GEOLOGICAL CONTROLS ON THE QUALITY OF POTASH

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Ages of exploitable potash deposits range from Quaternary to Devonian; no economic potash deposits are known to occur in Precambrian strata. Most exploited potash is derived from sylvinite ores although carnallitite slurries are processed in the Dead Sea Salt Works. Even though the various potash salts are highly soluble, subsurface solutions cannot alter them until a protective wrap of tight bedded or halokinetic halite has been etched away. Larger economic potash deposits, such as in the Zechstein and Prairie evaporite units, originally precipitated penecontemporaneously as part of the evaporite fill of basinwide settings. This probably reflects the very high salinities that are needed before any brine reaches camallite/sylvite saturation, be it marine, nonmarine or hybrid. The highly isolated conditions that can be attained in "saline giants" tend to favor the accumulation of potash salts in such settings. There is no modem day equivalent to a drawdown basin or saline giant such as formed the Zechstein or Prairie Evaporite basin fills.

Carnallite, not sylvite is the accumulating potash phase in modem depositional systems such as Lake Dabuxurn in the Qaidam Basin, China and the Dead Sea Salt Works, Israel. In Lake Qaidam, the carnallite forms as an early karst fill or cement in shallow halite beds. The driving mechanism is cooling of a dense potassium-saturated brine as it sinks into nearsurface lake beds. In the Dead Sea a camallitite slurry forms in artificial solar salt pans fed by dense subsurface brines. In both situations sylvite is not a widespread precipitate at the depositional surface. Primary growth-aligned sylvite forms the sylvinite ores in the Oligocene lacustrine deposits of the Mulhouse Basin in the Rhine Graben. In other major exploited potash deposits, such as the Devonian Elk Point Basin, Canada, the Permian Boulby Halite UK, and the Cretaceous Maha Sarakharn in Thailand, part of the sylvinite ore is primary but its subsequent enrichment is related to the recrystallization and throughfiow of subsurface brines. This potash enrichment within its thick halite host often occurs at or near an intrasalt unconformity or disconformity. It reflects times of brine fractionation and recrystallization related either to episodes of exposure and subaerial leaching/ concentration, or to episodes of subsurface flushing of the most soluble salts followed by their reprecipitation. In some deposits, such as the Maha Sarakham, near Khon Khan Thailand, the potash concentration process was aided by early synprecipitational salt flow and karsting of a bedded camallitite precursor.

WHAT IS POTASH?

Potash is a commercial term for a variety of ore-bearing minerals, ores and refined products, all containing the element potassium in water soluble form. Commercial forms of potash include: Muriate of potash (KCl); Sulphate of potash (K_2SO_4) Sulphate of potash magnesia ($K_2SO_4 \cdot MgSO_4$); Saltpetre (KNO_3); and Chilean saltpetre (sodium-potassium nitrate - $NaNO_3$+KNO_3). Geologically, the term potash ore describes ores containing varying proportions of the potassium bearing minerals sylvite and carnallite. The main potash producing ore is usually sylvinite [sylvite (KCl) + halite (NaCl)], although our increasing ability to economically manipulate brine chemistries means carnallitite [carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$) + halite] will be an increasingly important ore type, especially in regions with geology suitable for solution mining. Other potassic salts in ores include: kainite, kieserite, langbeinite, leonite and polyhalite.

Geologically there are two main ore associations, those potash salts associated with $MgSO_4$ salts and those without. Historically, the group of potash salts associated with the $MgSO_4$ salts (such as epsomite, kainite, kieserite) were interpreted as marine as this is the set of associated bittern salts that form via the evaporation of modem seawater. Those without $MgSO_4$ salts were interpreted as precipitating either from nonmarine or hydrothermal waters (Hardie 1990). Recently the notion of the constancy of chemistry of Phanerozoic seawater has been questioned and fluid inclusion work on halites and other salts in the ores is showing the chemistry of seawater (Na-K-Mg-Ca-Cl vs Na-K-MgCl-S04) is changing according to the changes in the rates of seafloor spreading (Kovalevich et al., 1998).

POTASH WORLD GEOLOGY

What follows is a summary of geological controls on potash purity in some economically important deposits (Table 1). Potash deposits, being part of the salt fill of basinwide evaporites tend to accumulate in particular plate tectonic settings; in the highly continental and hyperarid conditions that characterise the early stages of continental rifting or highly restricted parts of collision belts and transform basins (Warren, 1999). In both settings the inflow brines can be marine, nonmarine, or hybrid. World-wide, the potash deposits accumulating in these settings typically retain textural evidence of early depositional controls to mineral distribution with ore purity often modified and overprinted by subsequent diagenetic alteration. This alteration can be syndepositional and associated with reflux and cooling of K saturated brines, or much later and deeper in zones where the brine flow is driven by regional tectonic events.

There are no economic potash accumulations older than Cambrian (Table 1), with the largest reserves to be found in the Devonian salt basins of Canada. The only modem accumulations of potash minerals occur in highly continental playas in the interior of China within the Qaidarn Basin.

Modern carnallitite in Lake Qaidam, China

Carnallite is the dominant potash salt in the Lake Qaidarn Basin. It occurs both as a surface precipitate and as a nearsurface voidfilling cement. But it is preserved only in the near subsurface within the upper 13 m of the 45m thick interbedded clay-halite succession that underlies the Lake Dabuxurn strandline. These subsurface camallites are early diagenetic void-filling cements and displacive crystals, precipitated by the cooling of down-welling carnallite-saturated brines (Figure 1). As these dense carnallite-saturated lake brines sink into the underlying sediment they cool and precipitate carnallite in pre-existing karst holes and pits in the halite host bed (Casas et al., 1992). The host voids were created by an earlier lowering of the water table and freshening of the lake waters. This style of secondary nearsurface carnallite accumulating as early karst cements in a bedded halite host within the active phreatic zone is analogous to textures served in much of the camallitite and sylvinite seen in ancientpotash deposits in Thailand, Canada and the USA (Lowenstein and Spencer, 1990; Warren, 1999). Modem carnallitite is also produced at the southern end of the Dead Sea from brines pumped to the surface from their subsurface Miocene evaporite host into a series of gravity-fed solar evaporation ponds. There are no modern documented examples of widespread primary sylvite precipitation.

Sylvinite in the Mulhouse Basin

The lacustrine potash deposits in the Mulhouse Basin are part of a Tertiary rift basin fill that is some 150 km long and 10-25 km wide and straddles the Franco-German border (Figure 2). The total fill of Oligocene lacustrine evaporites is some 1,700m thick and is dominated by anhydrite, halite and mud stone. The ore is Oligocene sylvite with subordinate carnal lite, it lacks $MgSO_4$ and forms layers in a matrix of halite. The ore hosting section is made up of two thin potash zones: the Couche Inferieure (Ci, 3.9m thick), and Couche Superieure (Cs, 1.6m thick). Both are in turn made up of turn made up of stacked, thin, parallel-sided cm-dm-thick beds (averaging 8 cm thickness), which are in turn constructed of couplets composed of grey-colored halite overlain by red-colored sylvite (Lowenstein and Spencer, 1990). Each couplet has a sharp base that separates the basal halite from the sylvite cap of the underlying bed sometimes marked by a bituminous parting (Figure 2).

The sylvite-halite couplets in the ore preserve unaltered settleout and bottom-growth features of a primary chemical sediment, which accumulated in a shallow perennial surface brine pool. Based on their crystal size, the close association with cumulate halites in the sylvite layers, and the manner in which they mantle underlying chevron halites, sylvites are interpreted as precipitates that first formed at the air-brine surface (or within the upper brine) and then sank to the bottom, to form well-sorted primary accumulations. Similar cumulate deposits of carnallite, not sylvite, are found on the floor of modem Lake Dabuxurn in China, but are dissolved with each flood event. The deposits of the Mulhouse Basin are examples of primary

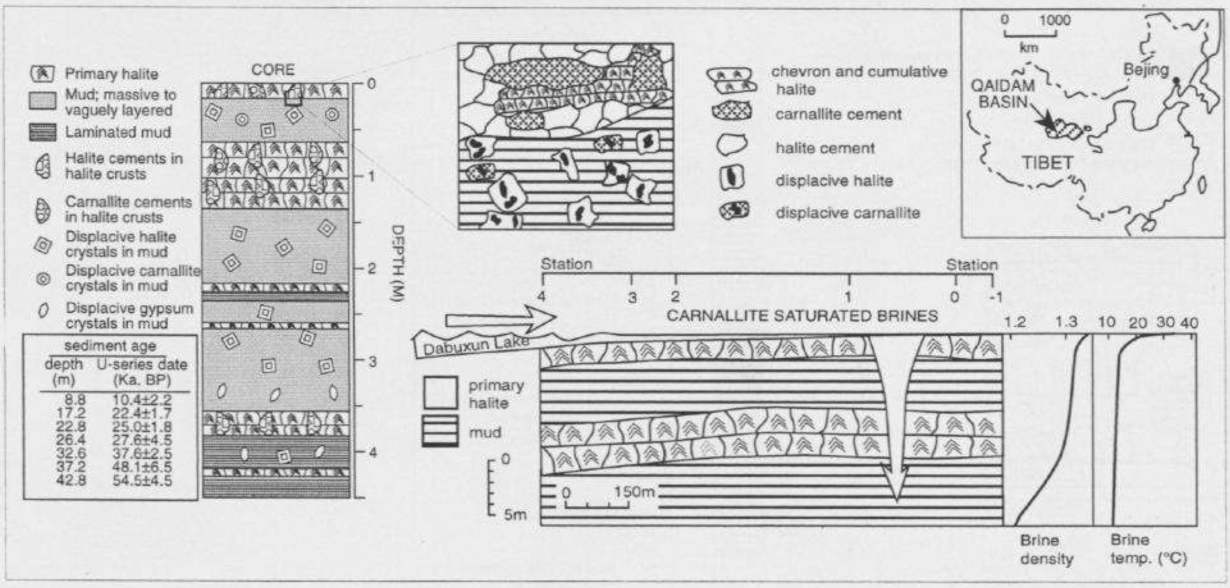

Figure 1. Carnallite formed as secondary cement in karst voids in bedded halite beneath the shores ofLake Dabuxum, Qaidam Basin, China(after Casas et al., 1992)

growth-aligned sylvite. The lack of secondary reworking of sylvite makes this style of deposit easier to predict in terms of ore purity.

Elk Point Basin, Canada

Stratiform potash ore occurs in the upper 70 m of the Middle Devonian Prairie Evaporite Formation at

Location	Mined?	Tectonic setting	$MgSO_4$	Main potash minerals	Style and origin of potash
Qaidam Depression, China Quaternary	Yes	Continental playa in foreland basin	Yes	Carnallite, lesser sylvite	Void filling cements and displacive crystals via cooling of syndepositional sinking brines.
Dead Sea Depression, Middle East Quaternary	Yes	Artificial brine recovery and pan evaporation in continental transform	No	Carnallite slurry with sodium and magnesium chloride	Sequential evaporation of brine pumped from pores and dissolution cavities in subsurface Miocene evaporates.
Mulhouse Basin, France Oligocene	Yes	Continental eastern, bedded in continental rift graben	No	Primary carnallite and sylvite	Interlayered primary potash and halite cm-scale couplets with settle-out/bottom growth textures.
Prairie Evaporite Fm., Elk Point Basin, Canada Devonian	Yes	Basinwide evaporite, mostly salterns, occasional deeper water	No	Syncepositional carnallite and sylvite within primary halite	Syndepositional potash textures, often overprinted by later alteration events related to tectonically driven episodes of fluid flushing by basinal brines or deeply circulating meteoric waters.
Maha Sarakham Fm., NE Thailand Cretaceous	Possibl y	Continental saltern, now halokinetic in part within continental foreland basin	No	Syndepositional carnallite and early secondary sylvite, also tachyhydrite	Syndepositional carnallite and secondary sylvite via brine cooling within karsted halite host.

Table 1. Geological characteristics of some worldclass potash deposits (after Warren, 1999)

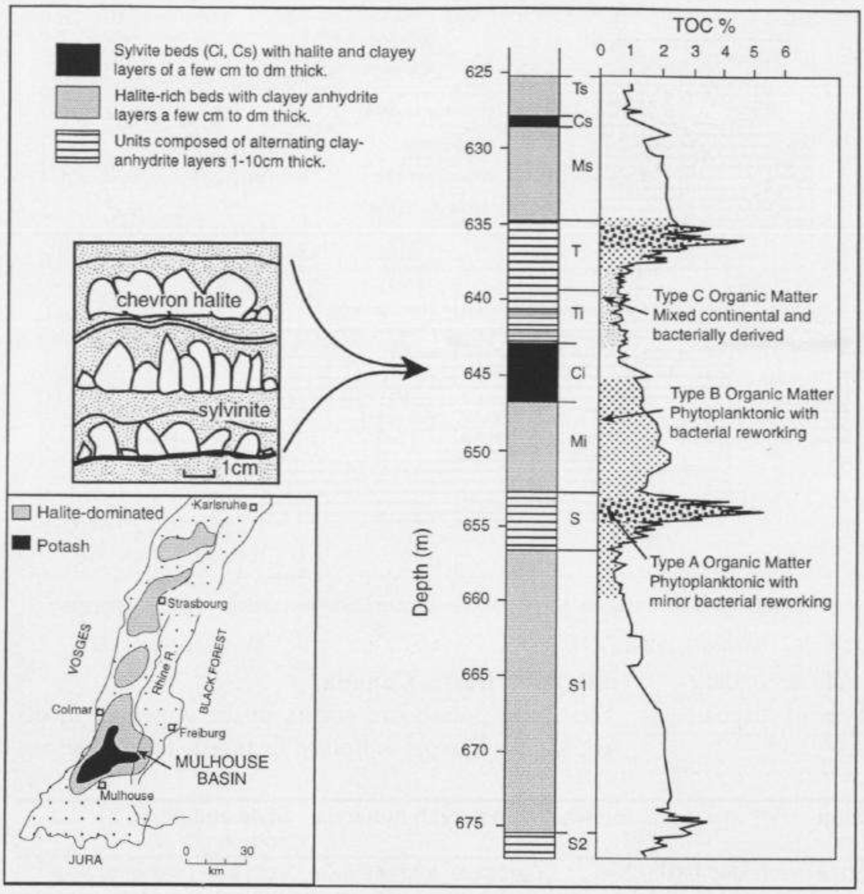

Figure 2. Depositional sylvite in the Mulhouse Basin, Europe (after Gely et al., 1993; Warren, 1999

depths of more than 300 metres (Figure 3a-c). The various potash members are composed of halite,sylvite, sylvinite, and camallitite. The Prairie Evaporite Formation does not contain any M9S04 minerals (kieserite, polyhalite). It typically thins southward in the basin, is 200 m thick near Saskatoon, while it is only 140 m thick in the Rocanville area. It also thickens locally where carnallite, not sylvite, is the dominant potassium mineral. Most mines are located about the basin perimeter, the near dissolution edge of what was once a much more widespread evaporite sequence.

Within the Prairie Evaporite there are four main potash-bearing members, in ascending stratigraphic order they are: Esterhazy, White Bear, Belle Plain and Patience Lake members. Atypical sylvinite ore zone in the Patience Lake Member can be divided into six units (Figure 3d). The units are mappable and can be correlated across mines and regionally with varying degrees of success, dependent on partial or complete loss of section from dissolution. The halite matrix that hosts the sylvinite ore lacks well-defined primary textures (aligned chevrons and geopetals) and is atypical when compared with the well-preserved depositional textures in the adjacent nonore halite beds. This implies some sort of leaching and enrichment process was important in generating the potash ores. This leaching and remobilization of sylvite probably began syndepositionally and continued whenever the ore was flushed by basinal fluids (Lowenstein and Spencer, 1990; Boys 1993; Koeffier et al., 1997).

Potash purity in the vicinity of salt anomalies (also called leached beds or salt horses) is typified by five postburial facies (Figure 4). All are related to an influx of subsurface water that is undersaturated with respect to potash. These collapse structures in the ore zones act as conduits for overlying formation waters and drive pervasive leaching and

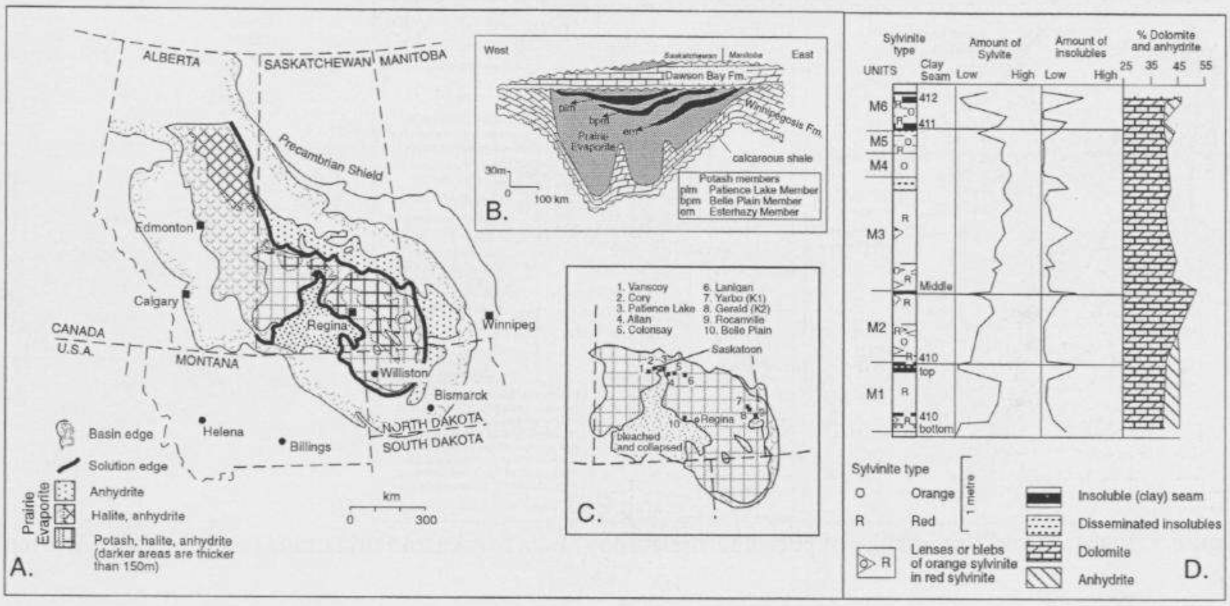

Figure 3. Potash distribution in the Elk Point Basin, Canada (after Worsley and Fuzesy, 1979; Fuzesy, 1982; Boys, 1993)

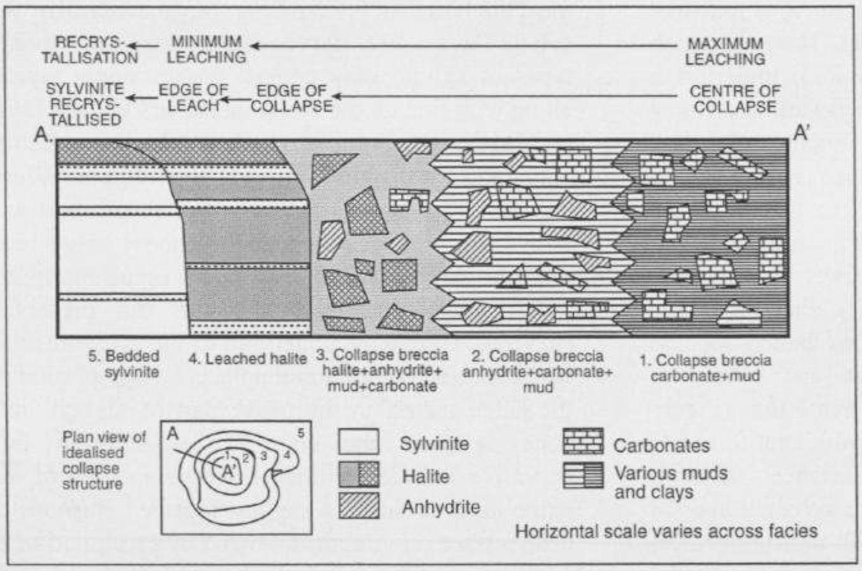

Figure 4. Idealised cross section through a collapse structure in the Prairie Evaporite showing sylvite remobilisation via fluid leaching (after Boys, 1993)

recrystallization of the Prairie Evaporite Formation while also forming salt anomalies. It is very likely that the same fluids that cause widespread recrystallization and possibly enrichment of the potash salts at the outer edge of the salt anomaly, can also dissolve huge cavities in the more central parts of the anomalies. It is also why the best ore zones are today located near the dissolution edge of the Prairie Evaporite. The effect of this postdepositional leaching is highly variable, with at least two major fluid influx events, possibly driven by uplift and tectonism: one occurred in the Late Devonian, the other in the Cretaceous.

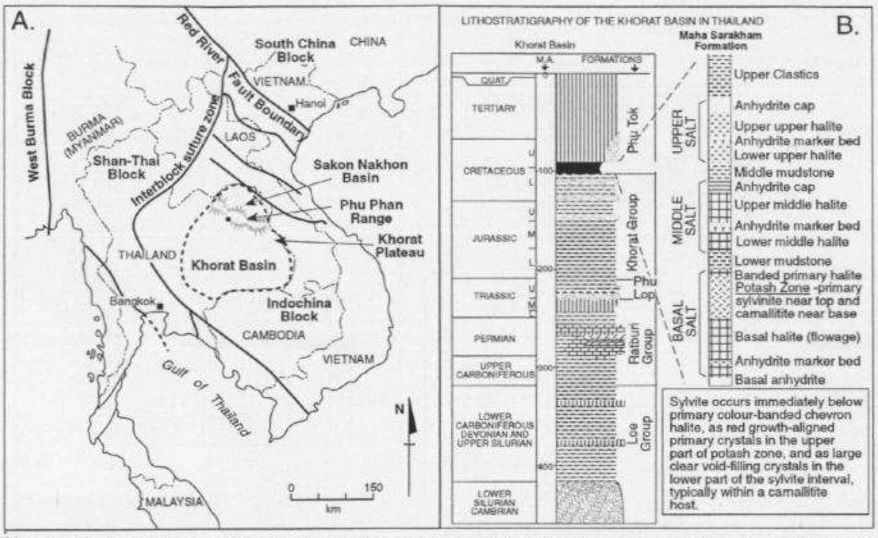

Figure 5. Location and stratigraphy of potash in Cretaceous Maha Sarakham Forination, Thailand, (after Warren, 1999)

Potash in Maha Sarakham Formation, Thailand

Potash in the Cretaceous Maha Sarakham Formation of Thailand occurs at the upper part of the Lower Salt Member and was deposited in a continental collision basin (Utha-aroon, 1992). The ore, which is dominantly sylvinite (0-6m thick), underlies a color banded halite (approx 6m thick) and sits atop a 15 to 30m thick carnallitite zone (Figure 5; Warren, 1999). Textures in the camallitite bed are identical to those karst-fill textures preserved in Lake Qaidarn (Figure 1). The carnallitite zone in rum sits atop massive to bedded halite of the Lower Salt Member (50-300m thick) with traces of carnallite. Halite crystals in the lower parts of this halite bed are flattened indicating salt flowage and pillowing, mostly in the lower part of this halite unit (Figure 6a-b). The sylvinite bed is regionally stratiforin but is not laterally continuousover distances of more than a few kilometres. Locally the sylvinite beds in the ore zone can dip up to 60-80' indicating local flowage and collapse of the sylvinite bed. At the transition between the camallitite and sylvinite zones some dissolution cavities are 25 cm across (in core) and can be filled with single clear sylvite crystals with a geopetal clay lining the base of the void. Higher in the sylvinite interval the sylvite tends to occur as stratiform primary layers showing subhorizontal bedding with textures near identical to those in the Mulhouse Basin. Each sylvinite bed ranges from 5 cm to 1 m thick. Individual aligned primary sylvite crystals in the stacked couplets within the bed may reach up to 2 cm in size, but most are less than 0.5 cm long. Macroscopically, the sylvite layers are not homogeneous and several types of sylvite may coexist within single layers, along with fine clastic components and halite. Halite beds altemating with sylvite layers in the sylvinite zone range in thickness from 1 cm to 15 cm. Where not destroyed by the processes of dissolution and recrystallization, NaCI crystals in these halite beds can still exhibit relict bedding and occasionally are milky white from inclusions in the preserved chevrons. Unlike the upper part of the sylvinite zone where chevrons are commonplace, a large portion of the halite matrix in the lower part of the sylvinite zone is clear and coarsely recrystallized into pervasive mosaic textures. Edge geometries of the halite in these mosaics suggest repeated episodes of near-surface dissolution followed by precipitation as passive void-fill cements. Seismic run in the vicinity of Khon Kaen clearly shows the pillowed nature of the Lower Salt member.

Seismic analysis, in combination with core textures, clearly shows that salt flow and solution controls sylvinite extent in the Khon Kaen area (Figure 6a-b). Sylvite ore fairways in this part of Thailand occur as sinuous trends located downdip of salt pillow crests, which were created by syndepositional salt flow and diagenesis of original stratiform camallitite. Pillows were deforming the carnallite zone and uplifting previously formed carnallite beds into a periodically freshened hydrological setting, while sylvite was precipitating on the pan floor and in karstic voids in the halite about the pan rim. The superimposed pillow hydrology was karstifying the halite at the same time that the upper portions of the carnallite member were dissolving and supplying K-rich brines to the adjacent pool floors. Brine pools were located atop subsiding rim synclines adjacent to the pillowing salt domes (Figure 6c; after Warren, 1999). The raising of the sedimentation surface, via pillowing, explains why sylvite in the lower sylvinite zone formed as clear coarse-crystal fills in large karst holes in the halite/ carnallite host, while sylvite in the upper sylvinite zone was a primary precipitate. That is in the early stages of uplift, prior to the formation of a perennial salt lake or pan, the raised camallitite unit was subject to karsting. Once the same area was buried beneath the sylvite pan it accumulated void-filling sylvite from cooling refluxing brine. At the same time, primary sylvite was accumulating above it on the pool floor as growth-aligned bottom nucleates and cumulates. When the rising pillow had dissolved the carnallitite bed from its top, only halite was dissolved. The cap of colour-banded primary halite was formed as this near monomineralogic feed brine flowed into the brine pool (Figure 6c; Warren, 1999).

In other words, the controls on the purity of Thai potash ore is both depositional and diagenetic with early salt flow controlling sylvinite purity with the thickest potentially exploitable sylvinite fairways lying in rim synclines adjacent to breached salt pillows. Sylvinite zones do not form laterally extensive horizons and, because of the effects of halokinesis, are not akin to the more extensive stratiform Devonian sequences of Canada.

SO WHAT CONTROLS PURITY?

The geology of potash and its purity evolves with time and burial. There are both depositional or diagenetic controls to sylvinite
ore purity and the textures must be examined petrographically to determine the timing and origin of the ore. Primary sylvite retains remnants of its crystallographic alignment. Most secondary sylvinite ore appears to retain evidence of having formed from a camallitite precursor.

Secondary potash enrichment in a thick halite host often occurs at an intrasalt unconformity or disconformity. This reflects an episode of brine fractionation and recrystallization related either to episodes of exposure and subaerial leaching/ concentration, or to episodes of subsurface flushing of the most soluble salts followed by their reprecipitation. In some deposits, such as the Maha Sarakham, near Khon Khan Thailand, the potash concentration process was aided by early synprecipitational salt flow and karsting.

Ore zones dominated by primary textures should tend to be more laterally predictable than those overprinted by burial effects. Primary ore zones appear to have formed in the most saline and topographically lowest part of the evaporite basin (at the time the ore was forming). In some basins this corresponds to its evaporite depocentre. In basins where the sylvinite ore shows a strong secondary overprint, it may be richest near a karstic margin on or near withdrawal sinks set up by synprecipitational ha lokinesis. Fluids mobilizing and enriching the potash may be meteoric or basinal. With diagenetic potash the high grade ore is typically not laterally continuous over kilometres. Hence, geological controls over ore purity must be understood and included in a mine model before any deposit can be profitably mined.

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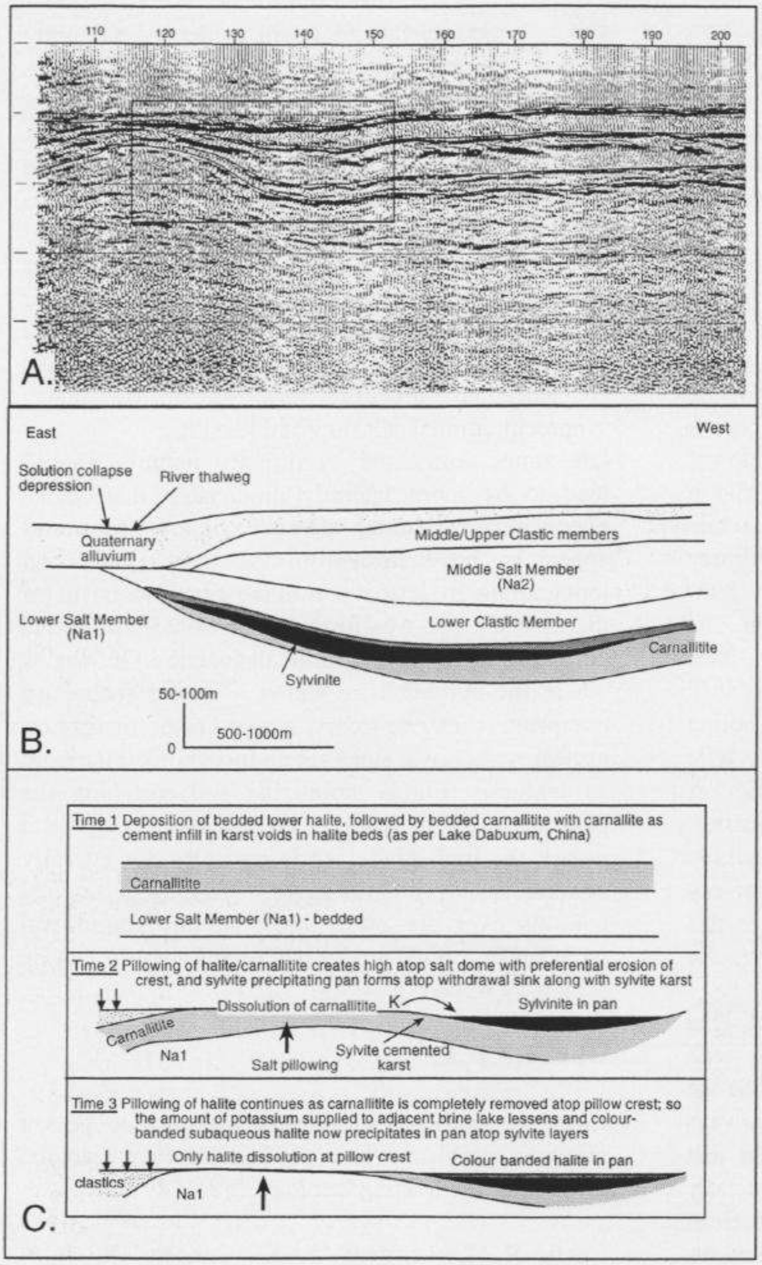

Figure 6. Maha Sarakhant Fm., Thailand. A) Seismic section in the vicinity of Khon Kaen. B) Interpretation of seismic shown in box in A. Q Evolution of sylvite ore section via potassic drainage off rising salt pillow prior to deposition of lower clastic member (see Figure 5bfor stratigraphy). After Warren, 1999.

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