a primary chemical sediment that accumulated in a shallow perennial surface brine pool. This in turn means that the brines must have been KCl-rich and $MgSO_4$-poor waters before evaporative concentration. As such they could not have been seawater with the composition of the modern oceans. Instead, typical potassium-rich $CaCl_2$ hydrothermal brines or mixtures of such brines with seawater (fig. 8) would provide the right composition of source waters to account for the halite $\longrightarrow$ halite + sylvite paragenesis recorded repeatedly in the succession of couplets in the Rhine Graben potash deposit. Support for such non-marine source waters comes from two quite different directions. First, Nielson (1967, 1972) has found that the $\delta^{34}S$ values in these Rhine Graben potash deposits are extremely low (+12 permil) compared to the value of about +20 permil thought to be typical for Tertiary marine deposits. Nielsen (1967, 1972) suggested, therefore, that the source waters for the Rhine Graben Oligocene evaporites were deep circulating brines, perhaps derived from the Zechstein evaporite basin over 300 km away. Secondly, Fettel (1982) has related the Pb-Cu-Zn-Fe-mineralization, barite veins, Ag-Co, and associated ores at Odenwald (northeast shoulder of the Rhine Graben) to "ascendant hydrothermal" fluids activated by Tertiary tectonic movements in the Rhine Graben. In that the primary mineralogy of the potash beds completely rules out a marine origin, these isotope data and the contemporaneous hydrothermal mineralization speak forcefully in favor of a non-marine origin for the Rhine Graben evaporites with upwelling hydrothermal $CaCl_2$ brines as the dominant inflow waters.

4. *Triassic of Morocco.*—The many Late Triassic (Keuper) fault basins in the Moroccan Meseta (table 3) are filled with non-marine red beds and evaporites (van Houten, 1977). A particular feature of these basins is the presence of thick basalt flows (up to 500 m in total thickness) interbedded with the saline deposits (Salvan, 1972; Cogney and Faugeres, 1975; van Houten, 1977). These lavas must have flowed across "subaerial mudflats into ponds and lakes, producing local interflow lenses of mudstone and lacustrine limestone" and across "extensive salt pans and associated mudflats" (van Houten, 1977, p. 85). In four of these basins the evaporites interbedded with volcanics carry potash deposits (tables 2 and 3; see Salvan, 1972; van Houten, 1977). These potash deposits consist essentially of halite, carnallite, sylvite, and rinneite with less than 1 percent of other minerals (anhydrite, kieserite, bischofite, douglasite) (Salvan, 1972). The $MgSO_4$-poor composition of these potash deposits led Salvan (1972) to point out "l'importance des influences continentales" in any consideration of their origin. These evaporites, interbedded with non-marine sediments and basaltic lava flows in isolated extensional fault basins, are prime candidates for deposition from upwelling $CaCl_2$ waters of hydrothermal origin. In this connection, it is significant that there exist hydrothermal Pb-Zn deposits of Triassic age in this block-faulted region of Morocco (Laznicka, 1976, p. 160–161).

5. *Mississippian of New Brunswick and Nova Scotia.*—The Windsor Group of Mississippian (Visean) age in New Brunswick and Nova Scotia carries $MgSO_4$-poor potash evaporites in several of the intermontane basins formed by extension related to post-Acadian strike-slip faulting (Howie and Barss, 1976; Ziegler, 1978; Bradley, 1982; see papers in Beaumont and Tankare, 1987). In the Moncton subbasin, the Potash Member (15–45 m) of the Cassidy Lake Formation consists of thin beds (centimeter scale) of halite and halite + sylvite, while the Upper Salt Member (65 m) is characterized by interlayering on a thin bed and lamina scale of argillaceous halite, sylvinite, and claystone-anhydrite (Anderle, Crosby, and Waugh, 1979). Notable is the presence of borate minerals in the Basal Halite (danburite) and Upper Salt (boracite, hydroboracite, szaibelyite, hilgardite, and ulexite) members. At Pugwash the potash deposit consists of halite, sylvite, and carnallite with minor rinneite and polyhalite (Evans, 1967).

A particularly remarkable feature of the Windsor Group of Nova Scotia and the gypsum-anhydrite deposits of equivalent age in Newfoundland is that they are hosts to contemporaneous Pb, Zn, and Ba hydrothermal mineralization (Swinden and Strong, 1976). For this reason serious consideration must be given to upwelling hydrothermal brines as major contributors of solutes to the waters from which the borate-bearing potash deposits of the Windsor Group precipitated.

Russell (1976) has documented that hydrothermal systems that deposited Pb, Zn, Ba, Cu, and other heavy metals were active in Lower Carboniferous times throughout the North Atlantic region. These hydrothermal systems were located in faults and fractures in zones along which Pangea later ruptured and separated. The driving force for this hydrothermal activity presumably was the igneous activity that was widespread in this area during the Carboniferous as the North Atlantic experienced the onset of regional tectonic extension (Russell, 1976; Ziegler, 1978).

6. *Pennsylvanian of the Paradox basin.*—The Pennsylvanian (Demoinesian) evaporites of the Paradox basin of Colorado-Utah appear at first glance to be unlikely candidates for anything but a marine origin because of the indisputable connection this evaporite basin had with the Carboniferous Sea, as evidenced by the fossiliferous black shales and dolomites interbedded with the evaporites and by the coeval marine carbonate facies at the southwestern edge of the basin (Person and Hite, 1969). These latter rocks contain abundant marine invertebrate fossils and mounds composed of red algae and the platy green alga *Ivanovia.* The evaporite facies is cyclical (total thickness over 1200 m, perhaps as much as 2000 m). Twenty nine cycles, individually ranging from less than 10 to over 300 m in thickness, have been identified in drillholes in the deepest part of the basin (Peterson and Hite, 1969, fig. 6). Internally, each cycle follows the general succession of black shale → argillaceous dolomite → anhydrite → halite ± potash salts, as would be predicted on evaporation of seawater. However, there are several features of these Paradox evaporites that do not conform to a seawater evaporation sequence. These features are: (1) lack of an $MgSO_4$ mineral zone in any of the eleven cycles capped by potash deposits. Instead, late bittern zones are represented by halite, carnallite, and sylvite (only very minor amounts of polyhalite and kieserite have been reported) (Hite, 1961); (2) Raup (1972) has found braitschite, a calcium rare-earth borate mineral, in anhydrite of potash-bearing cycle 5. The rare-earth distribution in this braitschite is similar to that in the bedrocks of the Uncompahgre uplift but quite different from that in seawater. This led Raup (1972) to postulate that the source waters from which the braitschite formed must have been derived from the surrounding highlands and not from the ocean; and (3) as noted earlier, the anhydrite of these evaporite cycles contains extraordinarily high concentrations of heavy metals (10,300 ppm Fe, 150 ppm Mn, 14 ppm Cu, 5.2 ppm Pb, see Stewart, 1963, table 23; and Dean, 1978, table 5.3). These values are much higher than those found in the anhydrites of the $MgSO_4$-rich potash deposits of the Permian Salado Formation and Zechstein 2 (Stewart, 1963, table 23; Dean, 1978, table 5.3). Such high values could not be the result of simple evaporative concentration of the low contents of these metals in normal seawater (see Riley and Chester, 1971).

All these non-marine chemical signals in the evaporites of the Paradox basin can be explained if the evaporating surface brines originated as mixtures of seawater and heavy metal-rich hydrothermal brines (or formation waters). Only relatively small additions of $CaCl_2$ brines upwelling into the basin along faults and other permeable pathways are needed to convert a restricted body of seawater into a $MgSO_4$-poor brine (fig. 8). Substantial amounts of anhydrite (enriched in heavy metals) could be precipitated from such mixtures (fig. 8), which in the late stages of evaporative drawdown, would deposit halite, sylvite, and carnallite in the absence of $MgSO_4$ salts.

The Paradox-type cyclic evaporites also fill the nearby Pennsylvanian-age Eagle Basin (Petersen and Hite, 1969), and a similar brine mixing mechanism could explain the $MgSO_4$-poor potash salts (carnallite, sylvite) in this downfaulted basin.

7. *Silurian of the Michigan basin.*—Finally, an example from a classic cratonic basin, the Michigan basin, demonstrates that $CaCl_2$ brines could be important in the formation of evaporites in this type of depositional basin. Chemical analyses of fluid inclusions in the halite of the Silurian Salina Formation of the Michigan basin show a considerably higher Ca/Cl ratio than modern seawater or halite precipitated from modern seawater (Holser, 1963, table 1; Kramer, 1965, table 5). Kramer (1965) concluded that the brine captured in the Salina halite "does not represent fossil seawater." More recent chemical analyses by H. D. Holland (personal commun., 1985) confirm this conclusion. Holland found that brine inclusions in the Salina halite are Ca-rich and SO_4-poor, and he suggested that Silurian seawater was altered by dolomitization before the halite stage of evaporite concentration was reached. That the Salina Formation brines were Ca-rich and SO_4-poor is strongly supported by the mineralogy of the potash facies in the center of the Michigan basin. Here, sylvite is intimately associated with primary, bottom-grown chevrons of halite (Nurmi and Friedman, 1977, fig. 13), clearly demonstrating that the original surface brines were $MgSO_4$-poor (whole rock analyses show only trace amounts of Mg and SO_4 in these potash beds). As with a number of other $MgSO_4$-poor potash deposits (see above), the Salina sylvinite carries calcium borate minerals (Nurmi and Friedman, 1977, p. 40–41) as major accessories.

The origin of cratonic basins is very uncertain, but Bally (1980) and Bally and Snelson (1980) stress that most if not all cratonic basins are underlain by ancient rift systems. This implies thinned crust underlying the basin, as suggested for the Michigan basin by Fowler and Kuenzi (1978), and perhaps also an increased geothermal gradient, as occurs today in the West Siberian basin (Tamrazyan, 1971). With regard to the significance of $MgSO_4$-poor potash deposits in cratonic basins underlain by rifts, it may be that these $CaCl_2$ evaporites are signals of periods of increased thermal activity in the thinned crust that supports the subsiding basin.

CONCLUSIONS AND SOME IMPLICATIONS

Ancient potash evaporites in the geologic column are of two major types:

1. *$MgSO_4$-rich type,* characterized by $MgSO_4$ salts such as polyhalite, kainite, and kieserite, predicted to form on evaporation of waters of modern seawater type:

2. *$MgSO_4$-poor type*, characterized by the paucity, or more commonly the complete lack, of $MgSO_4$-bearing salts; this type cannot be derived by evaporation of waters of modern seawater type.

The $MgSO_4$-poor type is by far the most common type (tables 1 and 2), and, where petrographical and sedimentological evidence proves a primary origin for such deposits (Hardie, Lowenstein, and Spencer, 1983), their mineralogy and chemistry require primary precipitation from *non-marine source waters* rich in $CaCl_2$. Based on modern analogs an explanation has been offered in this paper that calls on major contributions from subsurface $CaCl_2$ brines driven upward to the surface by hydrothermal circulation or by gravity in active extensional fault basins. It is hoped that the evidence from the Holocene, the geochemical arguments, and the discussion of ancient $MgSO_4$-poor potash deposits presented in this paper provide a strong enough case to have evaporitologists add the hydrothermal $CaCl_2$ brine hypothesis to their arsenal of multiple working hypotheses for their attacks on the origin of potash evaporites.

The hypothesis presented here has important implications for the evolution of $CaCl_2$-rich basinal brines and for a genetic connection among $MgSO_4$-poor potash evaporites, hydrothermal ore deposits, and hydrothermal alteration of the sediments in extensional fault basins.

The role of $CaCl_2$ basinal brines both as source waters for, and as by-products of, $MgSO_4$-poor potash evaporites has been outlined briefly in the discussion of the hypothesis and is summarized in figure 7. There is, however, yet a further dimension to the connection between $MgSO_4$-poor potash evaporites and $CaCl_2$ basinal brines. It follows as a logical consequence of the hypothesis that there should exist a direct connection between the abundance of $MgSO_4$-poor potash deposits and the volume of concentrated $CaCl_2$ formation waters in the major sedimentary basins of the world. The pattern would have been established in the early stages of tectonic development of the basins when active magmatism promoted abundant hydrothermal activity during crustal extension. These hydrothermal fluids, if they leaked to the surface, would have imposed a $CaCl_2$ signature on the evaporites, a signature that would have been strongly amplified in the evaporite mother-liquors by the simple but powerful process of evaporative concentration and saline mineral precipitation (fig. 5 is a perfect illustration of such an enhancement of the $CaCl_2$ component). These $CaCl_2$-enriched mother-liquors would continuously leak away into the porous sediments surrounding the evaporite depocenter down the descending pathways of the convection cells. After the thermal activity had subsided these dense $CaCl_2$ brines would be stored as near static formation waters in the subsurface of the basin. A subsequent thermal event could recirculate these concentrated formation waters (the hot pore fluids at Cheleken may be a modern example, see Lebedev, 1967, 1972) while at the same time making new hydrothermal brines from overlying less dense groundwaters (marine or non-marine) by interaction with heated bedrock (fig. 7). Upwelling of these old formation waters and the new generation of hydrothermal brines could lead to another cycle of $MgSO_4$-poor evaporites and in the process convert, by mixing, substantial new volumes of surface waters into $CaCl_2$ brines (fig. 8). In this way the pool of $CaCl_2$ formation waters would increase with each new thermal event in the history of the basin, and at the same time, the stock of $MgSO_4$-poor evaporites would grow. Interior basins with a long history of repeated tectonic movements and magmatism, like the West Siberian basin, will display a long record of $MgSO_4$-poor potash deposits (see Zharkov, 1984) and a substantial volume of $CaCl_2$ basinal brines. The thermal events that drive such a hydrothermal machine will be responsible for other very significant phenomena related to subsurface fluid transport, namely hydrothermal ore deposition and metasomatic alteration of basin sediments.

In presenting the case for hydrothermal brines as the source waters for the $MgSO_4$-poor potash evaporites of the Sergipe, Gabon-Congo, Canadian Maritimes, Rhine Graben, and Moroccan Meseta basins, the occurrence of coeval Pb–Zn–Cu–Fe–Mn–Ba mineralization was called on as critical supporting evidence. The same line of evidence has been used by Dzhinoridze (1987) in making his case for the "exhalatory-sedimentary" origin of salt deposits, and he gives examples from the USSR of hydrothermal ore mineralization in deposits underlying Permian, Jurassic, and Tertiary salt. This connection between potash evaporites and base metal ore deposits needs to be explored more thoroughly in all extensional basins that carry potash deposits because it may throw new light on the origin and evolution of both evaporites and hydrothermal ore deposits. For example, it would be worthwhile to look into possible genetic connections between Cu, Pb, Zn and other ore deposits in red beds and fanglomerates at the margins of downfaulted basins (see, for example, papers in Friedrich and others, 1986) and any evaporites in the basin center (for example, the many copper-bearing red beds that repeatedly occur throughout the Phanerozoic in Kazakhstan, USSR, some of which have coeval basin-center evaporites, Susura, Glyovsky, and Kislitsin, 1986). A special case of this is the mineralization associated with the Zechstein evaporites of the northeastern European basin. In Poland the Lower Permian Rotliegende sandstones are copper-bearing (also Pb-Zn, Banas and others, 1982), and they directly underlie the famous Kupferschiefer of the basal Zechstein, the Werra Series. In early Werra times the Rotliegende basin was flooded by seawater and developed into a deep, stratified system with anoxic bottom waters (a condition that lasted at least into the $CaSO_4$ evaporite stage, Schlager and Bolz, 1977). Hydrothermal brines could have leaked in through the bottom of this anoxic basin (as in modern Lake Kivu, Degens and Kulbricki, 1973) and left their record in the heavy metals chelated by the organic matter of the bottom layer (Cu, Pb, Zn, Ag, see Haranczyk,

1986) that is now the Kupferschiefer. The records of the subsurface pathways of the hydrothermal brines that circulated upward through the underlying Rotliegende sandstones are the ore zones characterized by replacement of quartz and feldspar grains by chalcocite, bornite, galena, and sphalerite, and by cements composed of anhydrite, chalcedony, quartz, and sulfide minerals (Banas and others, 1982).

Finally, alteration of the sediments of evaporite basins by hot brines circulating in the subsurface should be included in any linkage between hydrothermal fluids, ore mineralization, and potash evaporites. As discussed above at some length, this alteration will include albitization, chloritization, dolomitization (or calcitization depending on prevailing temperature and Ca/Mg ratio of the brine, Hardie, 1987, fig. 7), and cementation by anhydrite, calcite, dolomite, and silica phases (opal, chalcedony, quartz). Some of these changes may be easily missed unless specifically looked for as hydrothermal manifestations, as Muffler and White (1969) noted for the Salton Trough hydrothermal system.

All in all, connections in space and time among $MgSO_4$-poor potash evaporites, hydrothermal brines, base metal ore deposits, hydrothermal alteration of basin sediments, and thermal events are worth searching for in the stratigraphic record of extensional basins. It perhaps would not be stepping too far afield to suggest that migration of hydrocarbons derived from bituminous shales associated with evaporites or with pre-evaporite lacustrine deposits be included in this chain of connected phenomena driven by periodic thermal events.

ACKNOWLEDGMENTS

The author's basic ideas as outlined in the present paper were brought into sharp focus during numerous discussions with Jim Wood (now of Chevron) when Jim was a post-doctoral student at Hopkins in 1973–1975 interested in the hydrothermal circulation of brines in rift zones. Subsequently, the critical views of several generations of graduate students were most valuable in shaping my own views of the origin of calcium chloride brines and their relationship to evaporites and hydrothermal ore deposits. I would especially like to thank Tim Lowenstein (now at SUNY Binghamton) and Ron Spencer (now at University of Calgary) for their insightful discussions. Their sustained enthusiasm for and clear thinking about the study of evaporites and brines have been a constant source of encouragement for my own recent work on evaporites.

My colleagues, Owen Phillips and Grant Garven, have taken some of the mystery out of convective circulation of subsurface fluids for me. Discussions with Mark Person on many aspects of the subsurface flow of brines in fault basins have been particularly valuable. Dimitri Sverjensky helped considerably to "debug" the original manuscript and, in addition, provided much needed expertise about matters concerned with ore deposition. At his suggestion a number of changes were made to the manuscript. Valuable comments on the original manuscript were also made by Tim Lowenstein, Ron Spencer, Lynton Land, and Blair Jones. Charlotte Schreiber read the manuscript and kindly provided data on Tertiary potash deposits in France. The final version (lengthy as it is) remains entirely my own responsibility.

Finally, I would like to thank Kate Francis for her patience and skill with the typing, Paul Dunn for his invaluable help with the techniques of Macintosh graphics, and Kathleen Sweeney for a Russian translation.

DEDICATION

This study is dedicated to the late Hans Pieter Eugster (1925–1987), mentor, colleague, friend, and wise counselor. Hans got me into evaporites and geochemistry and thereby changed the course of my life. He will be sorely missed.

The charged atmosphere Hans Eugster created in his laboratories on the third floor of Latrobe Hall captured me completely — this was the "new geology" in action, the search for an understanding of geological processes using quantitative means. Hans' enthusiasm for the "new geology" was infectious, and I was fortunate to be an active part of the excitement of those times. This aspect of Hans' scientific legacy will not be forgotten by those of us who were there.

Hans understood most clearly that the study of evaporites needed more than an experimental approach (after all, van't Hoff years earlier had pioneered the field of experimental geochemistry based on thermodynamics using the Zechstein salts as his target). Modern saline lake systems, where brine-mineral processes could be monitored, seemed to offer an untapped resource from which new ideas about the origin of evaporites might be culled. This view proved to be uncannily accurate as well as pivotal, as Hans' own publications have demonstrated. This line of enquiry into modern non-marine evaporites, together with the parallel studies of modern marine sabkhas by Doug Shearman's group, has revolutionized our understanding of how evaporite systems work. The present study arises directly out of this way of looking for solutions to evaporite problems and so has the spirit of Hans Eugster firmly woven into its fabric.

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