Salty Matters

John Warren - Wed., November 30, 2016

Gases in Evaporites: Part 2 of 3: Nature, distribution and sources

This, the second of three articles on gases held within salt deposits, focuses on the types of gases found in salt and their origins. The first article (Salty Matters October 31, 2016) dealt with the impacts of intersecting gassy salt pockets during mining or drilling operations. The third will discuss the distribution of the various gases with respect to broad patterns of salt mass shape and structure (bedded, halokinetic and fractured)

What's the gas?

Gases held in evaporites are typically mixtures of varying proportions of nitrogen, methane, carbon dioxide, hydrogen, hydrogen sulphide, as well as brines and minor amounts of other gases such as argon and various short chain hydrocarbons (Table 2). There is no single dominant gas stored in salt across all evaporite deposits, although a particular gas type may dominate or be more common in a particular region. For example, CO_2 is commonplace in the Zechstein salts of the Wessen region of Germany (Knipping, 1989), methane is common in a number of salt dome mines in central Germany and the Five-Islands region in Louisiana, USA (Kupfer, 1990), nitrogen is dominant in other salt mines in Germany and New Mexico, while hydrogen can occur in elevated proportions in the Verkhnekamskoe salt deposits of the Ural foredeep (Savchenko, 1958).

Before considering the distribution of the various gases, we should note that older and younger sets of gas analyses conducted over the years in various salt deposits are not necessarily directly comparable. Raman micro-spectroscopy is a modern, non-destructive method for investigating the unique content of a single inclusion in a salt crystal. There is a significant difference in terms of what is measured in analysing gas content seeping from a fissure in a salt mass or if comparisons are made with conventional wet-chemical methods which were the pre Raman-microscopy method that is sometimes still used. Wet chemical methods require sample destruction, via crushing and subsequent dissolution, prior to analysis. This can lead to the escape of a variable proportion of

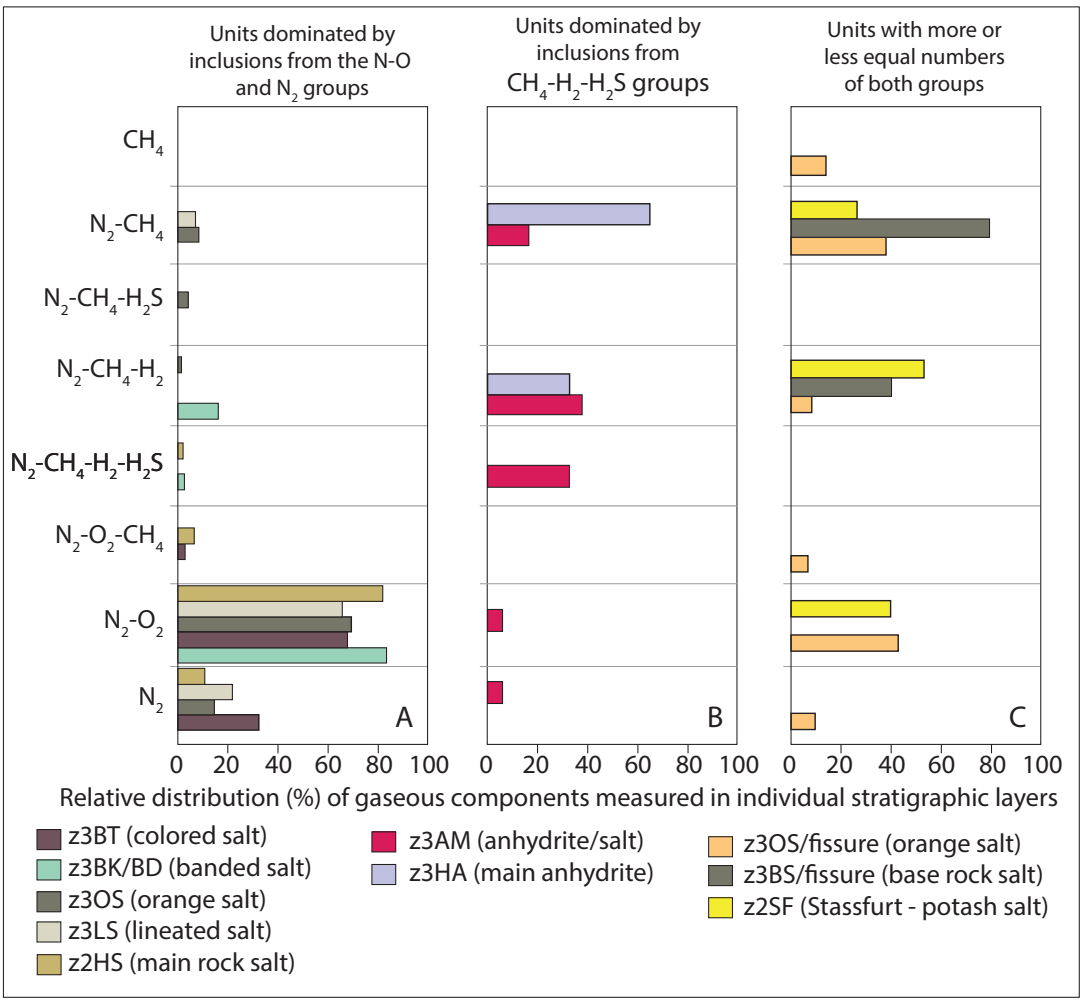


Figure 1. The relative distribution % of gaseous components in inclusions in salt as measured in individual stratigraphic layers (replotted from Siemann and Elendorff, 2001).

the volatile compounds during the crush stage, such as methane, hydrogen, ethane and aromatic hydrocarbons, especially of those components held in fissures and more open intercrystalline positions. Any wet chemical technique gives values that represent the average of all the inclusion residues and intercrystalline gases left in the studied sample, post preparation. In contrast, Raman Microspectroscopy indicates content and proportion within a single inclusion in a salt crystal. So, free gas results and wet chemical compositions, when compared to Raman microscopy determinations from inclusions, are not necessarily directly comparable. With this limitation in mind, let us now look at major gas phases occluded in salt.

Nitrogen

Gassy accumulations in salt with elevated levels of N2 occur in many salt basins in regions not influenced by magmatic intrusions (Table 1). In an interesting study of spectroscopic gases held in inclusions in the Zechstein salt of Germany, Siemann and Elendorff (2001) document a bipartite distribution of inclusion gases. With rare exceptions, the first group, made up of N_2 and N_2-O_2 inclusions reveals N_2/O_2 ratios close to that of modern atmosphere, which they interpret as indicating trapped paleoatmosphere (Figure 1). Similar conclusions are reached in earlier studies of nitrogen gas held in Zechstein salts, using wet chemical techniques (Freyer and Wagener, 1975). The second group documented by Sieman and Elendoorff (2001) is represented by inclusions that contain mixtures of N_2, CH_4 occasionally H_2 or H_2S. The most abundant subgroups in this second group are N_2-CH_4 and N_2-CH_4-H_2 mixtures, that is, the methane association (Figure 1). Siemann and Elendorff (2001) argue that these methanogenic and hydrogenic gas mixtures of the second group are the product of decomposition of organic material under anoxic subsurface conditions. They note that the methane and hydrogenic compounds, as well as some portion of the nitrogen, are not necessarily derived from decomposing organics held within the salt. They could have been generated by degassing of underlying Early Permian (Rotliegendes) or Carboniferous organic-rich sedimentary rocks with subsequent entrapment during early stages of fluid migration, possibly driven by Zechstein halokinesis.

Different origins and timings of both main nitrogen gas groupings in inclusions in the salt host is supported by stratigraphic correlations (Siemann and Elendorff, 2001). In the stratigraphic layers which contain mainly mixtures of N_2 and O_2 or pure N_2 inclusions of the Nv-CH_4-H_2-H_2S-group are rare (A in Figure 1) and vice versa: layers which are rich in N_2-4-H_2-H_2S do not contain many pure N_2-O_2inclusions (B in Figure 1). The majority of layers investigated in the salt mostly contain inclusions of the N_2-O_2 group, sans methane. Only two anhydrite-rich layers of Zechstein 3 (Main Anhydrite and Anhydrite-intercalated Salt) contain mainly inclusions of the second group (i.e. with abundant methane) as seen in B in Figure 1. The Zechstein 3 potash seams, as well as secondary halites, contain more or less the same population of inclusions from every main group (C in Figure 1). A comparison of the gas-rich inclusions and the gases in the brine-rich inclusions of the Zechstein 2 layer, Main Rock Salt 3, also shows distinct differences. Whereas, the

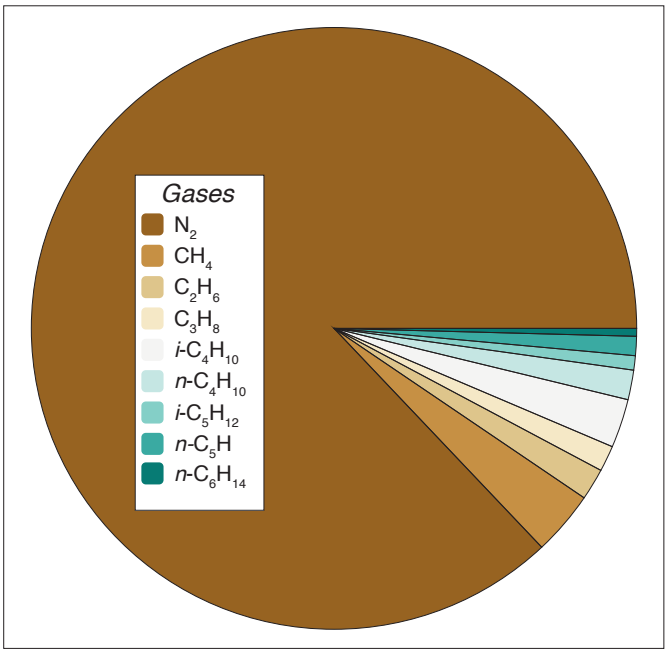


Figure 2. Composite of free gas compositions in Sylvinite Layer IV of Potash Horizon 3 in the Krasnoslobodsky Mine (Permian salt, Urals, after Andreyko et al., 2013)

gas-rich inclusions are mostly of the N_2-O_2 grouping, the gases from the brine-rich inclusions are mostly of the N_2-CH_{4d} group, emphasizing different origins for the gas-rich and brine-rich inclusions Siemann and Elendorff (2001) conclude that the latter gas group is a product of thermally evolved anhydrite-rich parts or potash seams that have generated hydrocarbons catagenically, with these products migrating into the overlying and deforming Main Rock Salt 3.

Work on the free gas released during mining of the Permian Starobinsky potash salt deposit in the Krasnoslobodsky Mine, Soligorsk mining region, Russia shows that the dominant free gas is nitrogen, along with a range of hydrocarbons, including methane (Figure 2; Andreyko et al., 2013). The compositional plot is based on free gases released from the main pay horizon of the Krasnoslobodsky Mine, which it the Potash Salt Horizon 3. The exploited stratigraphy is 16 to 18 m thick in the centre of the minefield and thins to 1 m thick at the edges of the ore deposit. Depth to the potash horizon varies from 477 to 848 m below the landsurface. It consists of three units: 1) top sylvinite unit, which is classified as non-commercial due to high insoluble residue content; 2) mid clay–carnallite unit, which is composed of alternating rock salt, clay and carnallite; and 3) bottom sylvinite unit, which is the main ore target and is composed of six sylvinite layers (I-VI), alternating with rock salt bands (Figure 3). The distribution of gas across the stratigraphy of units I-VI shows that the free gas yields are consistently higher in the sylvinite bands (Figure 3).

Oxygen levels in salt are not studied in as much detail as the other gas phases due to their more benign nature when released in the subsurface. Work by Freyer and Wagener (1975) focusing on the relative proportions of oxygen to nitrogen held in Zechstein salts was consistent with the inclusions retaining the same rela-

Well	Depth (m)	CO_2	N_2	CH_4	C_2H_4	C_2H_6	C_3H_8	SCO	H_2	H_2S	C-like	NH_4Cl	Oil
						Halite zones							
Siberia (average from 15 wells)	-	99.0	traces	traces						1.0	+	*no*	no
						Sylvinite zones in the vicinity of magmatic intrusions							
Nepa-7	927	*99.0*	*n.d.*	traces				*1.0*				*0.0*	yes
Nepa-13	698	99.7		0.1						0.2		0.0	no
		99.5	0.4							0.1			
	742	99.9								0.1			no
Nepa-116	937	96.8		1.7						1.5	+		no
		92.9		3.6						3.5	+		no
		97.7		1.3						1.0	+		no
		95.7		3.5						0.8	+		no
Nepa-185	1183	100.0									+		no
Nepa-194	839	54.4		43.4		0.9	1.3						no
	843	95.1	1.9	3.0		traces	traces						no
		23.0	6.5	89.3		0.6	0.6		0.6		+		no
	882		5.8	94.2	traces	traces	traces						aliphatics
	886			97.9	traces	0.5	1.6						no
Nepa-111	852	89.7		8.4						1.9	+	*0.0*	no
		91.5		6.4						2.1	+		
		92.8		5.6						1.6	+		
						Sylvinite zones with no magmatic intrusions in the drilling profile							
Zverevsk-1	832		6.3	93.7								*1.7*	no
			8.0	88.6		0.9	0.6		0.1			*0.3*	
			7.1	89.3		1.0	0.5		0.1				no
Nepa-154	843		22.6	73.7		2.3	0.9		0.5			*0.0*	no
			4.6	95.4									no
			15.5	85.5									no
Korshunovsk-3	917		98.2	1.1		0.3	0.4						aliphatics
			86.3	9.3		1.5	2.9						aliphatics
			74.5	11.2		3.8	10.6						aliphatics
	924		96.7	3.3								*0.3*	
			94.2	5.8								*0.0*	

Well	Depth (m)	CO_2	N_2	CH_4	C_2H_4	C_2H_6	C_3H_8	H_2	H_2S	C-like	NH_4Cl	Oil
						Other sylvinite intervals without magmatic intrusions (minor CO_2)						
Permian salts at Verhnekamsk (Russia) see also Anderyko et al., 2013			85.6	11.5		2.0	0.9					
			55.0	45.0							0.04	
			66.5	33.5							—	
		4.4	77.8	17.8						+	—	
		1.8	82.1	16.1						+	—	
		traces		100							0.4	aliphatics
Upper Eocene potassic salts (Spain) (Pironon et al., 1995)		2.5	74.2	23.0		0.3				+		
		3.9	77.0	18.8		0.3				+		
			87.0	13.0							0.3	

Table 1. Gas in inclusions in salt, mostly from Cambrian salt of Siberia, listed by well name, plus analyses of of Kungurian (Permian) salt of Urals foredeep and the upper Eocene of Spain. Listing is further divided based on the presence of absence of nearby magmatic intrusives (after Grishina et al., 1998).

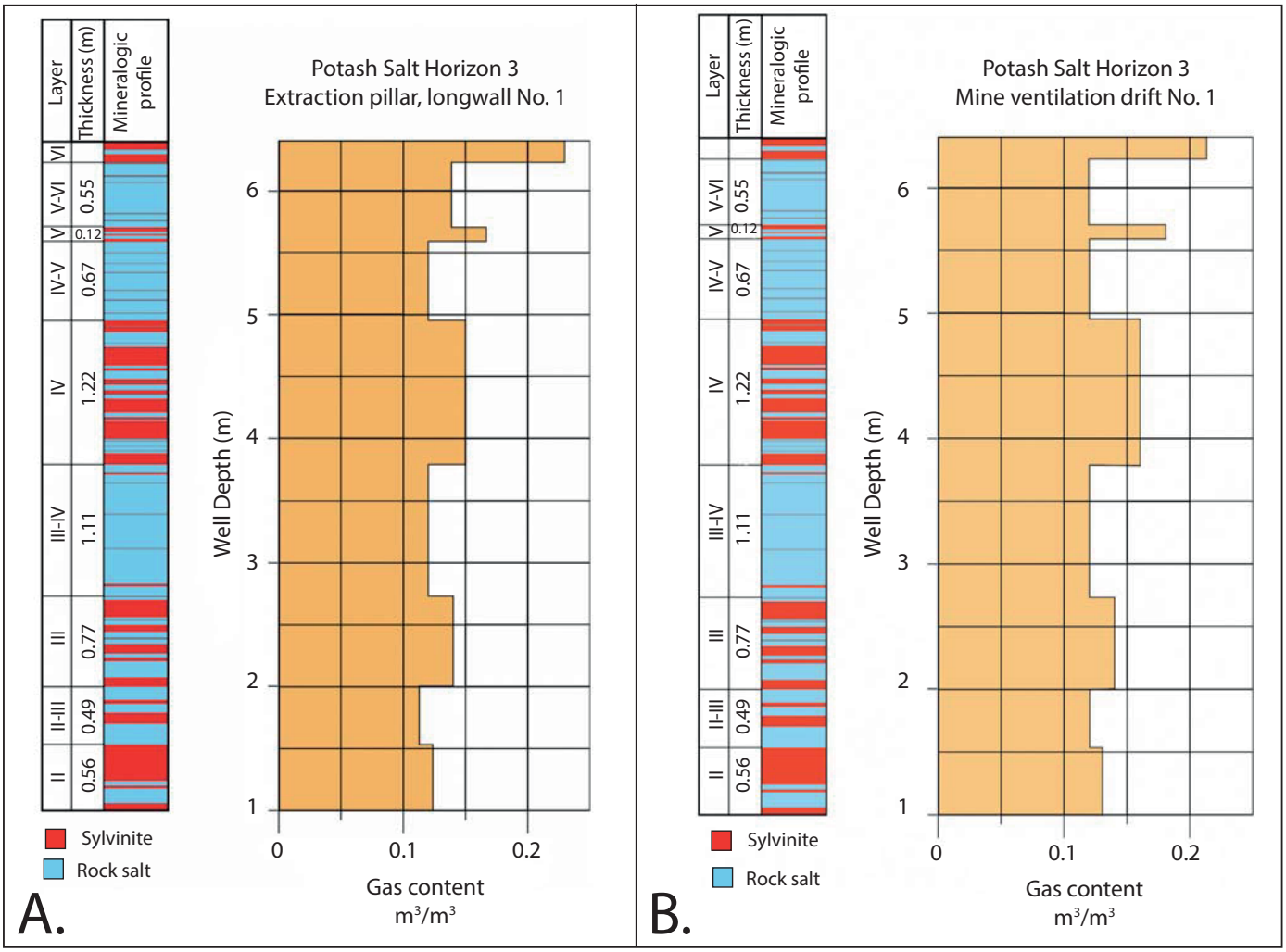


Figure 3. Gas content with repect to 2 measurement sites in the Krasnoslobodsky Mine (Permian salt, Urals, after Andreyko et al., 2013)

tive proportions of the two gases as were present in the Permian atmosphere when the salts first precipitated.

As well as being held within the salt mass, substantial nitrogen accumulations can be hosted in inter-salt and sub-salt lithologies. For example, the resources of nitrogen in the Nesson anticline in the Williston Basin are ≈53 billion m^3 and held in sandstones intercalated with anhydrite in the Permian Minnelusa Fm (Marchant, 1966; Anderson and Eastwood, 1968) and those in Udmurtia in the Volga–Ural Basin are ≈33 billion m^3 (Tikhomirov, 2014). In both these non-salt enclosed cases the evolution of the nitrogen gas is related to the catagenic and diagenetic evolution of organic matter. Tikhomirov (2014) concludes that nitrogen in the various subsalt fluids in the Volga–Ural Basin originates from two major sources. Most of the nitrogen in the subsalt has $\delta^{15}N > 0‰$ and is genetically related to concentrated calcium chloride brines, heavy oils, and bitumen in the platform portion of the basin and so ties to a catagenic origin. The other N2 source is seen in subordinate amounts of nitrogen across the basin with $\delta^{15}N$ values < 0‰. According to Tikhomirov (2014), this second group seems to be genetically related to methane derived at significant depths in the basement lithologies of Ural Foredeep and Caspian depression (possibly a form of mantle gas?).

Methane

Unexpected intersections with gas pockets containing significant proportions of methane can be dangerous, as evidence by the Belle Isle Salt Mine disaster in 1979 as well as others (see article 1). Many methane (earth-damp) intersections and rockbursts in US Gulf Coast salt mines can be tied to proximity to a shaley salt anomaly (Molinda 1988; Kupfer 1990).

Methane contents of normal salt (non-anomaly salt) in salt domes of the Five-Islands region of the US Gulf Coast were typically low (Kupfer, 1990). For example, the majority of the samples of normal salt, as tested by Schatzel and Hyman, (1984), contained less than 0.01 cm^3 methane per 100 g NaCI. Although there can be wide ranges of methane enrichment in normal versus outburst salts, outburst salts are typified by increases in halite crystal size, the number of included methane gas bubbles, contorted cleavage surfaces related to increased overpressured gas contents, and an increase in clay impurities in some of the more methane-rich salt samples.

Probably the most detailed study of controls on methane dis-

tribution in domal salt was conducted at the Cote Blanche salt mine in southern Louisiana (Molinda, 1988). Because outbursts were the primary mode of methane emission into the mine, he mapped more than 80 outbursts, ranging in size from 1 to 50 ft in diameter. The outbursts were aligned and elongate parallel to the direction of salt layering and such zones correlate well with high methane content (Figure 4). Halite crystal size abruptly increased upon entry into gassy zones subject to rockburst. The intensity of folding and kinking of the salt layering within the outburst zone also increased. The interlayered sand, shown in Figure 4, also occurred throughout the mine and not just in the mapped area shown, but was not a significant source of methane. Molinda (1988) and Schatzel and Hyman (188) all concluded that not all rockbursts were hosted by coarsely crystalline fine-grained salt, so the absence of coarsely crystalline salt may not be an indication that a rockburst cannot occur, although it is less likely. Sampling the salt for methane levels may be a better approach for rockburst prediction.

In some methane occurrences in Europe (in addition to generation from clayey intrasalt organic entraining bands) there is a further association with igneous-driven volatilization from nearby, typically underlying, coaly deposits. This igneous association with coals and carbonates likely creates an additional association with CO_2 and possibly H_2S.

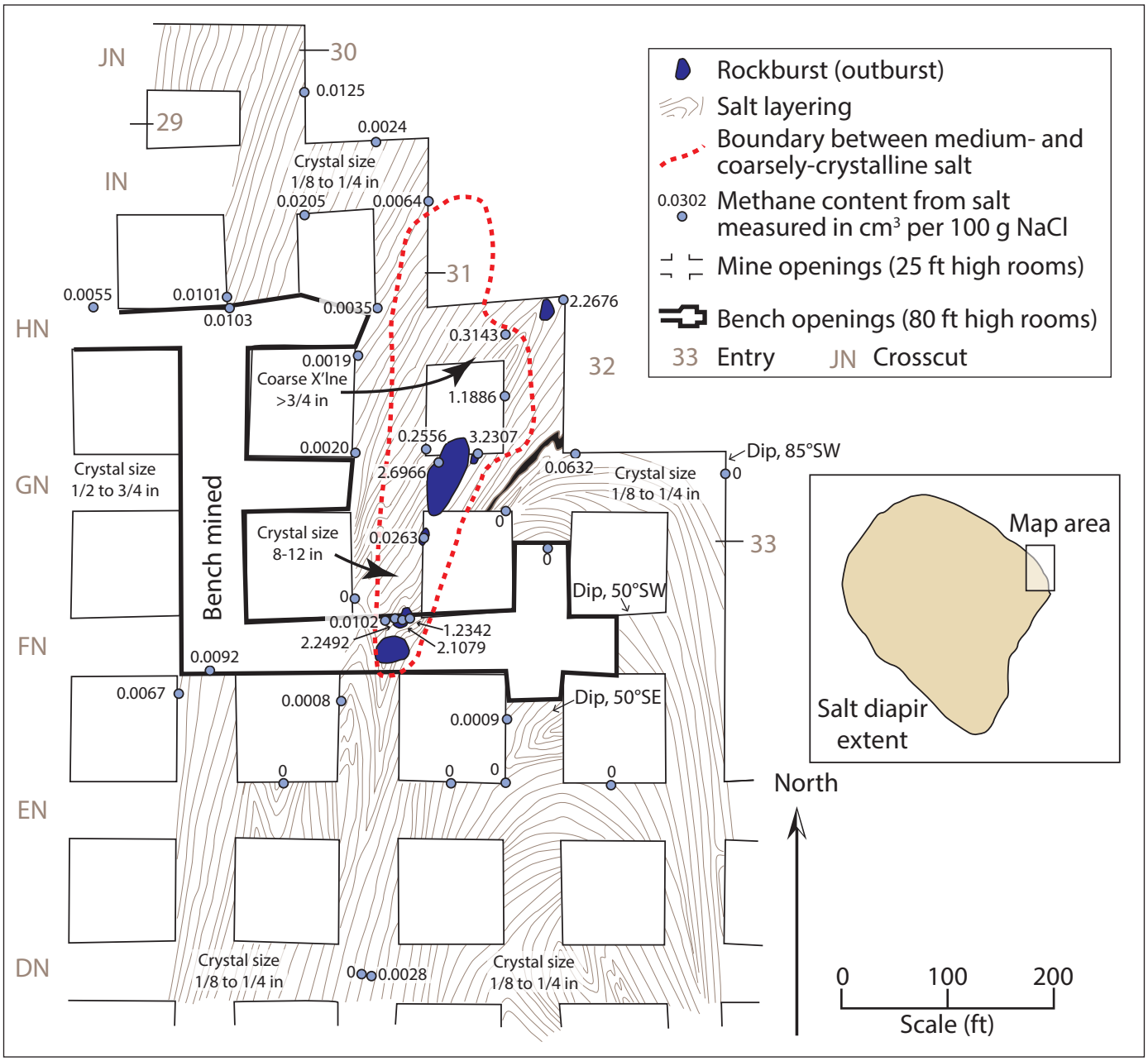
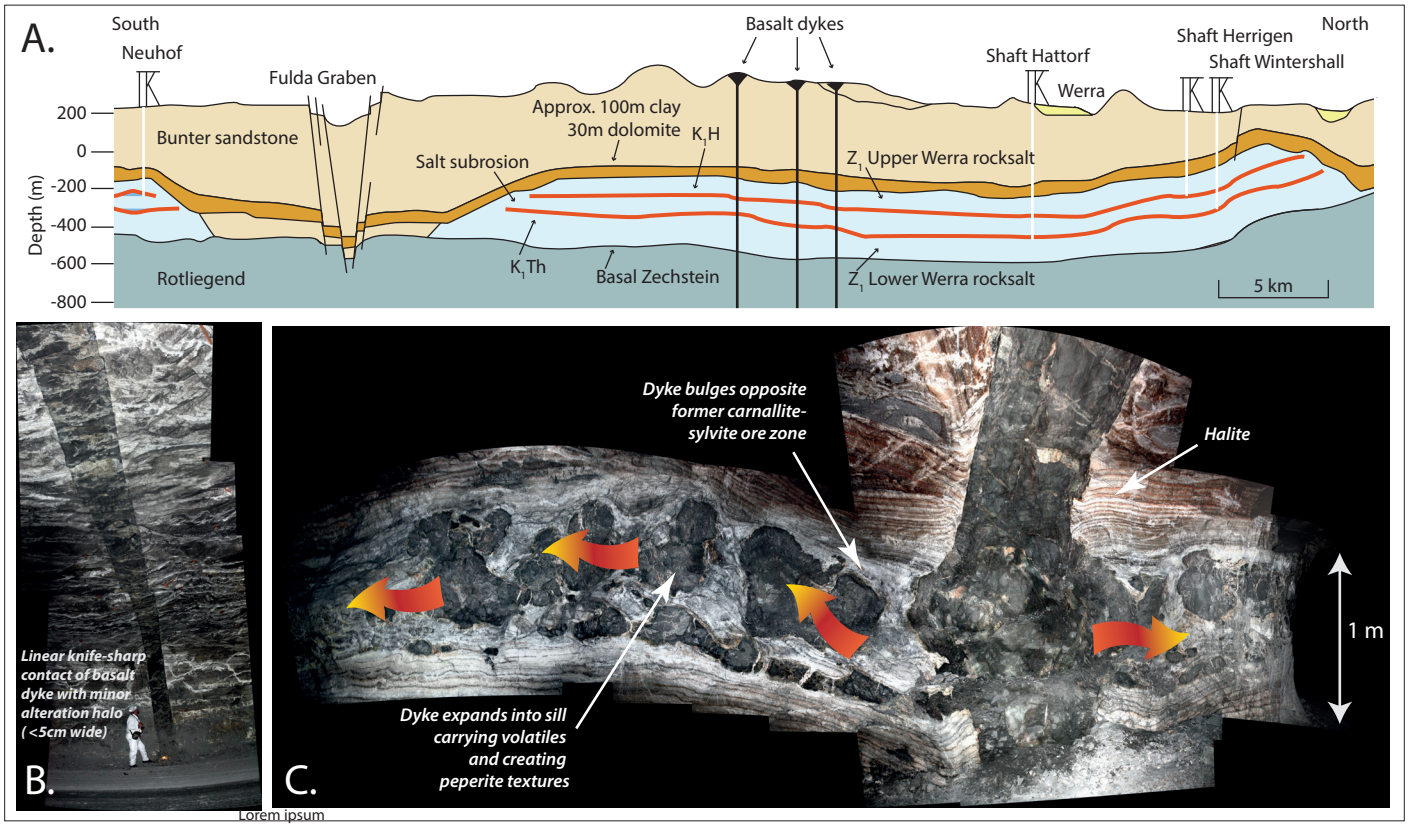


Figure 4. Cote Blanche salt mine, Louisiana. Detailed map showing a relationship between coarse halite crystal size, increased methane content in the salt and rockburst occurrences (Note this part of the former salt mine was located near the edge of the salt dome (after Molinda, 1988).

CO_2

Many CO_2-rich gas intersections tie to regions that have been heated or cross-cut with igneous intrusives. For example, many of the CO_2-bearing gas mixtures that were encountered in the Werra region during the initial exploratory drillings for potash salts(Table 1 in article 1; Frantzen, 1894). In 1901, shortly after mining at Hämbach had begun, coincident intersections of basalt dykes and releases of gas were observed (Gropp, 1919). Dietz (1928a,b) noted that a fluid phase was always involved in the fixation of the CO_2gas mixtures in the Zechstein evaporites, while Bessert (1933) reported on the enrichment of anhydrite, kainite, and polyhalite at the contact with the basaltic intrusive. Accumulations of CO_2-rich free gas in many Wessen mines became a safety issue and many subsequent studies underlined the association of CO_2 enriched gases with basalt occurrences (Knipping, 1989). In almost all instances in the Zechstein where native sulphur forms the at the contact of a basaltic dyke, knistersalz dominates the evaporite portion of the samples. According to Ackermann et al. (1964) gas-bearing drill core samples collected in the Zechstein K_1Th unit (carnallitite, sylvinite) in the Marx-Engels mine (formerly Menzengraben, East Germany) contained up to 0.6 - 14.0 ml gas/100 gm rock, with an average of 3.6 ml of gas fixed in 100 g of salt rock (Table 1)of. On average, the gas inclusions were composed of 84 vol% CO_2. Knipping (1989) concludes that quantities of volatile phases (mainly H_2O and CO_2) penetrated the evaporites during intrusion of basaltic melts. These gases influenced mineral reactions, particularly when intersecting with reactive K-Mg rock layers of the Hessen (K_1H) and Thuringen (K_1Th) potash seams in the former East Germany. The intensity of this reaction was likely greater when the evaporite layers contain hydrated salts such as carnallite and kainite. Such salts tend to release large volumes of water at relatively low temperatures when heat by a nearby intrusive (Warren, 2016; Chapter 16; Schofield et al., 2014). In doing so, significant volumes of CO2 enriched gases were trapped in the altered and recrystallising evaporites, so forming knistersalz.

While discussing CO_2 elevated levels, it is probably taking a little time to illustrate what makes this area of CO_2 occurrence so interesting in terms of the differential levels of reactivity when hydrated versus non-hydrated salt units are intruded and how this process facilitates penetration of volcanic volatiles (including CO_2) into such zones. The Herfa-Neurode potash mine is located in the Werra-Fulda Basin in the Hessian district of central Germany (Figure 5a). The targeted ore levels consist of the carnallite-rich Kaliflöz Hessen (K_1H) and Kaliflöz Thüringen (K1Th) intervals, which form part of the Zechstein 1 (Z1) bedded Werra salt succession(Warren, 2016). In the mine the K_1H and K_1Th units range in thickness from 2 m to 10 m, are generally subhorizontal and occur at a depth of 650–710 m below the present-day surface. In the later Tertiary, basaltic melts intruded these Zechstein evaporites as numerous sub-vertical dykes, but only a few dykes attained the Miocene landsurface. Basaltic melt production was related to regional volcanic activity some 10 to 25 Ma. Basalts exposed in the mine walls, where it cuts non-hydrous units of halite or anhydrite, are typically subvertical dykes, rather than subhorizontal sills. The basalts are phonolitic



Lorem ipsum

Figure 5. Influence of Tertiary basalt dyke intrusions on volatile distribution in Zechstein evaporites in the Fulda region, Germany. A) Geological cross section. B) steeply inclined dyke in laminated halite showing knife-sharp contacts. C) Near vertical dyke showing knife-sharp contacts opposite layered halite and alteration bulges extending tens ot hundreds of metres as peperite sill into level of former ore zone (see Schofield et al, 2014 for detail)

tephrites, limburgites, basanites and olivine nephelinites. Dyke margins are usually vitrified, forming a microlitic limburgite glass along dyke edges in contact with salt (Figure 5b; Knipping, 1989). At the contact on the evaporite side of the glassy rim there is a cm-wide carapace of high-temperature salts (mostly anhydrite and ferroan carbonates). Further out, the effect of the high-temperature envelope is denoted by transitions to clear halite, with higher temperature fluid inclusions (Knipping 1989). All of this metre-scale alteration is an anhydrous alteration halo, the salt did not melt (melting temperature of 804°C), rather than migrating, the fluid driving recrystallisation was largely from entrained brine/gas inclusions. The dolerite/basalt interior of the basaltic dyke is likewise altered and salt soaked, with clear, largely inclusion-free halite typically filling vesicles in the basalt.

Heating of hydrated salt layers, adjacent to a dyke or sill, tends to drive off the water of crystallisation (chemical or hydration thixotropy) at much lower temperatures than that at which anhydrous salts, such as halite or anhydrite, thermally melt (Figure 5c; Schofield et al., 2014). For example, in the Fulda region, the thermally-driven release of water of crystallisation within particular salt beds creates thixotropic or subsurface "peperite" textures in carnallitite ore layers. These are layers where heated water of crystallisation escaped from the hydrated-salt lattice. Dehydration-driven loss of mechanical strength focuses zones of magma entry into particular subhorizontal horizons in the salt mass, wherever hydrated salt layers were present. In contrast, dyke and sill margins are much sharper and narrower in zones of contact with anhydrous salt intervals and the intrusive is sub-vertical to steeply dipping (Figure 5b versus 5c).

Accordingly, away from the immediate vicinity of the direct thermal aureole, heated and overpressured dehydration waters can enter a former carnallite halite bed, and drive the creation of extensive soft sediment deformation and peperite textures in the former hydrated layer (Figure 5c). Mineralogically, sylvite and coarse recrystallised halite dominate the salt fraction in the peperite intervals of the Herfa-Neurode mine. Sylvite in these altered zone is a form of dehydrated carnallite, not a primary-textured salt. Across the Fulda region, such altered zones and deformed units can extend along former carnallite layer to tens or even a hundred or more metres from the dyke feeder. Ultimately, the deformed potash bed passes back out into the unaltered bed, which retains abundant inclusion-rich halite and carnallite (Schofield et al., 2014). That is, nearer the basalt dyke, the carnallite is largely transformed into inclusion-poor halite and sylvite, the result of incongruent flushing of warm saline fluids mobilised from the hydrated carnallite crystal lattice as it was heated by dyke emplacement. During Miocene salt alteration/thermal metamorphism in the Fulda region, NaCl-fluids were mixed with fluids and gases originating from thermally-mobilised crystallisation water in the carnallite, as it converted to sylvite. This brine/gas mixture altered the basalts during post-intrusive cooling, an event which numerical models suggest was quite rapid (Knipping, 1989): a dyke of less than 0.5 m thickness probably cooled to temperatures less than 200°C within 14 days of dyke emplacement. The contrast in alteration extent between anhydrous and hydrous salt layers shows alteration effects are minimal wherever the emplacement temperature of the magma is below that of the anhydrous salt body as it is next to a basalt dyke. If this is the mechanism driving entry of igneous-related volatiles (gases and liquids) into a salt body then the distribution of products (including $CO2_2$) will be highly inhomogeneous and related to the minerally of the salt unit adjacent to the intrusive.

Hydrogen

Many hydrogen occurrences are co-associated with occurrences of potash minerals, especially the minerals carnallite and sylvite. For example, mine gases (free gas) at Leopoldshall Salt Mine (Zechstein, Permian of Stassfurt, Germany) flowed for at least 4.5 years, producing hydrogen at a rate of 128 cubic feet per day (Rogers 1921). Bohdanowicz (1934) lists hydrogen gas as being present in evaporite intersection in the Chusovskie Gorodki well, drilled in 1928 near the city of Perm to help define the southern extent of the Soligamsk potash. Gases in the carnallitite interval in that well contained 33.6% methane and 17.4% hydrogen. More recent work in the same region clearly shows hydrogen is a commonplace gas in the mined Irenskii unit in the Verkhnekamskoe potash deposit within the central part of the Solikamsk depression in the Ural foredeep. Based on a study of free gas and inclusion-held gas in the Bereznikovshii Mine, Smetannikov (2011) found that the elevated H_2 levels are consistently correlated with the carnallite and carnallite-bearing layers (Table 2). Other gases present in significant amounts, along with the hydrogen, in the potash zones include nitrogen and methane. Interestingly, methane is present in much higher proportions in the free gas fraction in the ore zones compared to gases held in inclusions in the potash crystals (Table 2).

Smetannikov (2011) goes on to suggest that likely H_2 source is via radiogenic evolution of released crystallisation water hence the higher volumes of hydrogen in the carnallitite units in the mine (Table 2). He argues the most probable mechanism generating H2 is the radiolysis of the crystallisation water of carnallite (CaMgCl3.6H2O) driven by the effects of radioactive radiation. The most likely radiogenic candidates are ^{40}K and ^{87}Rb, rather than such heavy radiogenic isotopes as ^{238}U, ^{235}U, ^{234}U, ^{232}Th, and ^{226}Ra. His reasons for this are as follows: 1) U, Th, and partly Ra are sources of α radiation. U, Th, and Ra are concentrated in the insoluble residues of the salts, and the chloride masses contain only minor amounts of Th. Hence these components have no radioactive effect on carnallite because of the short distances of travel of α particles. Because of this, Smetannikov concludes these elements and not likely sources of radioactive radiation. He argues it is more likely that crystallisation water is more intensely affected by β and γ radiation generated by ^{40}K and ^{87}Rb. Hence, bombardment by β and γ radiation drives the radiolysis (splitting) of this water of crystallisation, so driving the release of hydrogen and hydroxyls. Free hydroxyls can then interact with Fe oxides to form hydro-goethite and lepidocrocite, i.e., both these minerals occur in the carnallite but are absent in the sylvinite.

The notion of hydrogen being created by radiolysis of potash salt layers is not new; it was used as the explanation of the hydrogen association with various potash units by Nesmelova & Travnikova (1973), Vovk (1978) and Knape (1989). Headlee

Average composition (vol %) of gas in microinclusions in crystals in the Bereznikovskii mine (extracted from Smetannikov, 2011)

Bed	$CO_2 + H_2S$	CH_4 + higher homologues	H_2	N_2 + i	Ar + Kr + Xe	Ne + He
Carnallite C (carnallitite)	22.0	7.0	32.6	38.3	0.954	0.003
Sylvinite C	14.5	1.9	4.6	78.5	n.a.	n.a.
Single-crystal sylvinite blocks	10.3	1.6	1.1	87.0	0.360	0.001
Bed B (carnallitite)	12.7	1.2	2.9	83.4	0.322	0.003
Bed A (banded sylvinite)	5.5	1.9	3.3	89.2	0.476	0.001
Bed RII (sylvinite)	7.1	5.3	9.6	85.6	1.724	0.001

Average composition (vol %) of free gases in the Bereznikovskii mine (extracted from metannikov, 2011)

Bed (dominant mineralogy)	$CO_2 + H_2S$	CH_4	C_2H_6 + higher homologues	H_2	N_2 + i	Ar + Kr + Xe	Ne + He
Carnallite C (carnallitite)	0.06	31.0	3.8	7.8	57.5	0.077	0.003
Bed B (carnallitite)	0.50	33.2	7.5	0.0	45.4	0.180	0.004
Bed A (banded sylvinite)	0.75	43.1	10.5	0.0	45.8	0.182	0.007
Bed RII (sylvinite)	0.00	31.4	13.3	0.0	55.0	0.196	0.008

Table 2. Gas compositions in the units dominated by potash salts in the Berenikovskii Mine (Permian, Urals foredeep). The analysis clearly shows how free gas and inclusion gas compositions can vary - Methane is the principal gas in the free gas, nitrogen and hydrogen are the dominant gases held in inclusions in the potash minerals in the same layers.

(1962) attributed the occurrence of hydrogen in salt mines to the absence of substances with which hydrogen could react within the salt beds once it was generated. It is likely that there are several different origins for hydrogen gas in evaporites: 1) Production during early biodegradation of organic matter, co-deposited with the halite or potash salts and trapped in inclusions as the crystal grew. This can explain some of the associated nitrogen and oxygen; 2) A significant proportion can be produced by radiolysis associated with potassium salts (when present) and 3) the hydrogen may be exogenic and have migrated into the halite formations, along with nitrogen.

Temperature and mineralogical effects on gas generation and distribution in salt (in part after Winterle et al., 2012)

Temperature can affect brine chemistry of volatiles released as natural rock salt is heated (is this an analogue to the generation of some types of free gas and other volatile released as salt enters the metamorphic realm? –see Warren 2013; Chapter 14). Uerpmann and Jockwer (1982) and Jockwer (1984) showed that, upon heating to 350°C [662°F], the gases H_2S, HCl, CO_2, and SO2 were released from blocks of natural salt collected from the Asse mine in Germany. Pederson (1984) reported the evolution of HCl, SO_2, CO_2, and H_2S upon heating of Palo Duro and Paradox Basin rock salt to 250°C [482°F]. Impurities within the salt apparently contain one or more thermally unstable, acidic components. These components can volatilize during heating and increase the alkalinity of residual brines. For example, pH of brines increased from near neutral to approximately 10 in solutions prepared by dissolving Permian Basin salt samples that were annealed at progressively higher temperature [up to 167°C [333°F] (Panno and Soo, 1983).

Zones of igneous emplacement and intrusion of interlayered halite and potash units create a natural laboratory for the study of the generation and migration of free and inclusion gases during the heating of various salts (Figures 5, 6 and Table 1). In the Cambrian succession of the Siberian platform evaporite intervals are dominated by thick alternating carbonate- sulphate and halite beds. Numerous basaltic dykes and sills intrude these beds. In a benchmark paper dealing with the zone of alteration of intrusives in evaporites, Grishina et al. 1992 found that, in potash-free halite zones intersected by basaltic intrusions, the evolution of the inclusion fluid chemistry is described as a function of the thickness of the intrusion (h) and the distance of the sample from the contact with the intrusion (d) and expressed as a response to the measure d/h. The associated gas in the halite is dominated by CO_2 (Table 1). Primary chevron structures with aqueous inclusions progressively disappear as d/h decreases; at d/h < 5 a low-density CO_2 vapour phase appears in the brine inclusions; at d/h < 2, a H_2S-bearing liquid-CO_2 inclusions occur, sometimes associated with carbonaceous material and orthorhombic sulphur, and for d/h < 0.9, $CaCl_2$, $CaCl_2$.KCl and n $CaCl_2$.n$MgCl_2$ solids occur in association with free water and liquid CO_2 inclusions, with H_2S, SCO, and Sg. The d/h values marking the transitions outlined above occur both above and below sills, but ratios are lower below the sills than above, indicating mainly conductive heating below and upward vertical fluid circulation above the sill. The water content of the inclusions progressively decreases on approaching the sills, whereas their

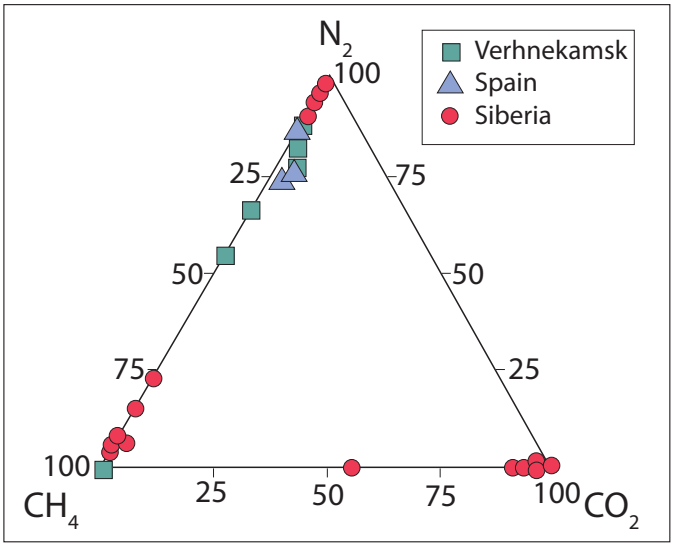


Figure 6. Ternary diagram showing gas composition deduced from Raman analyses of the inclusions of Siberia, Verhnekamsk and Spain (in mol%), deduced from Raman analyses (Tables I, 2 ; after Grishina et al., 1998).

CO_2 content and density increase.

Carnallite, sylvite and calcium chloride salts occur as solid inclusions in the two associations nearest to the sill for d/h<2. Carnallite and sylvite occur as daughter minerals in brine inclusions. The presence of carbon dioxide is interpreted to indicate fluid circulation and dissolution/recrystallization phenomena induced by the basalt intrusions. The origin of carbon dioxide is related to carbonate dissolution during magmatism. Similar conclusions as to the origin of the CO_2 in heated halite-dominant units were reached by many authors studying gases in the Zechstein salts in the Werra Fulda region of Germany (Figure 6; Table 1; see Knipping et al., 1989, Hermann and Knipping 1993 for a summary).

When the gas distributions measured in inclusions in potash units, other than the Cambrian salts of Siberia, are compared to those salts that have not experienced the effects of igneous heating, there is a clear separation in terms of the dominant inclusions gases (Table 1; Grishina et al., 1998). For example, inclusions in the Verhnekamsk deposit (Russian platform) are N_2-rich, in regions not influenced by magmatic intrusives (Figure 2, 3). It is an area marked by the presence of ammonium in sylvite (0.01-0.15% in sylvinite and 0.5% in carnallite, Apollonov, 1976). Likewise, nitrogen (via crush release of the samples) is the dominant gas according to the bulk analyses of the same salts by Fiveg (1973).

Later Raman studies of individual inclusions in these Cambrian salts reveals a more complicated inclusion story. There are three types of inclusion fill; a) gas, b) oil and c) brine + carnallite-bearing inclusions. Fe-oxides are sometimes associated with inclusions containing the carnallite daughter minerals. Detailed work by Grishina et al. (1998) shows there two kinds of gassy inclusion: 3) N_2-rich and 2) CH_4-rich 3) CO_2-rich in the same age salt (Table 1; Figure 6). That is, not all gassy brine inclusion in the Cambrian salts are nitrogenous. N_2 gas inclusions that also contain CO2 and are associated with sylvite with a low ammonium content (0.04 mol% NH4C1). In contrast, CH_4 inclusions are associated with ammonium-rich sylvite (0.4 mol% NH_4Cl) (Table 2). Older bulk analysis studies(Apollonov, 1976) showed that red sylvinite has a lower molar NH_4Cl content (0.01%) than pink and white sylvinites (0.05 to 0.19%)

Raman studies of inclusions in the potash-entraining Eocene basin of Navarra, (Spain) outside of any region with magmatic influence show that the gaseous inclusions are mostly N_2-rich with 10% to 20% methane (Table 1; Figure 6; Grishina et al., 1998). Traces of CO_2 are also detected in some of the Spanish inclusions. Sylvite inclusions in CO_2-free inclusions in Spain contain up to 0.3 mol% NH_4Cl (Table 2). Grishina et al. (1998) notes that salt formations in the Bresse basin (France) and Ogooue delta (Gabon) have no basalt intrusions and both occur in N2-free, oil-rich environments. The inference is that nitrogen in some salt units is not an atmospheric residual.

To test if there may be a mineralogical association with a gas composition in inclusions in various salt and evaporitic carbonate layers we shall return to the Zechstein of Germany and the excellent detailed analytical work of Knipping (1989) and Hermann and Knipping (1993). This work is perhaps the most detailed listing in the public realm of gas compositions inclusions sampled down to the scale of salt layers and their mineralogies. Figure 7 is a plot I made based on the analyses listed in Table 9 in Hermann and Knipping (1993). It clearly shows that for Zechstein salts collected across the mining districts of central Germany this is an obvious tie of salt mineralogy to the dominant gas composition in the inclusions. In this context, it should be noted that all Zechstein salt mines are located in halokinetic structures with mining activities focused into areas where the targeted potash intervals are relatively flat-lying. There is little preservation of primary chevrons in these sediments. Nitrogen is the dominant, often sole gas in the halite-dominant units, CO_2 is dominant in carbonate and anhydrite dominant layers, this is especially obvious in units originally deposited near the base of the Zechstein succession. Hydrogen in small amounts has an association with inclusions the same carbonates and anhydrites, but elevated hydrogen levels are much more typical of potash units, clays and in juxtaposed layers.

In my opinion, the gas compositions in inclusions that we see today in any salt mass that has flowed at some time during its diagenetic history will likely have emigrated and been modified to varying degrees within the salt mass. This is true for all the gases in salt, independent of whether the gas is now held in isolated pockets, fractures or fluid inclusions, Non of the gas in halokinetic salt is not in the primary position. Movement and modification of various gas accumulations in halokinetic salt is inherent to the nature of salt flow processes. Salt and its textures in any salt structure have migrated and been mixed and modified, at least at the scale of millimetres to centimetres, driven by vagaries of recrystallisation as a flowing salt mass flows (Urai et al., 2008). All constituent crystal sizes and hence gas distributions across various inclusions in the salts are modified via flow-induced pressure fields, driving pressure solution and reannealing (See Warren 2016 Chapter 6 for detail).

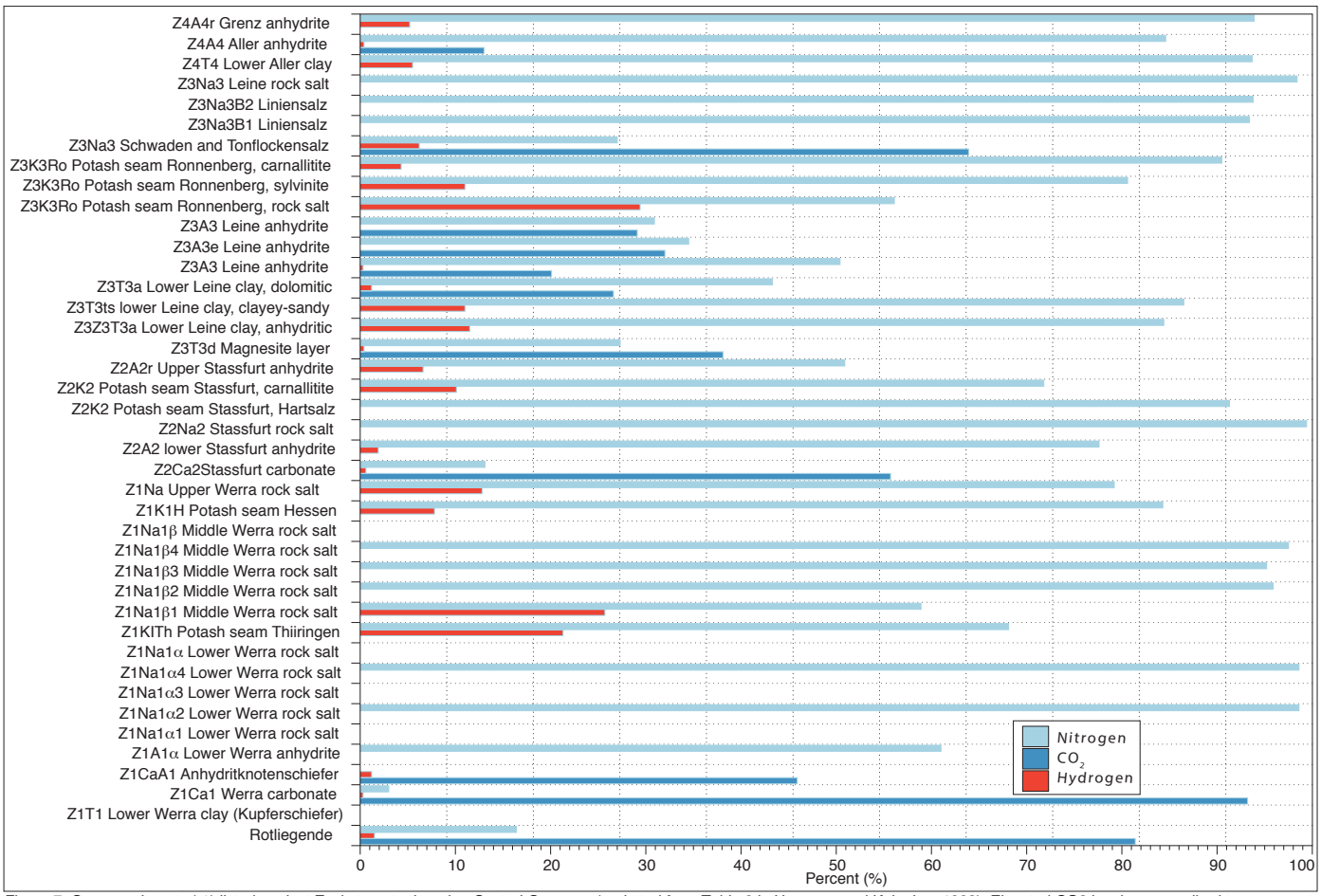


Figure 7. Gas constituents (%) listed against Zechsten stratigraphy, Central Germany (replotted from Table 9 in Hermann and Knipping, 1993). Elevated CO2 levels are ascribed to a magmatic source.

With this in mind we can conclude that for the Zechstein of central Germany, nitrogen was likely the earliest gas phase as it occurs in all units. On the other hand, CO_2, with its prevalence in units near the base of the succession or in potash units that have once contained hydrated salts at the time of igneous intrusion, entered along permeability pathways. This may also be true of carbonates and anhydrites which would have responded in more brittle fashion. Hydrogen is clearly associated with potash occurrence or clays and an origin via radiolysis is reasonable.

This leaves methane, which as we saw earlier is variable present in the Zechstein, but not studied in detail by Knipping (1989) or Hermann and Knipping (1993). There is another excellent paper by Potter et al. (2004) that focuses on the nature of methane in the Zechstein 2 in a core taken in the Zielitz mine, Northeastern Germany Bromine values show a salting-upward profile with values exceeding 200 ppm in the region of potash bitterns (Figure 8a). This is a typical depositional association, preserved even though textures show a degree of recrystallisation and implying there have not been massive fluid transfers since the time the salt was first deposited. Methane is present in sufficient volumes to be sampled in the lower 10 metres of the halite (Z_2NA_a) and in the upper halite (Z_2N_{ac}) and the overlying potash (Z_2K_{st}). If was variably present in the intervening middle halite. When carbon and deuterium isotope values from the methane in the lower and upper parts of the stratigraphy are cross plotted. Values from the lower few meters of the halite plot in the thermogenic range and imply a typical methane derived via catagenesis and possible entry into the lowermost portion of a salt seal. The values from the upper halite and the potash interval have very positive carbon values so that the resulting plot field lies outside that typical of a variety of methane sources (Figure 8b). Potter et al. (2004) propose that these positive values show preserve primary values and that this methane was sealed in salt since the rock was first deposited. That is positive values preserve evidence of the dominant isotopic fractionation process, which was evaporation of the mother brines. This generated a progressive ^{13}C enrichment in the carbon in the residual brines due to preferential loss of $^{12}CO_2$ to the atmosphere. The resulting CH_4 generated in the sediments, as evaporation and precipitation advanced, so recording this 13C enrichment in the carbon reservoir. Therefore, the isotopic profile observed in this sequence today represents a relict primary feature with little evidence for postdepositional migration. This is a very different association to the methane interpretation based on gases held the US Gulf coast or the Siberian salts.

The most obvious conclusion across everything we have considered in this article is that, at the level of gas in an individual brine inclusion measure, there is not a single process set that explains

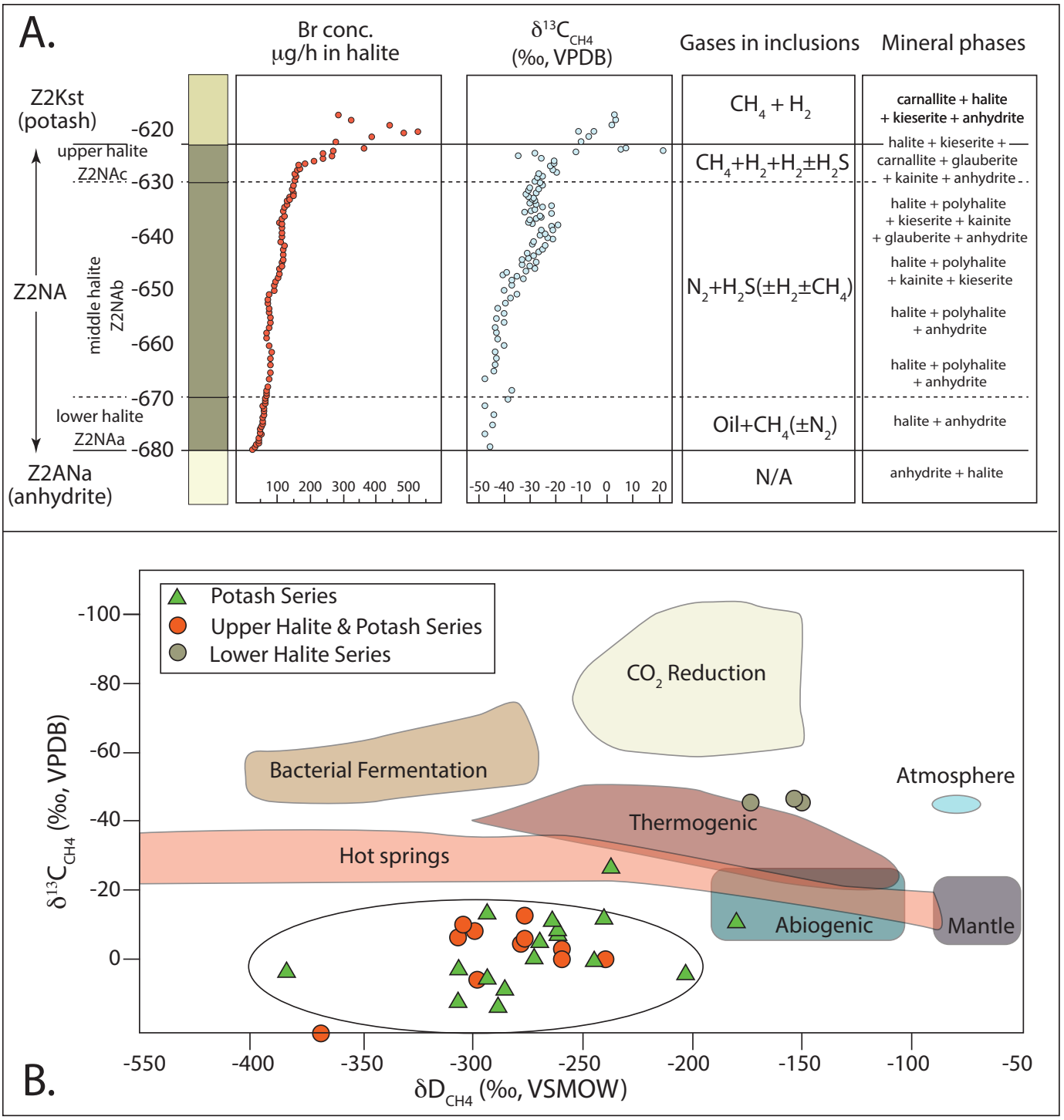


Figure 8. Methane in the Zechstein 2, core from Zeilitz Mine, NE Germany. A) Bromine levels and CH4 carbon isotope results plotted against depth (metres below sea level) for grain-boundary gases. Mineral phases: anhydrite ($CaS0_4$), halite (NaCl), polyhalite [$K_2MgCa_2(S0_4)_4.2H_20$], kainite ($KMgClS0_4 2.75H_20$), kieserite($MgS0_4.H_20$), glauberite [$Na_2Ca(S0_4)_2$], and carnallite ($KMgCl_3.6H_20$). VPDB—Vienna Peedee belemnite. B) $\delta^{13}C$ versus δD data for methane. Shaded zones outline isotope plotfields of methane source fields based on Schoell (1988). The recorded vaules with the exception of the lower halite series lie well ouside the plotted values of methane sources due to the unusually positive carbon values (after Potter et al., 2004).

gas compositions in salt. Any gas association can only be tied back to its origins if one studies gas compositions in the framework of the geological history of each salt basin. We shall return to this notion in the third article in this series when we will lock at emplacement mechanisms that can be tied to depositional and diagenetic features and compositions at the macro scale.

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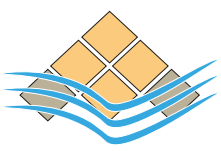

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