

# Controls on halogen concentrations in sedimentary formation waters

RICHARD H. WORDEN\*

BP Exploration Limited, Research and Engineering Centre, Chertsey Road, Sunbury on Thames,  
Middlesex, TW16 7LN, UK

## Abstract

Chlorine is the most abundant halogen in sedimentary formation waters with concentrations from <100 to >250000 mg/l. Bromine is the second most abundant halogen at <1 mg/l to >6000 mg/l with iodine from <0.1 mg/l to >100 mg/l and fluorine from <0.1 mg/l to 30 mg/l. Chlorine and bromine show a strong systematic covariation suggesting that they are subject to the same controlling mechanisms. Fluorine only shows relatively high concentrations at elevated chlorine and bromine concentrations showing that fluorine, chlorine and bromine are possibly controlled by the same processes. Iodine does not correlate with any of the other halogens indicating that unique processes control iodine.

Key geological parameters that influence chlorine and bromine (and possibly fluorine) concentrations are the presence of salt in a basin, the age of the reservoir unit and the kerogen-type within the main hydrocarbon source rock in a basin. The presence of salt in a basin shows that sea water was evaporated to halite saturation producing connate waters with high concentrations of chlorine and bromine. The presence of salt also leads to high salinity waters through water-salt interaction during burial and diagenesis. Tertiary reservoirs typically have much lower chlorine and bromine concentrations than Mesozoic or Palaeozoic reservoirs. The age of the reservoir unit may simply reflect the different amounts of time available for formation water to interact with salt. The dominance of type II marine kerogen in a basin leads to higher bromine concentrations. This may reflect the dominance of a marine influence in a basin which is more likely to lead to salt deposition than terrestrial depositional environments. Iodine concentrations are independent of all these parameters. Other geological parameters such as depth of burial, temperature, basin forming mechanism and reservoir lithology have no influence upon halogen concentrations.

Key processes that affect halogen concentrations are sea water evaporation and dilution, water-salt interaction and input from organic sources. Chlorine and bromine data lie close to the experimentally-derived sea water evaporation trend showing that sea water evaporation may be an important general control on halogens. Sea water dilution is probably responsible for most low salinity formation water chlorine and bromine concentrations for the same reason. Sea water dilution can occur either by meteoric invasion during burial, or following uplift and erosion, or by diagenetic dehydration reactions. Water can interact with salt in a variety of ways: halite dissolution by congruent processes, halite recrystallization by incongruent processes, sylvite dissolution or recrystallization and halite fluid inclusion rupture. Halite dissolution will lead to high chlorine and relatively low bromine waters because halite contains little bromine. In contrast, halite recrystallization will lead to bromine-enhanced waters because NaBr dissolves preferentially to NaCl. The occurrence of dissolution or recrystallization will depend on the water rock ratio, greater volumes of water will lead to more dissolution and waters with higher Cl/Br ratios. Sylvite is usually rich in bromine so dissolution will lead to bromine-enhanced waters. Primary aqueous inclusions in halite contain high bromine concentrations so that rupture, during deformation or recrystallization, will lead to bromine-enhanced formation water. A combination of these

\* Present address: School of Geosciences, Queen's University of Belfast, Belfast, Northern Ireland, BT7 1NN, UK

processes are responsible for the very limited range of Cl/Br ratios although congruent halite dissolution must have a limited role due to the absence of waters with high Cl/Br ratios.

Iodine is strongly concentrated in organic materials in the marine environment; oils and organic rich-source rocks have high I/Cl and I/Br ratios relative to sea water or evaporated sea water. All formation waters are enriched in iodine relative to sea water implying that there has been input from organic matter or interaction with oil. However, hydrocarbon source rock type in a basin has no discernible effect upon iodine concentrations.

KEYWORDS: halogens, sedimentary formation waters, sea-water evaporation, water–salt interaction.

### Introduction

HALOGENS are very important constituents of sedimentary formation waters. Chlorine is usually the main anion, often accounting for >90% of the anion content of formation waters. Halogens are thought to behave conservatively, i.e. they do not undergo diagenetic water-rock interaction. This is because there are no significant rock-forming halogen minerals in carbonate and clastic rocks. The only circumstances in which water-rock interaction is important for halogens is where water comes into contact with salt. Apart from evaporite minerals, chlorine can be present in very small quantities in hydroxyl-bearing minerals such as micas and apatite. These minerals probably have little effect upon the chlorine concentration of sedimentary formation waters. Bromine and iodine are considered not to form minerals in sedimentary basins but are concentrated in organic-rich mudrocks in the sedimentary rock record (Collins, 1975). Fluorine exists as the rare sedimentary mineral, fluorite (CaF<sub>2</sub>) and is probably the one halogen that can interact strongly with the rock matrix.

Halogen concentrations and ratios have been used as tracers of fluid movement due to their conservative behaviour. Formation waters can move great lateral distances in sedimentary basins (e.g. Bethke 1985) and can cross formation boundaries (e.g. Worden and Matray, 1995). The movement of waters obeys the same physical gradients as the movement of hydrocarbons in a basin, tracing water movement therefore has major economic significance to the oil industry. The movement of formation waters has also been cited as a mechanism of cement formation and porosity-loss in hydrocarbon reservoirs (e.g. Bjørlykke, 1994). Sedimentary formation waters have been proposed as the vehicle for mineralization in some Pb-Zn provinces; the source and movement of fluid therefore has great significance in mineral exploration (e.g. Sverjensky, 1984). The concentration of halogens in sedimentary formation waters is an important issue that must be addressed before the origin of formation waters can be understood.

This review examines the variability and controls on the concentrations and ratios of the halogens in

sedimentary formation waters. Data has been drawn from the open literature and covers sedimentary basins from most continents (Table 1). No new analytical data are presented here. Only analytical data from subsurface formations, that contain chlorine and at least one other halogen have been included in the database. The database contains over 1000 water analyses.

To understand the influence of the broad geological context of the formation water, the

TABLE 1. Sources of the halogen concentration data that have been used in this paper

Author	Area/basin
Carpenter and Miller, 1969	USA, Missouri
Carpenter <i>et al.</i> , 1974	USA, Mississippi
Carpenter, 1978	USA, Arkansas
Collins, 1969	USA, Anadarko
Collins, 1975	USA, general
Collins, 1987	USA, Appalachian
Conolly <i>et al.</i> , 1990	W Canada
Crossey <i>et al.</i> , 1986	USA, San Joachim
Edmunds <i>et al.</i> , 1982	UK, Wessex
Egeberg and Aargaard, 1989	Europe, North Sea
Ferguson <i>et al.</i> , 1993	Australia, Canning basin
Fisher and Boles, 1990	USA, San Joachim basin
Fisher and Kreitler, 1987	USA, Palo Duro basin
Fontes and Matray, 1993b	France, Paris Basin
Hitchon <i>et al.</i> , 1971	W Canada
Kharaka and Carothers, 1988	USA, North Slope
Kharaka <i>et al.</i> , 1986	USA, Texas
Kharaka <i>et al.</i> , 1987	USA, C. Mississippi
Land and Macpherson, 1989	USA, GOM Plio-Pleist
Lundegard and Trevena, 1990	Thailand, Pattani
Macpherson, 1992	USA, GOM Frio
Merino, 1975	USA, San Joachim basin
Moldovanyi and Walter, 1992	USA, Smackover
Morad <i>et al.</i> , 1994	N. Africa, S. Tunis
Morton and Land, 1987	USA, GOM Oligocene
Sanders, 1991	USA, Appalachian
Stueber and Walter, 1991	USA, Illinois
Stueber <i>et al.</i> , 1993	USA, Illinois
Wilson and Long, 1993a	USA, Michigan
Wilson and Long, 1993b	USA, Michigan

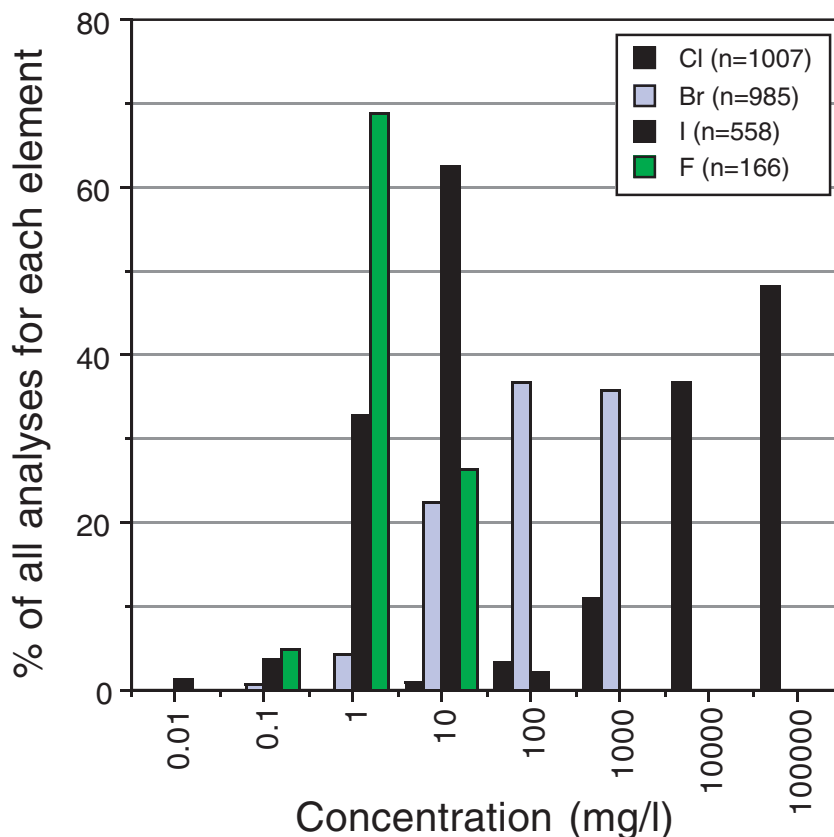


FIG. 1. Comparison of halogen concentrations in sedimentary formation waters. Chlorine is the most abundant halogen followed by bromine, then iodine and finally fluorine.

depth, temperature, basin type, reservoir lithology, reservoir age, source rock (kerogen) type and presence of salt in the record have been noted for each analysis. Depth, temperature, reservoir lithology and age are usually reported with the water analysis. The main basinal source rock type has been taken either from the published source of the analytical data or from Klemme and Ulmishek (1991). The basin type and presence or absence of salt in the record have been taken from the publications or from regional geology publications.

**Halogen concentrations in sedimentary formation waters**

Chlorine usually has the highest concentration of all the halogens although the concentration can vary from <100 to >250000 mg/l (Figs. 1 and 2). Chlorine, being the dominant anion in most formation waters, reflects formation water salinity. Bromine is usually

the second highest concentration halogen in formation waters having concentrations from <1 and >6000 mg/l (Figs. 1 and 2). Fluorine and iodine are usually the lowest concentration halogens in formation waters. Iodine has concentrations < 0.01 to >100 mg/l although examples of formation waters with iodine concentrations up to 1400 mg/l have been reported (e.g. Collins, 1969). Fluorine varies from <1 to about 30 mg/l (Figs. 1 and 2) although this low maximum concentration may reflect the size of the database. Far fewer fluorine analyses have been reported (166 in database) for sedimentary formation waters than chlorine and bromine (>1000 each) or even iodine (558).

**Halogen co-variation patterns**

The validity of the concept of the conservative behaviour of halogens may be assessed by plotting each against the other; if they are not affected by

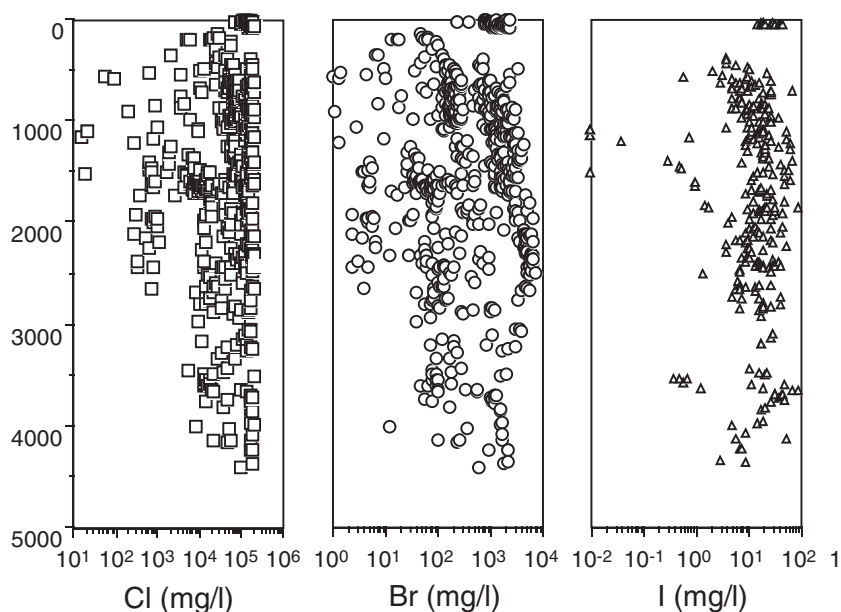


FIG. 2. Variation of halogen concentrations with depth of burial. Relatively high chlorine, bromine and iodine concentrations occur at all depths of burial. Very low chlorine and bromine concentrations only occur in shallow reservoirs.

water-rock interaction during diagenesis then simple correlations should emerge. Chlorine and bromine concentrations, plotted on a log-log diagram, have a largely sympathetic variation pattern (Fig. 3). Bromine increases proportionally with chlorine up to about 100000 mg/l chlorine, thereafter bromine increases at a greater rate than chlorine. There is some scatter in the data but they are tightly constrained to a compositionally-limited area. There are no high Cl/Br waters or vice versa. This covariation supports the notion that chlorine and bromine behave conservatively and shows that they are probably controlled by the same processes.

In contrast, neither chlorine-iodine nor bromine-iodine display any systematic variation patterns (Fig. 3). This indicates that iodine concentrations are affected by different processes than those that control chlorine and bromine concentrations.

Chlorine and fluorine data, plotted on a log-linear diagram due to the limited range of fluorine concentrations (Fig. 3), seem to show some systematic co-variation. Waters with >100000 mg/l chlorine have the highest fluorine concentrations (10–20 mg/l). Waters with lower chlorine concentrations have lower fluorine concentrations (<5 mg/l). It is possible that chlorine concentrations control fluorine concentrations. Bromine and fluorine show a similar pattern to chlorine and fluorine. Iodine and fluorine do not display a systematic pattern.

#### Geological controls on halogen concentration and ratios

Many features of diagenetic systems, such as the dissolved silica content in formation waters (e.g. Fournier and Rowe, 1977) and feldspar diagenesis (e.g. Morad *et al.*, 1990), evolve with depth of burial and the consequent increase in temperature. In contrast, halogen concentrations in formation waters show little correlation or relationship with depth or temperature of the reservoir (Fig. 2). The one discernible feature is that very low chlorine concentrations only occur at shallow depths of burial (<2500 m).

The subdivision of the database by basin type is problematic because the basin-forming process may evolve through time. For example, passive margin basins are rifted basins at their inception. The present day basin forming process has been used in this study. The type of basin has no effect upon formation water halogen geochemistry suggesting that formation water is not directly influenced by tectonic setting.

There is no relationship between the lithology of the host reservoir and halogen concentrations. Carbonate and sandstone reservoirs contain the same wide spread of chlorine, bromine, iodine and fluorine concentrations supporting the notion that halogens do not undergo reservoir-water interaction.

The presence of salt in the stratigraphic record has a major impact upon the concentrations of chlorine,

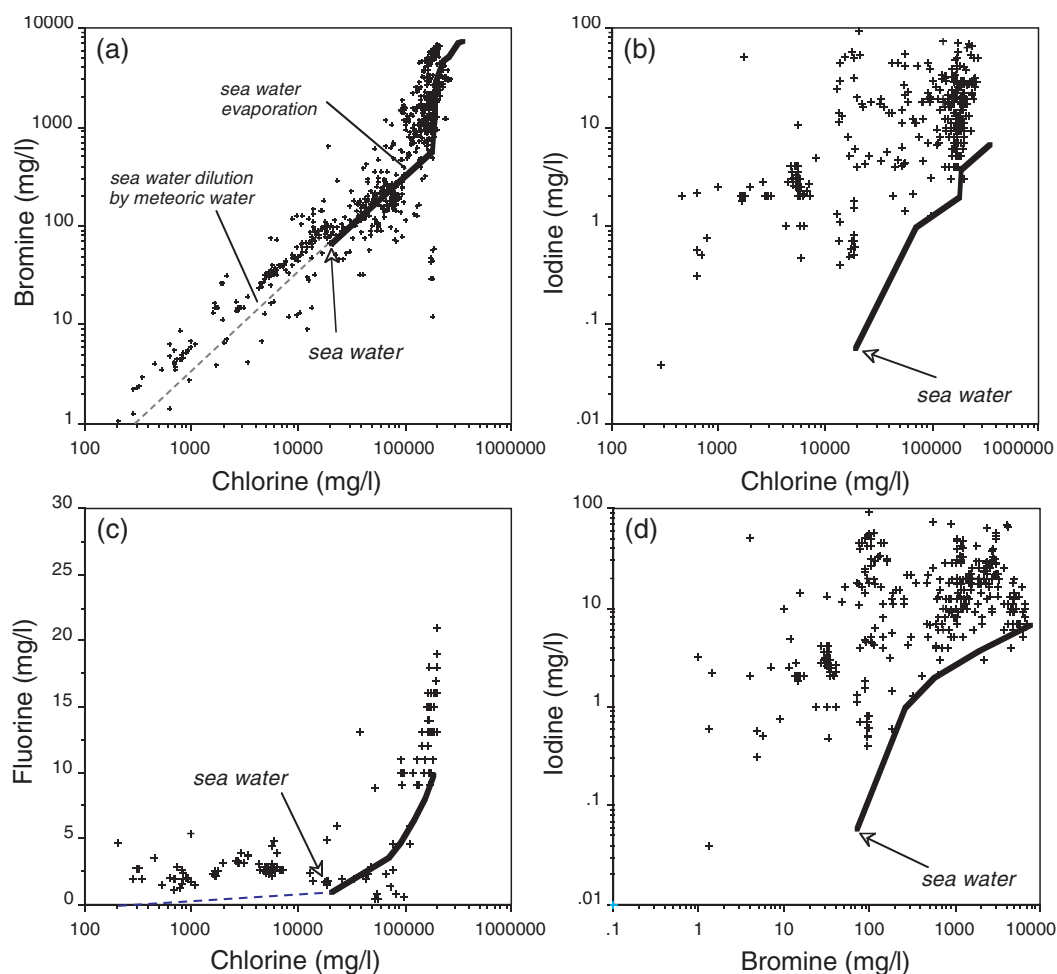


FIG. 3. Comparison of halogen concentrations in sedimentary formation waters. The data may be compared to halogen concentrations in evaporated and diluted sea water. Halogen concentrations during sea water evaporation have been taken from Zherebtsova and Volkova (1966); McCaffrey *et al.*, (1987) and Fontes and Matray (1993a). (a) Cl-Br; the data show a strong correlation between chlorine and bromine suggesting that their concentrations are genetically linked. The data show significant correlation with the sea water trends. (b) Cl-I; there is no correlation between chlorine and iodine suggesting that they are controlled by different processes. The sea water evaporation curve provides a floor to the iodine concentrations but most formation waters are more enriched in iodine than can be explained by evaporation of sea water. (c) Cl-F; (note log-linear plot) the highest fluorine concentrations are associated with the highest chlorine concentrations. The sea water evaporation curve assumes evaporative concentration of fluorine at the same rate as chlorine up to halite precipitation. (d) Br-I; similar to the Cl-I cross plot; there is little pattern in the data indicating separate sources of bromine and iodine in formation waters.

bromine and fluorine in formation waters. Salt-containing basins have average Cl and Br concentrations of 118392 and 1583 mg/l respectively (Fig. 4 and Table 2). Basins that do not contain salt have average Cl and Br concentrations of 48640 and 155 mg/l respectively. The presence of salt has no discernible effect upon the iodine concentration in formation water.

The age of the host reservoir appears to have a major impact upon chlorine and bromine concentrations (Fig. 5). Tertiary reservoirs have lower chlorine concentrations than Mesozoic reservoirs. Palaeozoic reservoirs tend to have still higher chlorine concentrations. The bromine concentration tends to be lowest in Tertiary reservoirs and is similar in both Mesozoic and Palaeozoic reservoirs. The Cl/Br ratio

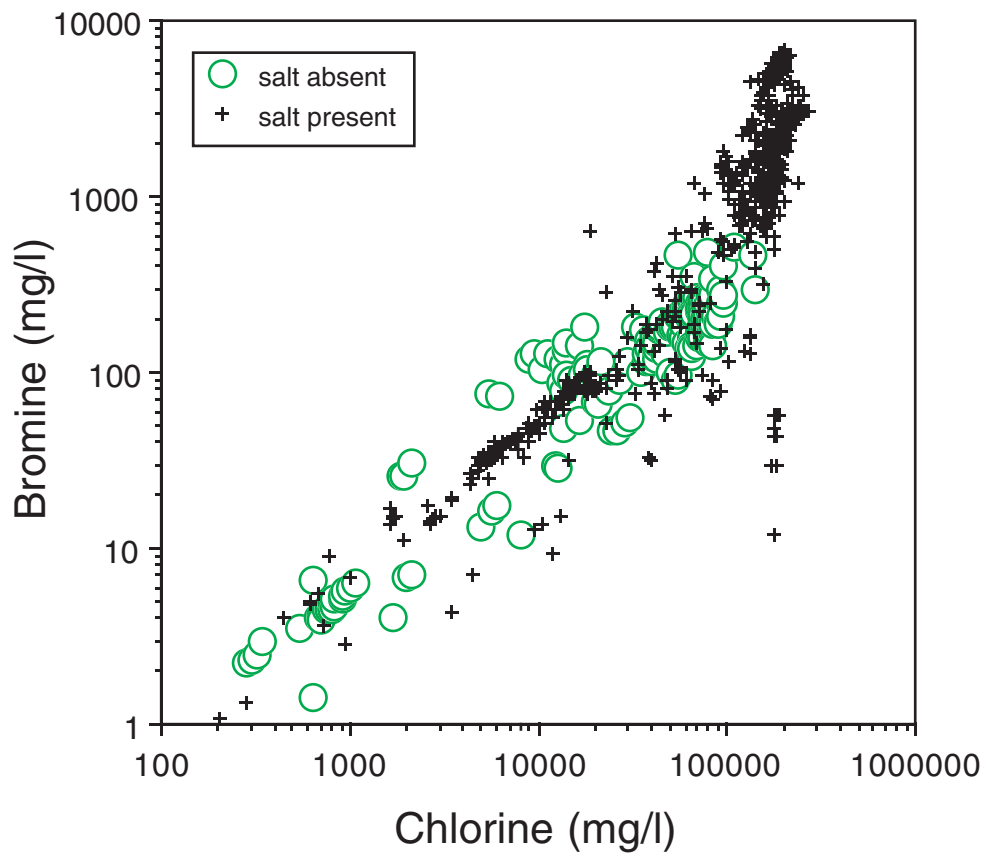


FIG. 4. Comparison of chlorine and bromine concentrations in basins with and without salt in the stratigraphic record. Basins with salt can have much higher chlorine concentrations than those without salt. This difference is even more extreme for bromine than for chlorine. In general, basins without salt do not get higher chlorine concentrations than those associated with halite saturation. Iodine concentrations are not influenced by the presence of salt in the basin.

TABLE 2. Illustration of the influences of the broad geological context on average halogen concentrations

Control	Condition	Total data	Cl	Br	I	F	Cl/Br	Cl/I	Cl/F	Br/I
Salt in record	absent	204	48640	155	23	2	314	2115	383	12
	present	670	118392	1583	15	7	75	7893	16913	2
Age of reservoir	Tertiary	92	34695	109	22	2	320	1569	17391	11
	Mesozoic	402	99157	1630	10	7	61	9447	14361	2
	Palaeozoic	383	116412	988	17	1	118	6852	109564	16
Source type	II (marine)	720	107816	1333	14	7	81	7930	15615	2
	III (terrestrial)	170	60186	239	18	1	251	3268	56646	17
Seawater	—	—	19870	68	0.05	1.35	292	397400	14719	1360

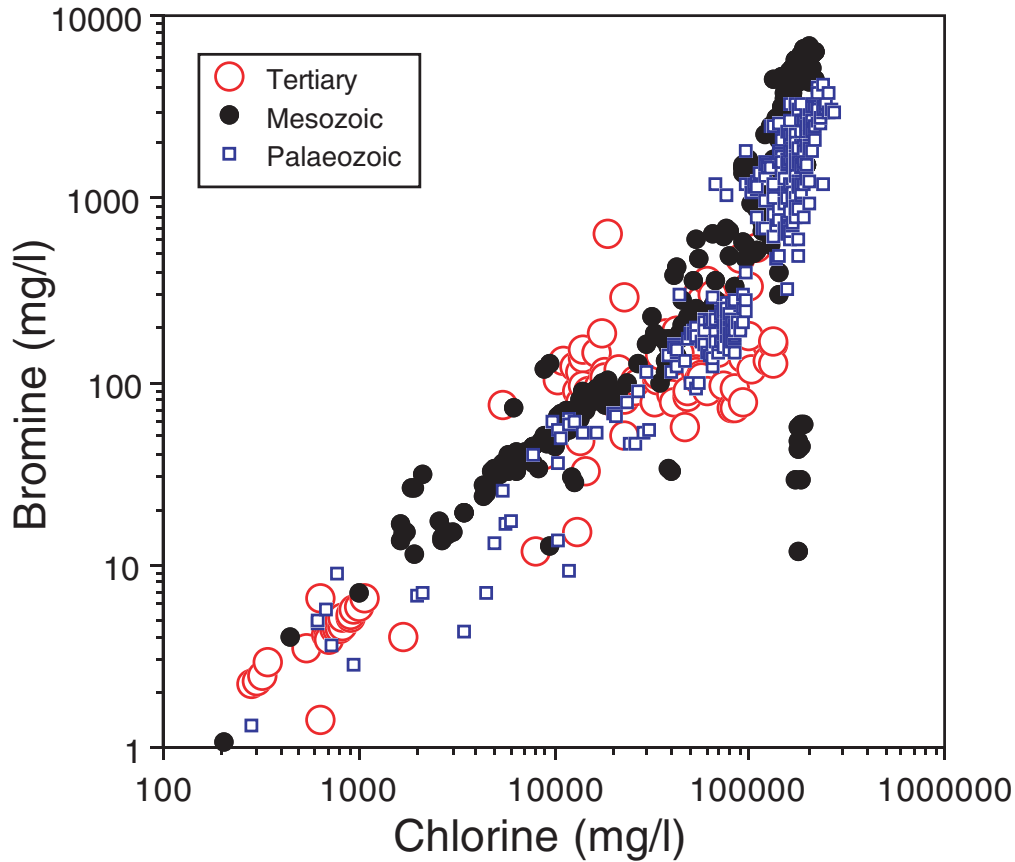


FIG. 5. Comparison of chlorine and bromine concentrations in formation waters grouped by age of host formation. Mesozoic and Palaeozoic reservoirs can have much higher chlorine and bromine concentrations than Tertiary reservoirs. Note that iodine concentrations are not influenced by the age of the reservoir.

in Tertiary reservoirs is similar to that of sea water, the ratio is much lower than sea water in the older reservoir classes.

It has been proposed that iodine (and in some cases bromine) are at least partially derived from organic sources (e.g. Collins, 1969). Formation waters have been subdivided according to the main hydrocarbon source rock (kerogen) type in the relevant basin because source rocks are a major organic component of a basin. There is only sufficient information to subdivide the data into either type II (algal-marine, oil-prone) or type III (land-plant dominated, gas-prone) kerogen. Iodine concentrations are not influenced by the main kerogen type in a basin (Fig. 6). Type II source rock basins can have higher bromine concentrations and lower Cl/Br ratios than type III source rock basins.

**Processes affecting halogen concentrations**

Most of the broad geological controls that influence halogen concentrations are related to the presence of salt in a basin. The deposition and dissolution of salt play a major role in controlling halogen concentrations. These, and several other processes, are discussed below to define the mechanisms that control the halogen concentrations of sedimentary formation waters

*Sea water evaporation*

Sea water evaporation has often been proposed as the origin of elevated chlorine and bromine concentrations in formation waters. Halogen concentrations during evaporation are controlled by the partition

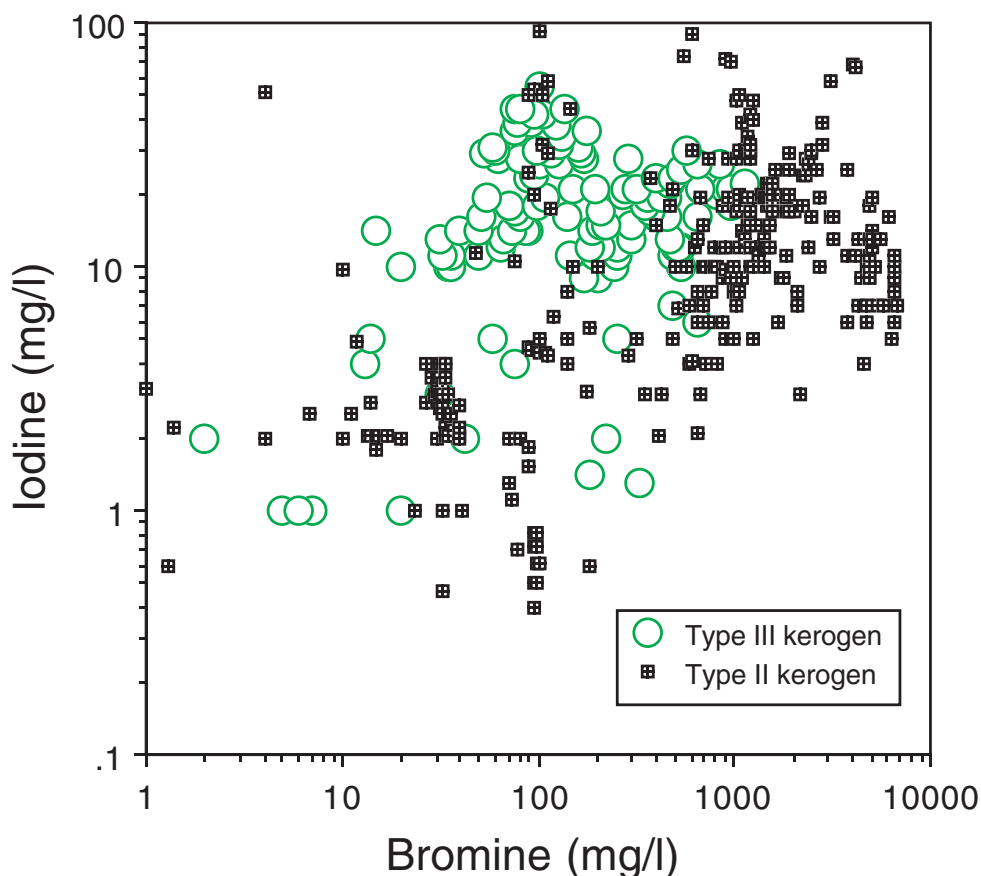


FIG. 6. Comparison of bromine and iodine concentration data grouped by the main kerogen type in the basin. Iodine concentrations are independent of the main kerogen type despite the relationship between marine organic matter and iodine (e.g. Collins *et al.*, 1971; Martin *et al.*, 1993 and see Fig. 9). In contrast, basins with type II, marine algal-dominated kerogen can have higher bromine concentrations than those with type III terrestrial kerogen.

coefficients of the different elements into the precipitating minerals (e.g. data in Holser, 1979*b*). The chlorine-bromine ratio during evaporation is well established (e.g. McCaffrey *et al.*, 1987; and data in Fontes and Matray, 1993*a*). Chlorine and bromine increase in concentration during evaporation until halite precipitation commences. During halite precipitation, bromine is preferentially excluded from the halite lattice, bromine increases in concentration in the water much faster than chlorine (Fig. 3). Further evaporation leads to carnallite and sylvite precipitation, which have higher Br partition coefficients than halite so that both chlorine and bromine increase in concentration.

The high salinity chlorine-bromine data show a marked similarity to the sea water evaporation curve (Fig. 3). There is scatter about the evaporation

trajectory but the overall pattern of the data is the same as sea water evaporation.

Sea water evaporation also affects iodine concentrations. Iodine-chlorine relations during sea water evaporation are taken from Zherebtsova and Volkova (1966). Iodine has very low partition coefficients for halite, sylvite, carnallite etc. (Zherebtsova and Volkova, 1966; Holser, 1979*b*). Salt contains little iodine so that iodine is strongly enriched in the remaining water (Fig. 3). However, the sea water evaporation curve merely defines a minimum iodine concentration limit for formation waters. Iodine concentration is not simply the result of sea water evaporation; there must be another source of iodine in formation waters.

There are no published data on fluorine behaviour during sea water evaporation. However, if fluorine is



concentrated at the same rate as chlorine during evaporation, then it will have a concentration of about 10 mg/l when chlorine reaches halite saturation (Fig. 3). Simple evaporative concentration of fluorine bears some resemblance to the data plotted in Fig. 3.

#### *Non-marine water evaporation*

Sea water is not the only surface water that can be concentrated by sub aerial evaporation, lacustrine and hydrologically-closed environments can also produce salt pans and therefore result in brines. The specific evolution of halogen concentrations and ratios during evaporation will depend on the initial water chemistry (e.g. Eugster and Jones, 1979; Hardie, 1984; Sanford and Wood, 1991). Few details of halogen geochemistry resulting from this process have been published.

#### *Sea water meteoric dilution*

Sea water dilution by meteoric water flushing should have a predictable affect upon halogen concentrations and should reduce the halogen concentrations proportionally (Fig. 3). The data show that formation waters with chlorine concentrations lower than sea water closely follow the meteoric dilution chlorine-bromine trend (Fig. 3). Almost all formation waters have iodine concentrations greater than that found in sea water (Fig. 3), therefore meteoric dilution of sea water iodine is not an important part of the iodine budget.

#### *Sea water freezing*

Sea water freezing has been proposed by Herut *et al.* (1990) to account for Canadian Shield brines. Up to the point of halite precipitation, freezing has the same effect upon chlorine-bromine relations as sea water evaporation (Fig. 4). Sea water freezing may be an important process affecting formation water composition in rare sub-glacial environments but this cannot be discerned from chlorine-bromine data.

#### *Hydration/dehydration processes*

Clastic and carbonate diagenesis may have an influence upon the overall salinity of formation water, although it is unlikely that it will affect halogen ratios. Hydration reactions reduce salinity. For example, under appropriate diagenetic conditions of pH and silica activity, anhydrous K feldspar reacts with water to form kaolinite. This reaction can reduce water volume by 10-20% and increases halogen concentrations proportionally. In a sandstone with 10% K-feldspar and 10% water-filled porosity, chlorine and bromine concentrations would increase by approximately 9% if all the feldspar were reacted

to kaolinite. Extensive hydration reactions during retrograde metamorphism are thought to be responsible for high salinity fluid inclusions in metamorphic minerals (Bennett and Barker, 1992).

Dehydration reactions, which decrease halogen concentrations, also occur in sedimentary basins (e.g. the transformation of gypsum to anhydrite or smectite to illite). Examples where clay mineral transformation have resulted in significant reduction in salinity are given by Morton and Land (1987) and Hanor (1994a). An example of dramatic formation water salinity decrease following anhydrite-hydrocarbon reaction was given by Worden and Smalley (1993). Dehydration reactions reduce chlorine and bromine concentrations proportionally.

#### *Waters associated with salt bodies and salt diagenesis*

Dissolution of rock salt is a major mechanism for increasing halogen concentrations. Halite has a low partition coefficient for bromine (Holser, 1979b). If halite recrystallises in the presence of waters with a bromine concentration less than that associated with halite precipitation from sea water, then the waters will become bromine-enriched (Fig. 7) because NaBr dissolves preferentially to NaCl (Land and Prezbindowski, 1981; Stoessel and Carpenter, 1986). This is known as incongruent dissolution and is associated with recrystallization of salt at low water-rock ratios. Incongruent dissolution must operate in salt bodies because most salt bodies are bromine-depleted relative to primary evaporites, bromine presumably escaping from salt into the water (Holser, 1979b; Land *et al.*, 1988, Posey and Kyle, 1988). Conversely, congruent (or total) dissolution involves bulk dissolution of salt resulting in high chlorine concentrations and low Cl/Br ratios (Fig. 7). This probably occurs at high water-rock ratios (Land and Prezbindowski, 1981).

Newly deposited halite commonly contains abundant inclusions filled with bromine-enriched evaporated sea water. Rupture of these inclusions may lead to bromine-enriched formation waters (Fontes and Matray, 1993a). The significance of this process is difficult to assess.

Sylvite and other potash salts are typically bromine-enriched relative to halite (Holser 1979b). Sylvite dissolution will lead to different formation water Cl/Br ratios than halite dissolution (Fig. 7). Both congruent and incongruent dissolution of sylvite by either sea water or meteoric water will lead to bromine-enriched waters relative to evaporated sea water. Hanor (1994a) proposed K-salt dissolution as a likely process for producing bromine-enriched waters.

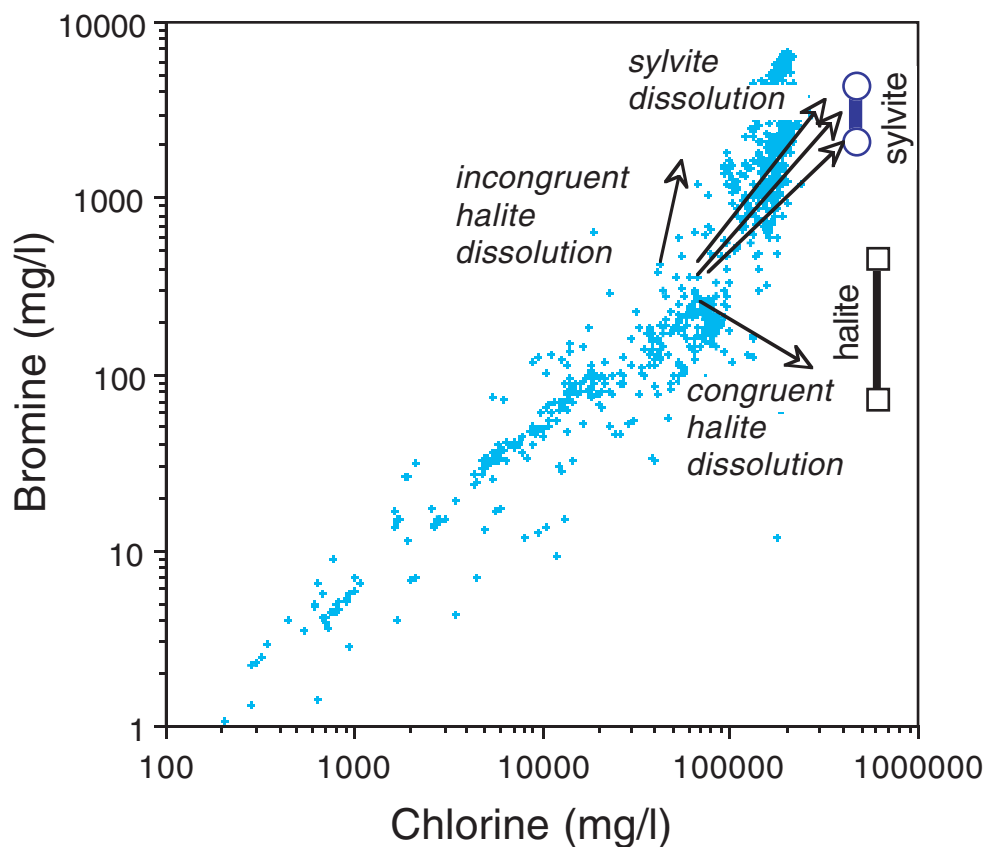


FIG. 7. Comparison of formation water Cl-Br data with modelled effects of halite and sylvite dissolution. Congruent (i.e. total) dissolution of halite leads to bromine depletion relative to evaporated sea water because halite has a low bromine content. In contrast, incongruent dissolution (recrystallisation and preferential dissolution of NaBr) leads to bromine-enrichment relative to sea water evaporation. Congruent or incongruent dissolution of sylvite could be responsible for bromine-enrichment of water relative to sea water evaporation because sylvite usually has a relatively high bromine content.

#### *Membrane filtration and reverse osmosis*

Membrane filtration has been proposed as a way increasing halogen concentrations in formation waters (e.g. Hitchon *et al.*, 1971; Kharaka and Berry, 1973; Graf, 1982). This entails water being forced under pressure from one aquifer through a clay membrane, into an adjacent aquifer. In this model, solutes are retarded relative to pure water by the membrane. Downstream water should have relatively low halogen concentrations and upstream water should have relatively high halogen concentrations. Experimental work has shown that membrane filtration affects halogens differently. The order of filtration efficiency is  $Br > Cl > I$  (Kharaka and

Berry, 1973) so that, for example, the Cl/Br ratio of the upstream water should decrease as membrane filtration proceeds.

The significance of membrane filtration is still under debate (see for example Fontes and Matray, 1993a and Hanor, 1994b), with major questions surrounding the efficiency of this process under natural pressures and mudrock permeabilities. Collins (1975) suggested that sulphate and carbonate scale would form on the upstream side of the membrane completely blocking fluid movement. Whilst arguments about significance of this mechanism rage, it is unclear whether it may be important in determining the absolute and relative concentrations of halogens in formation waters.

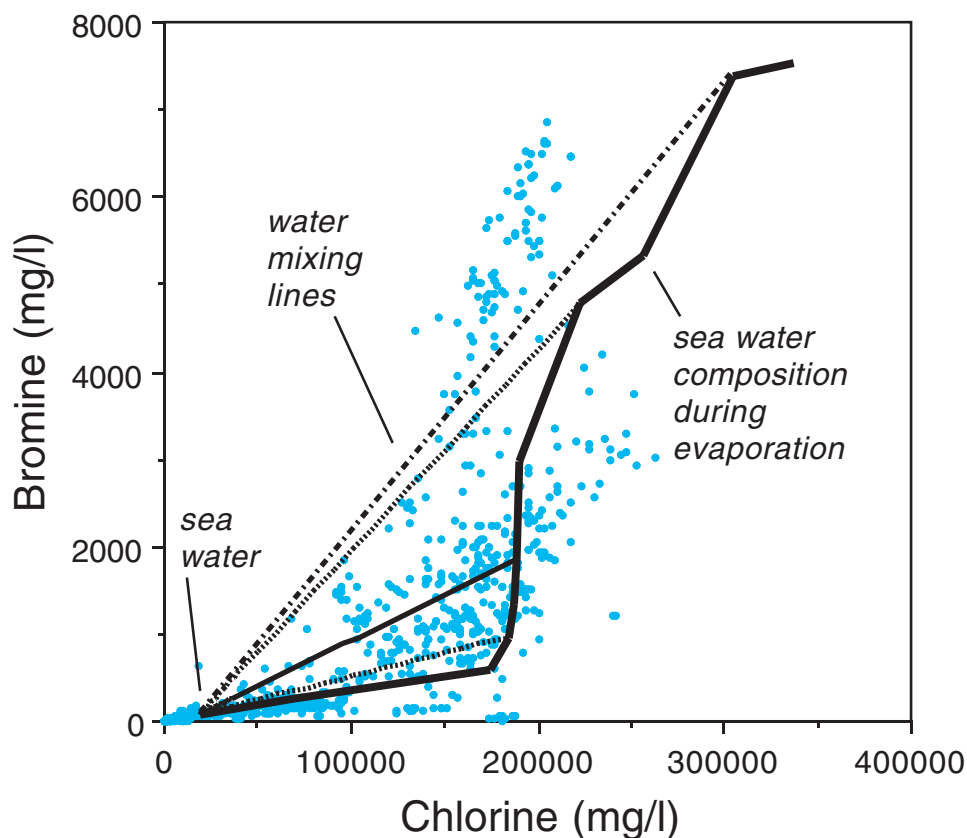


FIG. 8. The effect of mixing sea water with variably evaporated sea water upon chlorine-bromine relations (note linear-axes employed to produce straight mixing lines). Mixing of different water types may be responsible for bromine-enriched waters.

#### *Mixing of water sources*

Mixing of different formation waters may explain waters enriched in bromine relative to sea water evaporation (Carpenter, 1978). Fig. 8 illustrates modelled mixing curves between fresh sea water and sea water evaporated to different degrees. The curves pass through the bulk of the bromine-enriched waters to the left of the sea water evaporation curve and may account for bromine-enrichment. Different mixing trends could be modelled for the addition of meteoric water or sea water evaporated to below the point of halite saturation with highly evaporated water to produce a whole suite of mixing curves.

#### *Organic sources of halogens*

Formation waters are up to 3 orders of magnitude enriched in iodine relative to sea water evaporation

(Fig. 3). There are few options available to provide the excess iodine. Organic material is the main reservoir of iodine in recent marine environments, sediments enriched in organic material are therefore potential sources of iodine in formation waters (Collins, 1969, Collins *et al.*, 1971). Iodine enrichment in formation waters has been associated with proximity of hydrocarbon pools (e.g. Marsden and Kawai, 1965; Smirnova, 1969). Oil contains bromine and iodine in similar low concentrations, from 0.1 to about 10 mg/l (Fig. 9, this paper, and Ellrich *et al.*, 1985). Organic-rich mudrocks and their pore waters can contain substantial amounts of iodine and elevated I/Br ratios (Fig. 9, this paper, and Cosgrove, 1970; Price *et al.*, 1970; Martin *et al.*, 1993). Bromine is also preserved in organic-rich mudrocks (Cosgrove, 1970; Martin *et al.*, 1993). Mudrocks release their organic iodine to pore fluids upon burial and thermal maturation of the organic

matter. Iodine increases in concentration in pore waters with increasing depth of burial at a faster rate than bromine (Martin *et al.*, 1993).

### Discussion

The presence of salt in the basin and the degree and type of water-salt interaction are probably the most important factors that control the chlorine, bromine and fluorine concentrations. Iodine in formation waters is largely controlled by input from organic sources.

Basins that contain salt in the stratigraphic record tend to have higher chlorine and bromine concentrations than basins without salt. The presence of salt also depresses the Cl/Br ratio. The presence of salt tends to lead to very high chlorine and bromine concentrations due to water-salt interaction (Fig 4). The presence of salt is important for two reasons. Firstly its presence proves that basin has undergone evaporation at a greater rate than marine incursion. Surface waters have reached halite saturation and have a chance to be preserved as highly saline connate water following burial. Secondly, the presence of salt means that any circulating basinal waters, that are undersaturated with respect to halite, will increase in salinity if they come into contact with the salt. The Cl/Br ratio is low when salt is present presumably due to the release of bromine from salt at a greater rate than chlorine (Stoessel and Carpenter, 1986) and due to the presence of sea water evaporated to beyond halite saturation.

Tertiary reservoirs have much lower chlorine and bromine concentrations than Mesozoic and Palaeozoic reservoirs (Fig. 5). This may be because reservoirs formed in the Tertiary have had less access to, and time to interact with, salt than Mesozoic or Palaeozoic reservoirs.

Basins dominated by type II (oil-prone) kerogen tend to have higher bromine concentrations than basins dominated by type III (gas-prone) kerogen (Fig. 6). Type II kerogen has a marine origin, type III kerogen has a terrestrial origin. Salt is most likely to form in basins with a strong marine influence. The correlation between basin type and bromine concentrations may be a function of the dominance of marine sedimentation in a basin. Iodine concentrations in formation waters are independent of kerogen type (Fig. 6) despite the abundance of iodine in marine organic matter (Collins *et al.*, 1971).

Other major geological factors have no influence upon formation water halogen concentrations. Processes that control halogen concentrations are independent of the way in which the sedimentary basin formed. Reservoir lithology has no effect upon the halogen concentrations. Sandstones and carbonates do not contain abundant halogen minerals and

therefore do not affect halogen concentrations. Present day depth of burial and temperature do not strongly influence halogen concentrations in formation waters (Fig. 2). Depth of burial has no effect upon halogen concentrations presumably because halogens do not undergo depth- or temperature-dependent water-rock interaction. High chlorine concentrations can occur at any depth from near surface to >4500m despite the assertions to the contrary by Dickey (1966). Very low chlorine and bromine concentrations only occur in shallow reservoirs (Fig. 2). This may reflect the fact that invasion by meteoric water is more common in shallower formations.

Key processes that affect chlorine and bromine concentrations and ratios are sea water evaporation, sea water dilution, salt dissolution, salt recrystallization and fluid inclusion rupture. Elevated chlorine and bromine concentrations in formation waters follow the same pattern as evaporated sea water (Fig. 3). This figure shows scatter in the data but the vast majority of the data fall close to the evaporated and diluted sea water trends. Sea water evaporation may be at least partly responsible for the character of high salinity waters. The scatter at the highest concentrations may be the result of modified initial sea water compositions due to factors such as the basin being hydrologically restricted thus influencing the water chemistry and mineral precipitation order (e.g. Hardie, 1984; Sanford and Wood, 1991).

Many formation waters are enriched in bromine relative to sea water evaporation (Fig. 3a). There are several possible explanations for this including incongruent halite recrystallization (Fig. 7), K-salt dissolution or recrystallization (Fig. 7), mixing of pristine sea water with evaporated sea water (Fig. 8) and fluid inclusion rupture. Interaction of water with salt will always lead to increased chlorine concentrations and can lead theoretically to either high or low chlorine-bromine ratios. The effect depends on initial salt mineralogy, water-rock ratio, nature of the initial water and whether the salt is undergoing total or partial dissolution (congruent and incongruent dissolution respectively). All these factors must be accounted for in attempting to determine the origin of a formation water. Halite can contain abundant fluid inclusions (Roedder, 1984). The primary fluid in these inclusions represents the water present during halite growth and is therefore bromine-enriched. Rupture of these inclusions will release water with a high concentration of bromine into the formation water. This may be another process responsible for waters enriched in bromine relative to sea water evaporation (Fontes and Matray, 1993a).

Sedimentary formation waters with chlorine and bromine concentrations less than that in sea water tend to have similar Cl/Br ratios to sea water (Fig 3).

This suggests that the halogens in these waters are the result of sea water being diluted by very low salinity water. Even in very low salinity formation waters, the chlorine and bromine concentrations probably originate from sea water. Meteoric water input can occur during burial of the initial sediments (Lundegaard and Trevena, 1990) or during uplift and erosion (Fontes and Matray, 1993a). Mineral dehydration reactions may also cause local dilution and reduced halogen concentrations.

Iodine concentrations in sedimentary formation waters are ubiquitously greater than the concentration of iodine in sea water (Fig 3). Salt dissolution

probably has little effect upon the iodine concentration of formation waters because salt contains very little iodine. Waters associated with mudrocks contain elevated iodine concentrations (Fig. 9). Iodine is concentrated in algal matter typically preserved as potential hydrocarbon (marine) source rocks (Collins, 1969). It is possible that iodine is released from organic-rich mudrocks during burial and heating. However, there is no correlation between source rock type (marine or terrestrial kerogen) and the iodine concentration (Fig. 6). Oil contains trace iodine and bromine (Ellrich *et al.*, 1985) although the iodine content of oil is much

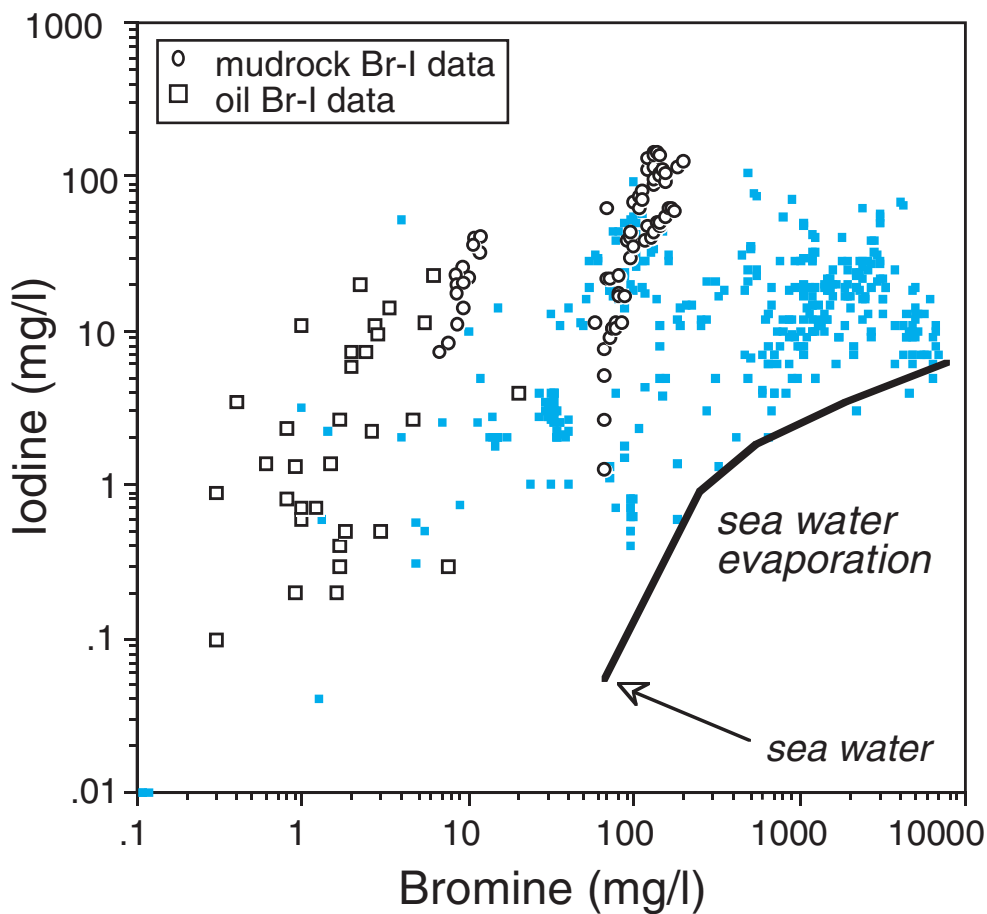


FIG. 9. The I/Br ratios of organic-rich mudrocks and oils are generally higher than the I/Br ratios of formation waters. Mudrock data are from Cosgrove (1970) and Martin *et al.* (1993); oil data are from Ellrich *et al.* (1985). Organic matter in mudrocks and oil is enriched in iodine relative to sea water or evaporated sea water and is probably the source of the elevated concentrations of iodine in formation waters. Organic matter may also be slightly enriched in bromine relative to sea water (or diluted sea water) and may be an important source of bromine in low salinity formation.

higher than sea water. The elevated iodine contents of oils and organic-rich mudrocks supports an organic source of iodine in formation waters (Fig. 9). In contrast, the organic contribution to the bromine budget is probably much less significant. However, an organic source of bromine in low salinity formation waters has been proposed by Fisher and Boles (1990) and MacPherson (1989).

The correlation between chlorine and fluorine (Fig. 3) suggests that evaporative concentration/salt dissolution may be part of the origin of fluorine-chlorine relations. However fluorite solubility relations probably play an important role in determining the fluorine concentration (Collins, 1975).

There are problems with the conclusions that chlorine and bromine are strongly influenced by sea water evaporation to the point of salt precipitation and water-salt interaction. One significant problem with sea water evaporation as a major source of elevated chlorine and bromine concentrations is that only a small volume of water remains after extreme evaporative concentration of sea water. By the point at which halite commences precipitation, 91% of the volume of the water has been lost, by the point at which K-salts commence precipitation, about 98% of the original water volume has been lost (Holser, 1979a). Large volumes of sea water must be evaporated in order to produce the large volumes of sedimentary formation water with elevated chlorine and bromine concentrations if sea water evaporation is a key process influencing formation water halogen concentrations. The Illinois basin has formation waters that record both halite dissolution and sea water evaporation although there is no record of salt in the stratigraphic record (Stueber *et al.*, 1993). However, anhydrite beds are present in the Illinois Basin. These are thought to represent the remnants of salt beds; the salt being removed through dissolution by convecting formation water (Stueber *et al.*, 1993). Thus, the absence of salt at the present day in a basin does not necessarily mean that salt has not been present in the past.

#### Acknowledgements

I would like to thank Jean-Michel Matray for his useful, informal review of an early version of this paper. Two anonymous reviewers provided plenty of food for thought which led a much-improved paper. Sarah Acland is thanked for spotting those stubborn stains that persist in nearly-finalised manuscripts.

#### References

- Bennett, D.G. and Barker, A.J. (1992) High salinity fluids: the result of retrograde metamorphism in thrust zones. *Geochim. Cosmochim. Acta*, **56**, 81–95.

- Bethke, C.M. (1985) A numerical model of compaction driven groundwater flow and heat transfer and its application to the palaeohydrology of intracratonic sedimentary basins. *J. Geophys. Res.*, **90(B8)**, 6817–28.
- Bjørlykke, K. (1994) Fluid flow processes and diagenesis in sedimentary basins. In *Geofluids: origin, migration and evolution of fluids in sedimentary basins*. (J. Parnell, ed.). Geol. Soc. Spec. Publ. **78**, 127–40.
- Carpenter, A.B. (1978) Origin and chemical evolution of brines in sedimentary basins. *Oklahoma Geol. Surv. Circ.*, **79**, 589–606.
- Carpenter, A.B. and Miller, J.C. (1969) Geochemistry of saline subsurface water, Saline County, (Missouri). *Chem. Geol.*, **4**, 135–67.
- Carpenter, A.B., Trout, M.L. and Pickett, E.E. (1974) Preliminary report on the origin and chemical evolution of lead- and zinc-rich oil field brines in Central Mississippi. *Econ. Geol.*, **69**, 1191–206.
- Collins, A.G. (1969) Chemistry of some Anadarko Basin brines containing high concentrations of iodine. *Chem. Geol.*, **4**, 169–87.
- Collins, A.G. (1975) *Geochemistry of oilfield waters*. Elsevier, 496 pp.
- Collins, A.G. (1987) Properties of produced waters. Ch. 24 in *Petroleum Engineering Handbook*. (H.B. Bradley, ed.) Soc. Petrol. Eng., Richardson, Texas, U.S.A.
- Collins, A.G., Bennett, J.H. and Manuel, O.K. (1971) Iodine and algae in sedimentary rocks associated with iodine-rich brines. *Geol. Soc. Amer. Bull.*, **82**, 2607–10.
- Connolly, C.A., Walter, L.M., Baadsgaard, H. and Longstaffe, F.J. (1990) Origin and evolution of formation waters, Alberta basin, Western Canada sedimentary basin. I. Chemistry. *Appl. Geochem.*, **5**, 375–95.
- Cosgrove, M.E. (1970) Iodine in the bituminous Kimmeridge shales of the Dorset coast, England. *Geochim. Cosmochim. Acta*, **34**, 830–6.
- Crossey, L.J., Surdam, R.C. and Lahann, R. (1986) Application of organic/inorganic diagenesis to porosity prediction. In *Roles of organic matter in sediment diagenesis*, (D.L. Gautier, ed.), Soc. Econ. Paleo. Mineral., Spec. Publ. **38**, 147–55.
- Dickey, P.A. (1966) Increasing concentration of subsurface brines with depth. *Chem. Geol.*, **4**, 361–70.
- Edmunds, W.M., Bath, A.H. and Miles, M.L. (1982) Pore fluid of the Bridport (Lower Jurassic) and the Sherwood sandstone (Triassic) intervals of the Winterborne Kingston borehole, Dorset. In *The Winterborne Kingston borehole, Dorset*. (G.H. Rhys, G.K. Lott and M.A. Calver, eds.). Rep. Inst. Geol. Sci. No 81/3, 149–63.
- Egeberg, P.K. and Aargaard, P. (1989) Origin and

- evolution of formation waters from oilfields on the Norwegian shelf. *Appl. Geochem.*, **4**, 131–42.
- Ellrich, J., Hirner, A. and Stark, H. (1985) Distribution of trace elements in crude oils from Southern Germany. *Chem. Geol.*, **48**, 313–23.
- Eugster, H.P. and Jones, B.F. (1979) Behaviour of major solutes during closed-basin brine evolution. *Amer. J. Sci.*, **279**, 609–31.
- Ferguson, J., Etminan, H. and Ghassemi, F. (1993) Geochemistry of deep formation waters in the Canning basin, Western Australia, and their relationship to Zn-Pb mineralization. *Austral. J. Earth Sci.*, **40**, 471–83.
- Fisher, J.B. and Boles J.R. (1990) Water-rock interaction in Tertiary sandstones, San Joaquin basin, California, U.S.A.: Diagenetic controls on water composition. *Chem. Geol.*, **82**, 83–101.
- Fisher, R.S. and Kreitler, C.W. (1987) Geochemistry and hydrodynamics of deep basin brines, Palo Duro basin, Texas, U.S.A.. *Appl. Geochem.*, **2**, 459–76.
- Fontes, J.Ch. and Matray J.M. (1993a) Geochemistry and origin of formation brines from the Paris basin, France 1. Brines associated with Triassic salts. *Chem. Geol.*, **109**, 149–75.
- Fontes, J.Ch. and Matray J.M. (1993b) Geochemistry and origin of formation brines from the Paris basin, France 2. Saline solutions associated with oil fields. *Chem. Geol.*, **109**, 177–200.
- Fournier, R.O. and Rowe, J.J. (1977) The solubility of amorphous silica in water at high temperatures and pressures. *Amer. Mineral.*, **64**, 1052–6.
- Graf, D.L. (1982) Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines. *Geochim. Cosmochim. Acta*, **46**, 1431–48.
- Hanor, J.S. (1994a) Physical and chemical controls on the composition of waters in sedimentary basins. *Mar. Petrol. Geol.*, **11**, 31–45.
- Hanor, J.S. (1994b) Origin of saline fluids in sedimentary basins. In *Geofluids: origin, migration and evolution of fluids in sedimentary basins*. (J. Parnell, ed.), Geol. Soc. Spec. Publ. **78**, 151–74.
- Hardie, L.A. (1984) Evaporites, marine or non-marine? *Amer. J. Sci.*, **284**, 193–204.
- Herut, B., Starinsky, A., Katz, A. and Bein, A. (1990) The role of sea water freezing in the formation of subsurface brines. *Geochim. Cosmochim. Acta*, **54**, 13–21.
- Hitchon, B., Billings, G.K. and Klovam, J.E. (1971) Geochemistry and origin of formation waters in the Western Canada basin -III. Factors controlling chemical composition. *Geochim. Cosmochim. Acta*, **35**, 567–98.
- Holser, W.T. (1979a) Mineralogy of evaporites. In *Marine minerals* (R.G. Burns, ed.), *Reviews in Mineralogy*, **6**, Mineral Soc. Amer., Washington D. C., 211–94.
- Holser, W.T. (1979b) Trace elements and isotopes in evaporites. In *Marine Minerals* (R.G. Burns, ed.), *Reviews in Mineralogy*, **6**, Mineral Soc. Amer., Washington D. C., 295–346.
- Kharaka, Y.K. and Berry, F.A.F. (1973) Simultaneous flow of water and solutes through geological membranes, I. Experimental investigations. *Geochim. Cosmochim. Acta*, **37**, 2577–603.
- Kharaka, Y.K. and Carothers, W.W. (1988) Geochemistry of oil-field waters from the North Slope. *US Geol. Survey Prof. Paper*, **1399**, 551–61.
- Kharaka, Y.K., Law, L.M., Carothers, W.W. and Goerlitz, D.F. (1986) Role of organic species dissolved in formation waters from sedimentary basins in mineral diagenesis. In *Roles of organic matter in sediment diagenesis*, (D.L. Gautier, ed.), Soc. Econ. Paleo. Mineral., Spec. Publ. **38**, 111–22.
- Kharaka, Y.K., Maest, A.S., Carothers, W.W., Law, L.M., Lamothe, P.J. and Fries, T.L. (1987) Chemistry of metal-rich brines from Central Mississippi salt dome basin, U.S.A. *Appl. Geochem.*, **2**, 543–61.
- Klemme, H.D. and Ulmishek, G.F. (1991) Effective petroleum source rocks of the world: stratigraphic distribution and controlling depositional factors. *Amer. Assoc. Petrol. Geol. Bull.*, **75**, 1809–51.
- Land, L.S. and MacPherson, G.L. (1989) Geochemistry of formation water, Plio-Pleistocene reservoirs, offshore Louisiana. *Gulf Coast Geol. Soc. Trans.*, **39**, 421–30.
- Land, L.S. and Prezbindowski, D.R. (1981) The origin and evolution of saline formation water, Lower Cretaceous carbonates, south-central Texas, U.S.A., *J. Hydrol.*, **54**, 51–74.
- Land, L.S., Kupecz, J.A. and Mack, L.E. (1988) Louann salt geochemistry (Gulf of Mexico sedimentary basin, U.S.A.): a preliminary synthesis. *Chem. Geol.*, **74**, 25–35.
- Lundegaard, P.D. and Trevena, A.S. (1990) Sandstone diagenesis in the Pattani basin (Gulf of Thailand): history of water rock interaction and comparison with the Gulf of Mexico. *Appl. Geochem.*, **5**, 669–85.
- MacPherson, G.L. (1989) Bromide in Gulf basin formation waters: organics as an additional source. *Geol. Soc. Amer. 1989 meeting abstracts*, A316.
- MacPherson, G.L. (1992) Regional variations in formation water chemistry: Major and minor elements, Frio formation fluids, Texas. *Amer. Assoc. Petrol. Geol. Bull.*, **76**, 740–57.
- Marsden, S.S. and Kawai, K. (1965) "Suiyosei-Ten'Nengasu," a special type of Japanese natural gas deposit. *Amer. Assoc. Petrol. Geol. Bull.*, **49**, 286–95.
- Martin, J.B., Gieskes, J.M., Torres, M. and Kastner, M. (1993) Bromine and iodine in Peru margin sediments and pore fluids: implications for fluid origin. *Geochim. Cosmochim. Acta*, **57**, 4377–89.

- McCaffrey, M.A., Lazar, B. and Holland, H.D. (1987) The evaporation path of sea water and coprecipitation of  $\text{Br}^-$  and  $\text{K}^+$  with halite. *J. Sed. Petrol.*, **57**, 928–37.
- Merino, E. (1975) Diagenesis in Tertiary sandstones from Kettleman North Dome, California - II. Interstitial solutions: distribution of aqueous species at 100°C and chemical relation to the diagenetic mineralogy. *Geochim. Cosmochim. Acta*, **39**, 1629–45.
- Moldovanyi E.P. and Walter, L.M. (1992) Regional trends in water chemistry, Smackover formation, Southwest Arkansas: Geochemical and physical controls. *Amer. Assoc. Petrol. Geol. Bull.*, **76**, 864–94.
- Morad, S., Bergan, M., Knarud, R. and Nystuen, J.P. (1990) Albitization of detrital plagioclase in Triassic reservoir sandstone from the Snorre Field, Norwegian sector. *J. Sed. Petrol.*, **60**, 411–25.
- Morad, S., Ben Ismail, H.N., De Ros, L.F., Al-Aasm, I.S. and Serhini, N.-E. (1994) Diagenesis and formation water chemistry of Triassic reservoir sandstones from Southern Tunisia. *Sedimentology*, **41**, 1253–72.
- Morton, R.A. and Land, L.S. (1987) Regional variations in formation water chemistry, Frio Formation (Oligocene), Texas Gulf coast. *Amer. Assoc. Petrol. Geol. Bull.*, **71**, 191–206.
- Posey, H.H. and Kyle, J.R. (1988) Fluid-rock interactions in the salt dome environment: an introduction and review. *Chem. Geol.*, **74**, 1–24.
- Price, N.B., Calvert, S.E. and Jones, P.G.W. (1970) The distribution of iodine and bromine in the sediments of the south-western Barents Sea. *J. Mar. Res.*, **28**, 22–34.
- Roedder, E. (1984) *Fluid inclusions. Reviews in Mineralogy* **12**, Mineral Soc. Amer., Washington D. C., 644 pp.
- Sanders, L.L. (1991) Geochemistry of formation waters from the Lower Silurian Clinton Formation (Albion sandstone), Eastern Ohio. *Amer. Assoc. Petrol. Geol. Bull.*, **75**, 1593–608.
- Sanford, W.E. and Wood, W.W. (1991) Brine evolution and mineral deposition in hydrologically open evaporite basins. *Amer. J. Sci.*, **291**, 687–710.
- Smirnova, A.Y. (1969) Genesis of boron, bromine and iodine in ground waters of western Ciscaucasian Cretaceous deposits. *Int. Geol. Rev.*, **12**, 703–10.
- Stoessel, R.K. and Carpenter, A.B. (1986) Stoichiometric saturation tests of  $\text{NaCl}_{1-x}\text{Br}_x$  and  $\text{NaCl}_{1-x}\text{Br}_x$ . *Geochim. Cosmochim. Acta*, **50**, 1465–74.
- Stueber, A.M. and Walter, L.M. (1991) Origin and chemical evolution of formation waters from Silurian-Devonian strata in the Illinois basin, U.S.A.. *Geochim. Cosmochim. Acta*, **55**, 309–25.
- Stueber, A.M., Walter, L.M., Huston, T.J. and Pushkar, P. (1993) Formation waters from Mississippian-Pennsylvanian reservoirs, Illinois basin, U.S.A.: Chemical and isotopic constraints on evolution and migration. *Geochim. Cosmochim. Acta*, **57**, 763–84.
- Sverjensky, D.A. (1984) Oil field brines as ore-forming solutions. *Econ. Geol.*, **79**, 23–37.
- Wilson, T.P. and Long, D.T. (1993a) Geochemistry and isotope chemistry of Michigan basin brines: Devonian formations. *Appl. Geochem.*, **8**, 81–100.
- Wilson, T.P. and Long, D.T. (1993b) Geochemistry and isotope chemistry of Ca-Na-Cl brines in Silurian strata, Michigan basin, U.S.A. *Appl. Geochem.*, **8**, 507–524.
- Worden, R.H. and Matray, J.M. (1995) Cross formational flow in the Paris Basin. *Basin Res.*, **7**, 53–66.
- Worden, R.H. and Smalley, P.C. (1993) Making water in sour gas deep carbonate reservoirs. In *Geofluids '93: Contributions to an international conference on fluid evolution, migration and interaction in rocks* (J. Parnell, A.H. Ruffell, N.R. Moles, eds.) 21–5.
- Zherebtsova, I.K. and Volkova, N.N. (1966) Experimental study of behaviour of trace elements in the process of natural solar evaporation of Black Sea and Sasyk-Sivash brine. *Geochem Int.*, **3**, 656–70.

[Revised manuscript received 10 July 1995]