- REVIEW ARTICLE -

Relationships of Formation, Migration, and Trapping Between Petroleum and Iodine

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Abstract

Iodine scarcely finds on Earth's crust. 99.6 % of Earth's crust is composed of 32 main elements. Remaining 0.4 % is shared among 64 trace elements. Ranking 61 among these 64 elements concerning abundance, iodine is one of scarcest non-metal elements within the composition of Earth's crust. Biological connection between iodine and carbon systems are well established. There is a strong relation between organic C and iodine concentrations in marine sediments. Iodine founds in low concentration in sedimentary rocks. Compliance of iodine with evaporite minerals is lower than that of bromine. Shales generally contain high iodine concentrations like 1-20 ppm. It is more related to preserved organic C. High amounts of iodine concentrations have measured in shales containing kerogen, the primary organic matter. As the iodine content increases in shales, the oil and organic carbon content also increase. Organic-rich sediments or their volatile derivatives (hydrocarbons) are the primary sources of iodine in many sedimentary basins. Iodine enrichment in waters increases with the proximity to the petroleum reservoirs and the depth of burial. Russians have asserted iodine as a hydrogeochemical indicator for petroleum. Iodine has been used in many studies as a sensitive tracer to discover oil or gas field. Iodine generally migrates together with organic matters due to its proximity to organic matters and is a good tracer for hydrocarbon migration and the movement history of the related waters. In this study, it has been shown that the 129I isotope system can provide useful information to decrease the costs of oil and gas exploration activities and to increase efficiency. Current studies showed that supporting the geological and geophysical survey with iodine hydrogeochemistry and soil geochemistry increases the efficiency of petroleum exploration. Use of iodine for the discovery of oil or gas fields has the advantage of both having reliable and consistent results and being simple and cost-effective.

Keywords: Petroleum exploration, iodine, geochemical indicator, geochemistry, oilfield brine, formation water

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Introduction

Kartsev et al. (1959) stated that a vast amount of iodine in waters is originating from petroleum, and, iodine is a direct hydrogeochemical indicator for petroleum. Kovda and Salvin (1951) determined in their studies that the iodine content in soil usually is 10^{-4} %, however, iodine content of soils covering oil and gas fields increase up to 10^3 % or 10^2 %. Iodine has been used to discover an oil and gasfield in the many studies (e.g. Ginis, 1966; Kudel'sky, 1977; Gallagher, 1984; Allexan et al., 1986; Sing et al., 1987; Tedesco et al., 1987; Gordon and Ikramuddin, 1988; Tedesco and Goudge, 1989; Leaver and Thomasson, 2002; Goudge, 2007, 2009; Mani et al., 2011; Hummel, 2011). Collins and Egleson (1967), Collins (1969, 1975), Bojarsky (1970), Schoeneich (1971), Kudel'sky (1977), Levinson (1980) and Özdemir (2018), in these studies, have proved the relationship between petroleum and iodine-rich waters in hydrocarbon production basins.

Iodine, which was discovered by Courtois in 1811 by extracting from seaweed ash, is scarcely found on Earth's crust. 99.6 % of Earth's crust is composed of 32 main elements. Remaining 0.4 % shared among 64 trace elements. Ranking 61 among these 64 elements concerning abundance, iodine is one of scarcest non-metal elements within the composition of Earth's crust (Hora, 2016). It is a halogen with Symbol I, atomic number 53, atomic mass 126.92, density 4.93 gr/cm^3 and valency -1, +1, +3, +5, +7. In seawater, there is 0.05 ppm iodide ion. The behaviors of iodine significantly differ from that of chlorine, since it has the most biophilic features among the halogens. The most significant reservoir of chlorine in the world is seawater (2.66 x 10^{16} tonnes, 72.2% of total chlorine), whereas the source of iodine is marine sediments (5.90 x 10^{12} tonnes, 68.2% of total iodine) (Muramatsu and Wedepohl, 1998). Thus, iodine enrichment is more related to the accumulation of iodine by marine phytoplankton, algae and organic matter deposition on the marine sediments rather than seawater (Tsunogai, 1971; Price and Calvert, 1977; Elderfield and Truesdale, 1980; Harvey, 1980; Lloyd et al. 1982; Tomaru et al., 2009a, b). Iodine distribution in seawaters and oceanic waters shows that sediments closer to the shore include more iodine than the deep sea sediments (Figure 1; Shishkina and Pavlova, 1965)
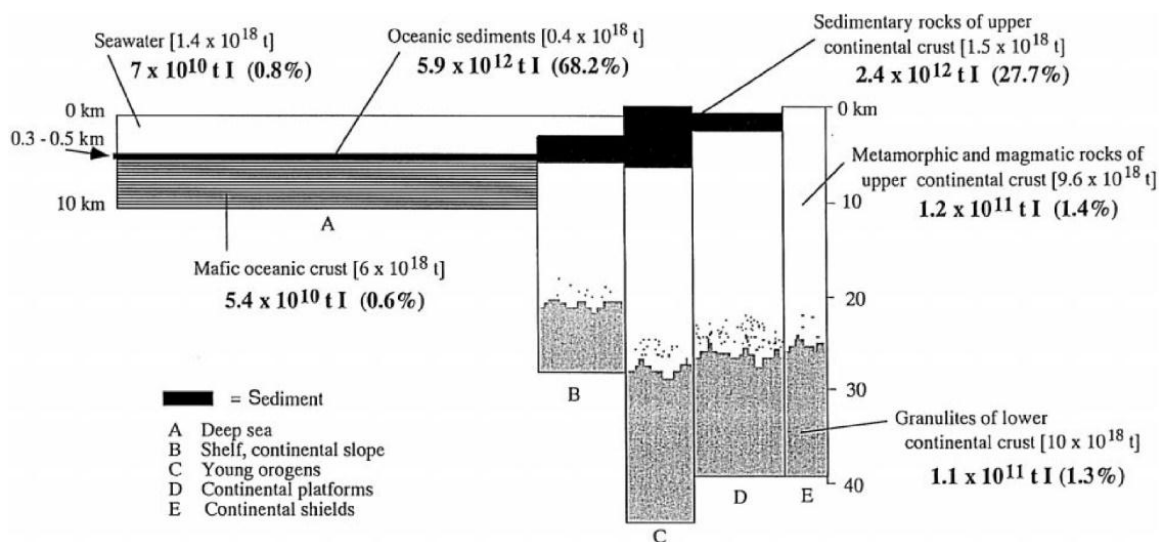

Figure 1. Distribution of iodine in Earth's crust (Muramatsu and Wedepohl, 1998)

Huang (1984) stated that most available geologically places for iodine accumulation of large and well covered, less deformed structures in areas where young and thick marine sediments are found (external neritic/bathyal reduction environment). Also, he defined the porous and permeable sandstones as the iodine reservoirs, the thick organic-rich shales as the source of iodine and the algae-rich organic matters as the accumulation regions of iodine. A vast amount of iodine (excluding potassium nitrate-caliche deposits in the Chile and seaweeds) find in the formation waters in oil and gas fields. Alvarez et al. (2015 and 2016) have determined that the source of the iodine in the Atacama (Chile), the most significant iodine deposit in the world, is the Jurassic, old organic-rich sedimentary basement. Some marine organism types like some seaweeds, planktonic algae, and corals take the iodine from the seawater and accumulate it in their bodies (Huang, 1984). Iodine accumulation mechanism in the mud of seafloor is as follows; 1) Accumulation in seaweeds, plankton diatoms, algae, and other marine organisms, 2) Accumulation of dead organisms on the seafloor. Iodine finds on the surface of organic sediments absorbed by colloid surfaces or bound to carbon components, and it is mostly immobile (Fuge, 1974). Marine organisms accumulate the iodine on external neritic seafloor together with inorganic matters and in bathyal reduction environment, and also in clayed sediments which are primary sources of iodine in oil and gas reservoir waters. Iodine-rich waters have classified in two groups; (1) iodine-rich waters with gaseous or petroliferous in oil and gas fields, (2) iodine-rich waters with the dry gas (dissolved natural gas) (Figure 2; Huang, 1984).

The main reservoir of iodine in actual marine environments is organic matters. Organic-rich sediments or their volatile derivatives (hydrocarbons) are primary sources of iodine in many sedimentary basins. Iodine enrichment in waters increases with proximity to petroleum reservoirs and depth of burial. Iodine increase in porewaters is faster than bromine (Warren, 2006; Martin et al., 1993). Salt lakes either contain a little iodine or no iodine at all (Warren, 2006).
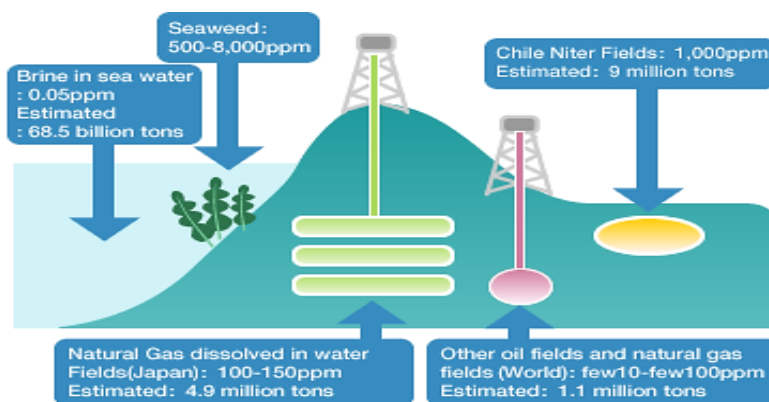

Figure 2. Environments where iodine is present (http://www.gasukai.co.jp/english/iodine/index4.html)

Organic-rich marine sediments and halite are primary sources for iodine in the terrestrial environment (Figure 3). These sources can be differentiated with I/Br ratios (Elderfield and Truesdale, 1980; Moran et al., 1995; Muramatsu and Wedepohl, 1998). Buried marine organic matter produces microbial/thermal methane and releases iodine. Meanwhile, iodine and methane (CH_4) which leave sediments accumulate in pore waters. These fluids which are rich in methane and iodine achieve to surface with leakages or trapped in sedimentary rocks in terrestrial

environments. There is a vast amount of iodine in oil and gas field waters (Moran et al., 1995). The amount of decomposed organic matter during generating of hydrocarbon in the marine environment affects the amount of released iodine (Fuge and Johnson, 1986).

It is known that algae and foraminifera muds contain a large amount of iodine (Figure 3). Also in micropaleontology studies, algae fibers are determined in iodine-rich rocks (Collins et al., 1971). Various ecological and biological factors control the environmental distribution of such organisms forming the reefs and carbonate build-ups (Tuzcu and Karabıyıklıoğlu, 1991).

Iodine concentrations, isotopic ratios, and ages indicate that iodine in volcanic fluids has derived from (together with iodine contribution of old sediments carried over from the crust) lower parts of the subducted marine sedimented column in the old subduction zone. High contents of iodine in geothermal fluids (according to observed iodine ages) indicate that reactivated iodine in the primary volcanic region is an essential part of the marine cycle (Figs., 4 and 5; Synder and Fehn, 2002). Alvarez et al. (2015 and 2016) have examined the effects of organic-rich sediments, volcanic (related with the arc) and meteoric (atmospherical) sources on iodine enrichment in the Atacama (Chile), the most significant iodine deposit of the world. Among all these sources are determined that the source of iodine is the Jurassic, old organic-rich sedimentary basement. Geochemical mixture models of these fluids have presented. Besides, this study has shown that iodine isotopic system (^{129}I/I) could be successfully used in the continental environment to monitor the water cycle (groundwaters and deep fluids in sedimentary basins) over ten billion years of time. Reich et al. (2013) prepared a graphic for determining the source of iodine found in the water sample according to the ratio of ^{129}I/I (Figure 6).
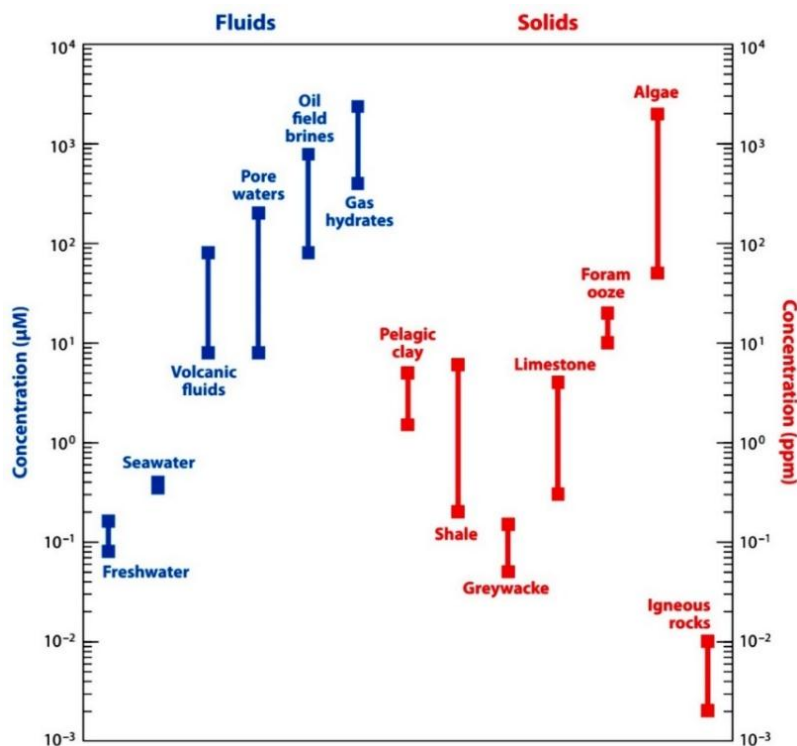

Figure 3. Concentration ranges of iodine in fluids and solids (Fehn, 2012)
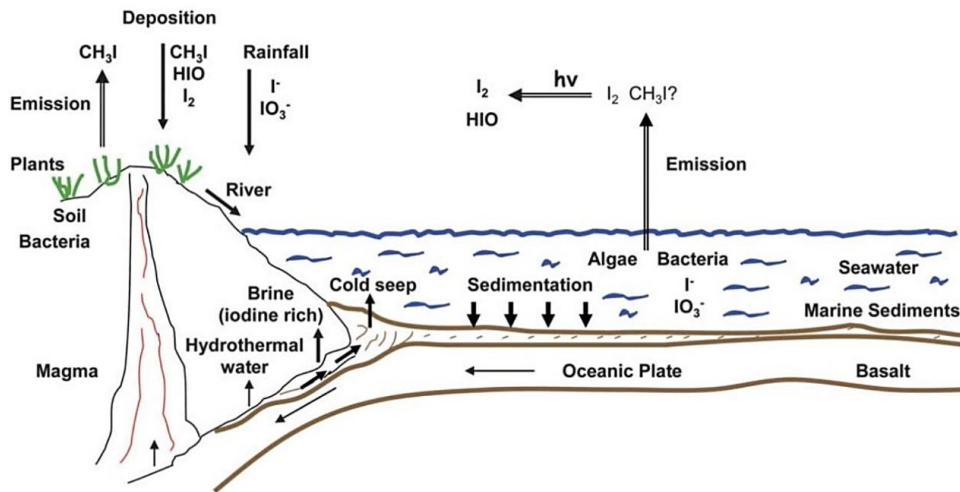
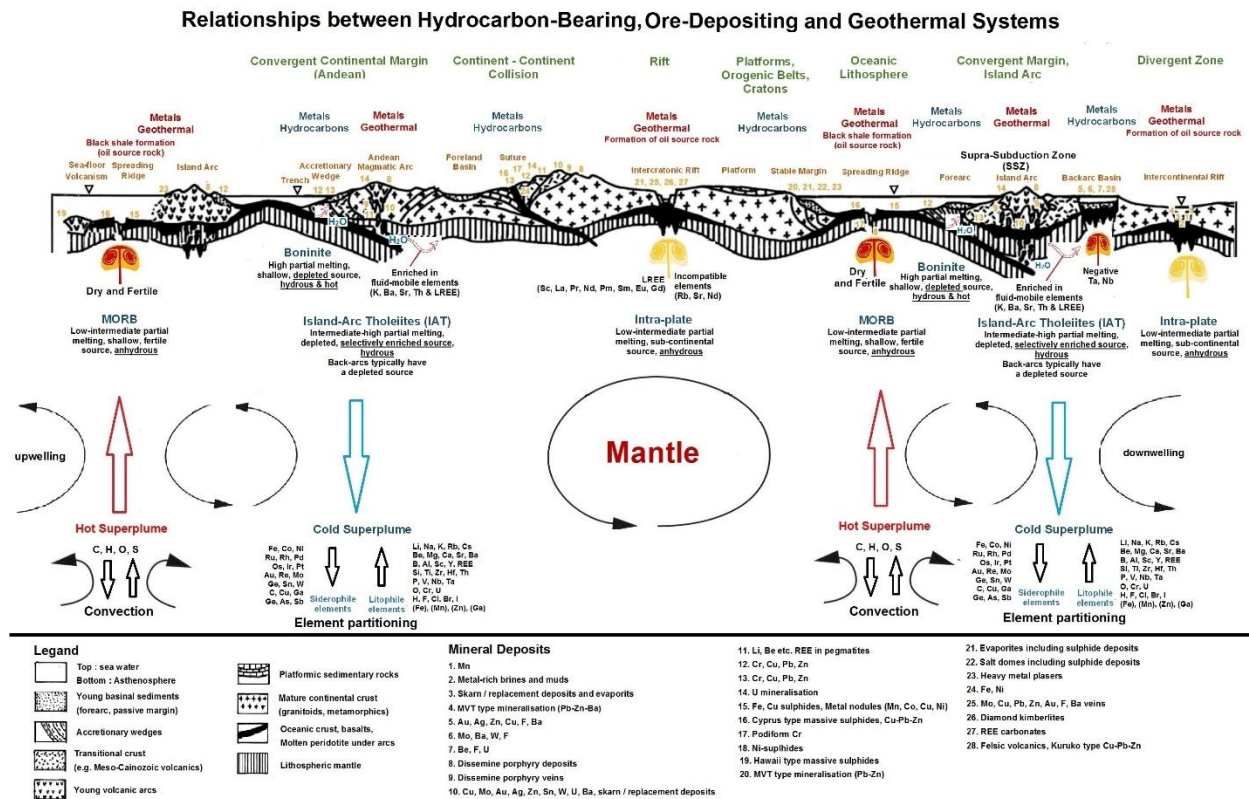Figure 4. Global iodine cycle (Muramatsu et al., 2004)

Figure 5. The relationship between iodine, which is a lithophile element, and geological, tectonic environments, and petroleum systems. Oil and gas fields containing iodine-rich waters are formed in convergent continental margins, continent-continent collision zones, platforms, orogeny zones, and craton margins. The iodine-rich petroleum source rocks are formed in rifts/mid-ocean ridges (Also see Figure 4)
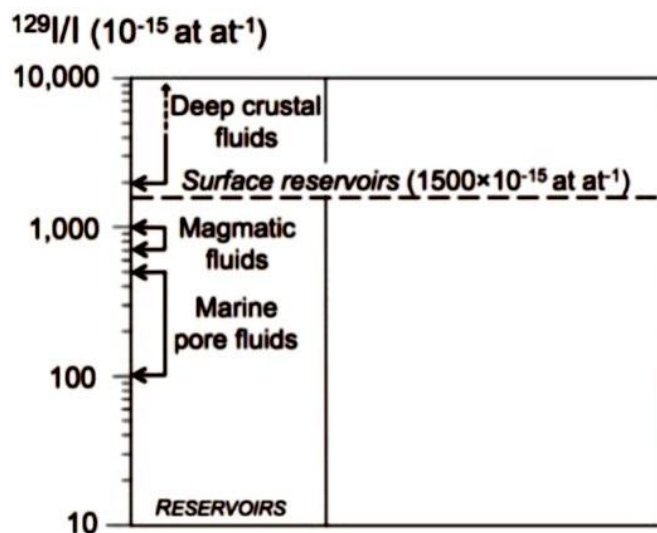
Figure 6. Source of iodine in water. The left scale shows the known [129]I/I ratios of different reservoirs, and the horizontal segmented line represents the preanthropogenic [129]I/I ratio for surface reservoirs (Reich et al., 2013)

Relationships Between Iodine, Organic Matter and Organic Carbon

High concentration of iodine accumulation in near-coastal and continent margin sediments has reported in various studies (Vinogradov, 1939; Shishkina and Pavlova, 1965; Price et al., 1970; Pavlova and Shishkina, 1973; Price and Calvert, 1973). In sediments in the early stages of diagenesis are seen that the iodine and bromine contents generally decrease with the increasing burial depth (Shishkina and Pavlova, 1965; Pavlova and Shishkina, 1973; Price and Calvert, 1977).

The loss of iodine in sediments is accompanied by the gradual decrease in organic carbon content and by iodine increase in pore waters (Pavlova and Shishkina, 1973). A similar increase can be expected in the content of bromine in pore waters. It is found that iodine increase in surface sediments is in direct proportion with organic carbon content (Figure 7). Unlike iodine is seen that $Br = k \, (C_{org})$ relation is independent of the redox potential of surface sediments (Peterson, 1979).
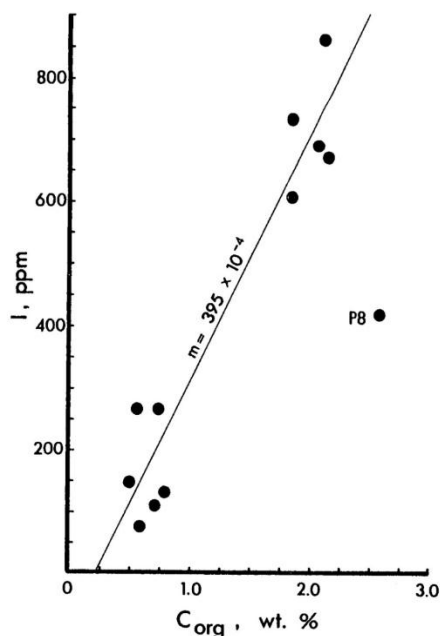
Figure 7. The relationship between salt-free iodine and organic carbon in Panama Basin area surface sediments. Sample P8:0-4: was omitted from the regression calculations since it deviates strongly from linearity. This deviation may be due to the presence of reworked, relatively refractory carbon in the core (Peterson, 1979)

The early diagenetic chemistry of iodine is considered as sequential in the context of four reaction regions defined in the light of information gathered from pore water (Figure 8). One of the distinctive features of Zone 1 is iodine concentration on surface sediments. As is evident from former and current studies are seen that the iodine concentration on the surface of oxic marine sediments stems from a semi-closed cycle with sediment-water contact. Such a cycle can be summarized as; within the vicinity of the sediment-water contact surface, iodine enters porewater through the dissolution of organic matter. Most of this iodine get does not lose by seawater above and probably trapped by clinging on new sediment particles in reactive organic areas. Decomposition of reactive organic matter near sediment-water contact surface returns iodine to pore waters and iodine is constantly regenerated on sediment-water contact surface or within its vicinity. High iodine content of uppermost pore waters reflects the increasing decomposition of iodine-rich organic matter on the sediment-water contact surface. Under the surface, little amount of iodine regenerated, and I/C ratio is changing with depth reflects the history of iodine concentration on the sediment-water contact surface.

ΣI concentrations and iodine species in porewaters cause four reaction regions in the sediment column (Figure 9). Zone 1 is the seawater/sediment contact zone where ΣI concentration increases and iodide (I^-) production prevails. Zone 2 is the base zone of the oxic part of sediment column where I^- turns into IO_3^- and iodide oxidation prevails. Zone 3 is the less oxygenic zone of the sediment column where iodate (IO_3^-) reduction reigns and IO_3^- turns back into I^-. Zone 4 is an anoxic subzone of the sediment column where iodide generation prevails (Kennedy and Elderfiel, 1987). In the analysis of porewater is observed that the iodine contents on the sediments increase with depth. In all sediments, the linear decrease of I/C_{org} with depth is independent of the amount, and it shows that there is more iodine loss than carbon during diagenesis (Peterson, 1979). Iodine

enrichment is a precise indicator of iodine-rich organic buried matter and is related to the rate of sedimentation (Figure 10). In zones with rapid sedimentation, iodine-rich organic matter buried rapidly, and most of the iodine trapped in pore waters. In slow sedimentation zones most of the iodine is also released into seawater (Martin et al., 1993).
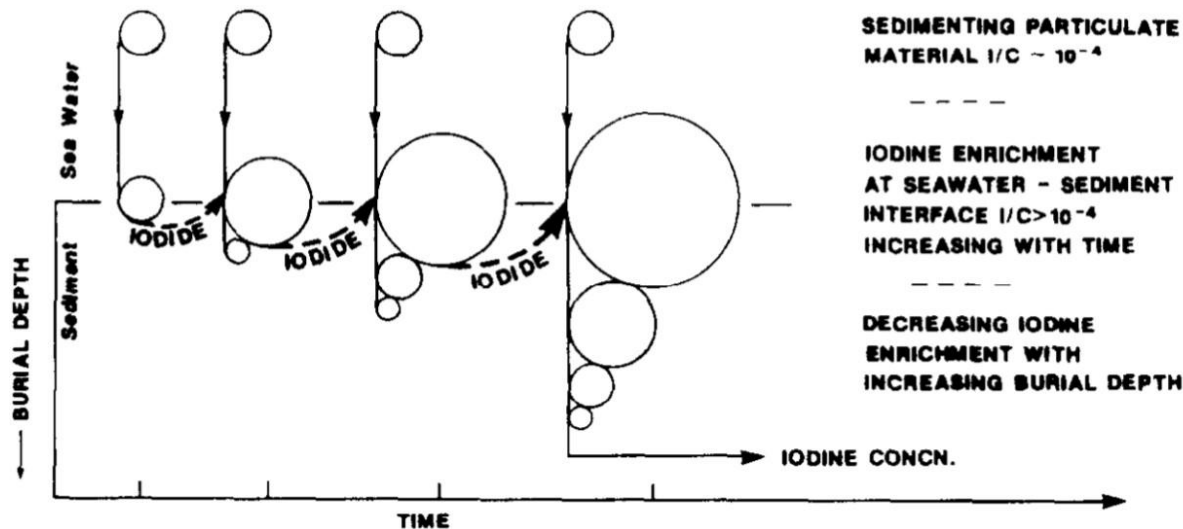

Figure 8. Cartoon of iodine cycling at the sediment-water interface (Kennedy and Elderfiel, 1987)

The biological connection between iodine and carbon systems have well established. There is a strong relation between organic C and iodine concentrations in marine sediments. Iodine is found in low concentration in sedimentary rocks (for instance in carbonates < 1 ppm, in marine evaporites < 0.1 ppm). Shales generally contain high iodine concentrations like 1-20 ppm. The iodine amount found in sedimentary rocks cannot be found in any rock-forming mineral and cannot be absorbed in clay. It is more related to preserved organic C (Cosgrove, 1970; Collins et al., 1971). High amounts of iodine concentrations have measured in shales containing kerogen, the primary organic matter (Cosgrove, 1970). Wilke-Dörfurt (1927) and Cosgrove (1970) studies are shown the close link between oil contents of shale ($r^2 = 0.98$) and organic carbon content ($r^2 = 0.76$), and iodine content of Lias (Posidonia) shales and Kimmeridge shales, the source rocks of North Sea (England) oil and gas fields. As iodine content is increasing in shales, oil and organic carbon contents are seen that increased (Figs., 11 and 12). Greenhalgh (2016) stated that TOC (Total Organic Carbon) value of Kimmeridge shales is > % 10, Hilger (2003) stated that carbon content of Lias shales is % 9 and oil yield as 40-45 liter/tonnes.
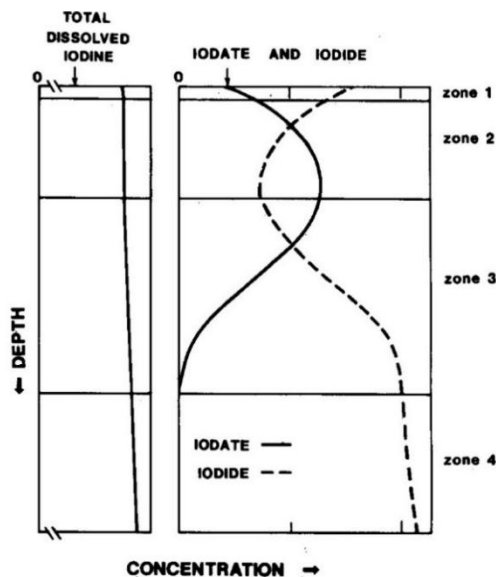
Figure 9. Schematic representation of the vertical sequence of iodine reaction zones based upon porewater data. Zone 1: iodide production; Zone 2: iodide oxidation; Zone 3: iodate reduction; Zone 4: iodide production (↓ marks seawater concentrations) (Kennedy and Elderfiel, 1987)

1) $y = 1.3765x + 0.0209$ ($r^2 = 0.91$),
2) $y = 0.8442x - 0.0868$ ($r^2 = 0.75$),
3) $y = 0.2891x - 0.0165$ ($r^2 = 0.97$),
4) $y = 0.1805x + 0.0221$ ($r^2 = 0.99$),
5) $y = 0.0637x + 0.0069$ ($r^2 = 0.93$).

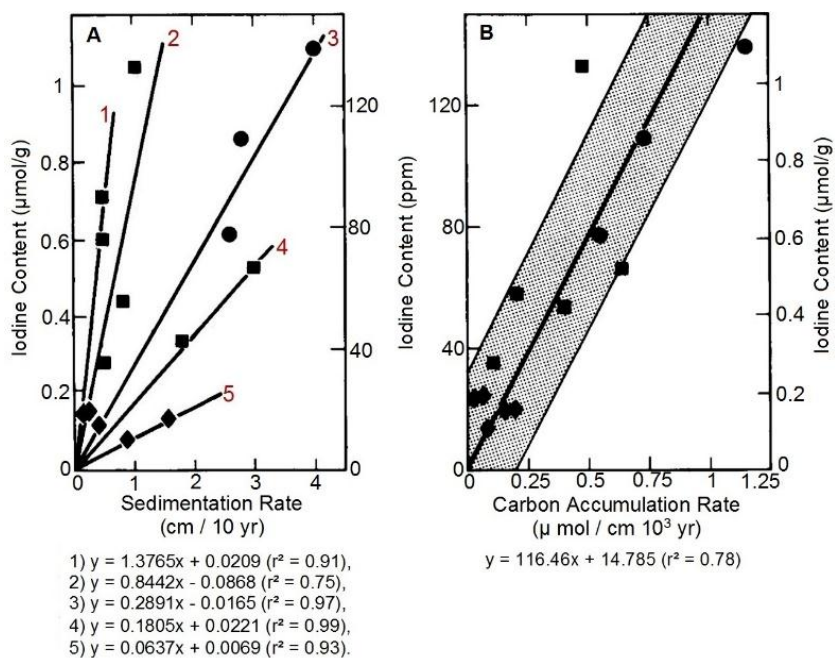$y = 116.46x + 14.785$ ($r^2 = 0.78$)

Figure 10. Relationships between iodine content of surficial sediment, sedimentation rate (A), and carbon accumulation rate (B). The equations were determined from the graphics by the author (from Kennedy and Elderfiel, 1987)
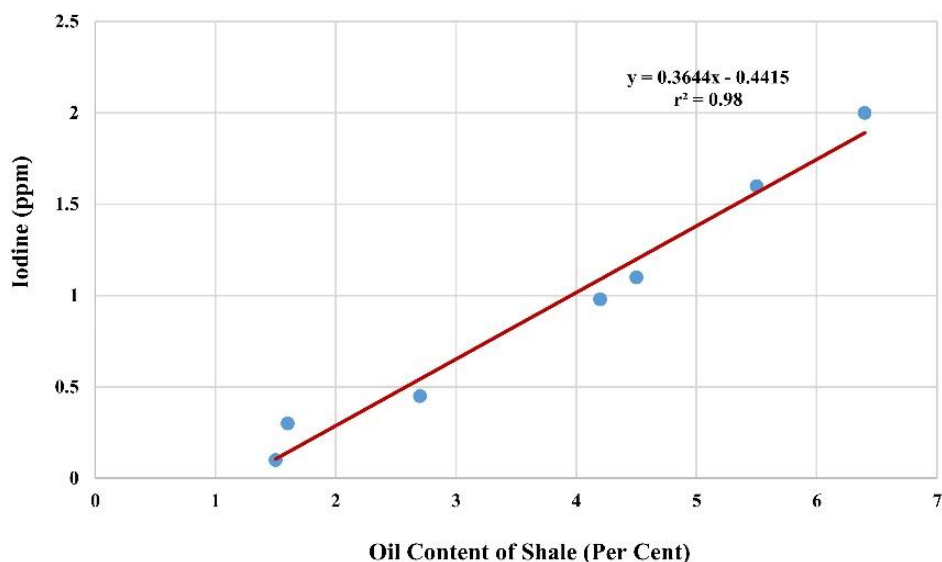
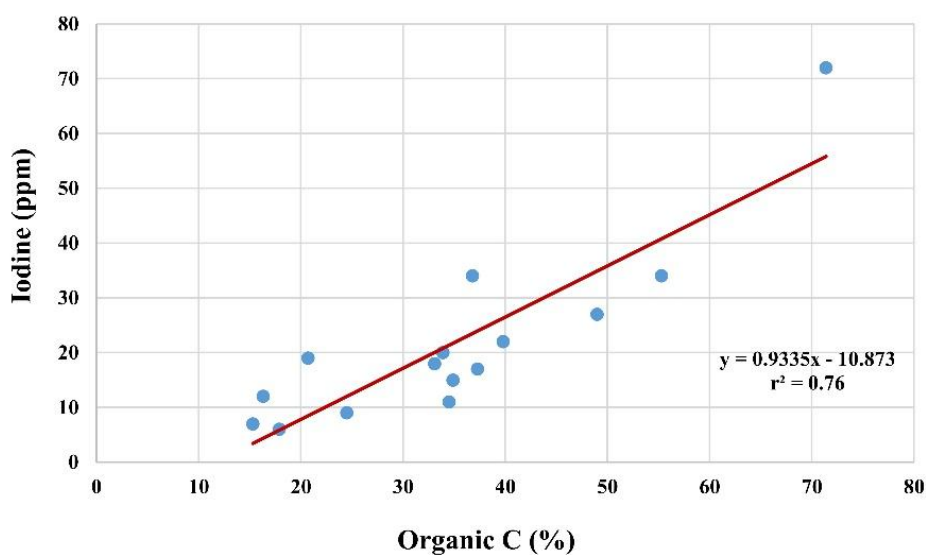Figure 11. The relationship between oil and iodine contents of Lias shales (Data: Wilke-Dörfurt, 1927)

Figure 12. The relationship between organic carbon and iodine contents of Kimmeridge petroleum source rocks (Data: Cosgrove, 1970)

Relationships Between Iodine with Formation, Migration, and Trapping of Petroleum

Iodine is a strong biophilic element and allows for determining the occurrence environments of geothermal sources (i.e., Fabryka-Martin et al., 1985; Fehn et al., 1992; Snyder and Fehn, 2002) and oilfield waters and gas hydrates, etc. (Moran et al., 1995; Fehn et al., 2000; Muramatsu e al., 2001; Fehn et al., 2003; Birkle, 2006; Tomaru et al., 2007; Tomaru et al., 2009a,b) the help of stable cosmogenic isotope [129]I. Formation of hydrocarbons is a result of increase in the iodine

content in deep porewaters with depth and the release of iodine from decomposed iodine-rich organic matter (Price and Calvert, 1977; Mayer et al., 1981; Martin et al., 1993; Egeberg and Dickens, 1999; Muramatsu et al., 2007), because iodine content of seawater is 0.05 ppm (Broecker and Peng, 1982). Iodine content of marine particles is generally between 200-1300 ppm (Wong, 1991). As a result of the decomposition of such iodine-rich organic matters and release of iodine to aqueous phase during diagenesis, iodine content increases over 250 ppm in sedimentary pore waters (Martin et al., 1993; Moran et al., 1995, Egeberg and Dickens, 1999; Tomaru et al., 2009a). That is why dissolved iodine can act as a representative of hydrocarbon migration in continental margins (Tomaru et al., 2009a). The iodine concentrations of formation waters in Lunnan oilfield (Tarim basin, China) are between 3.70 - 31.2 mg/L. The reason for such a significant amount of iodine enrichment in waters cannot be seawater evaporation, halite dissolution or any mineral transition process (i.e., plagioclase albitization or dolomitization). Such high iodine concentration is an indicator of the presence of organic matter related to the biophilic character of iodine (Chen et al., 2016). The high iodine content of organic-rich mudrocks and oil shows that iodine in formation waters (oilfield waters) have the organic origin (Figure 13). I/Br ratios of organic-rich mudrocks and oil are generally the bigger than I/Br ratios of formation waters. They are the richer in iodine compared to seawater or evaporated seawater and the source for high iodine content in the formation waters. Besides, organic matter is the richer in bromine compared to seawater (or diluted seawater). The low saline environment can be a significant source of bromine (Worden, 1996).
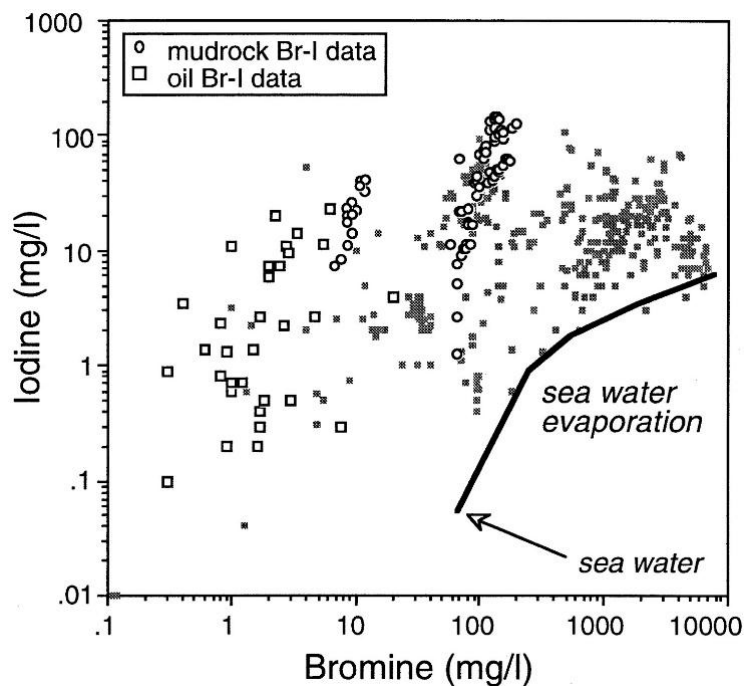
Figure 13. The I/Br ratios of organic-rich mudrocks and oils are generally higher than the I/Br ratios of formation waters. Organic matter in mudrocks and oil is enriched in iodine relative to seawater or evaporated sea water and is probably the source of the elevated concentrations of iodine in formation waters. Organic matter may also be slightly enriched in bromine relative to seawater (or diluted seawater) and may be an essential source of bromine in low salinity formation (Worden, 1996).

Waters associated with hydrocarbons sometimes expand to the other parts of sedimentary basins as a result of burial of basin (within geological time) (Bethke, 1985). Such waters are formed together with petroleum (Collins, 1975) and contain some natural tracers presenting the geochemical evolution of source rocks (Hummel, 2011). In many studies stated that iodine indicates organic matter presence in sedimentary basin (Vinogradov, 1959; Collins and Egleeson, 1967; Collins, 1969; Cosgrove, 1970; Whitehead, 1973, 1978; Ullman and Aller, 1980; Sheppard et al., 1995; Fuge, 1996; Moran, 1996; Fehn et al., 2007). Iodine concentrations show good relations with changes in organic matter amounts in marine sediments (Price and Calvert, 1973). Source of iodine in sedimentary basin brines, which is a large amount of hydrocarbon accumulation, is organic-rich dehydrated sediments in the buried basin (Mani et al., 2011; Collins, 1969; Collins et al., 1971; Moran, 1996; Correns, 1956). It is known that oilfield waters contain iodine with higher concentrations compared to seawater (Collins and Egleson, 1967). Therefore, in early stages of diagenesis, iodine in petroleum source rocks is preserved to a great extent, and this is most probably an indicator of anoxic conditions on the surface of original sediment (Price and Calvert, 1973). Brines of Canada shield characterizes by both iodine and high concentrations of ^{129}I, which reflects diagenetically modified seawater origin. Iodine concentration in Yellowknife brine is high (18 mg/L) and shows that there is iodine contribution from an external marine reservoir. Iodine in waters has formed as a result of iodine release during diagenesis stage of organic-rich marine sediments in the basin (Figure 14; Bottomley et al., 2002). Chen et al. (2016) have determined using ^{129}I isotope system that paleo-seawaters with high iodine content (~31 mg/L) in Lunnan oilfield reservoirs (Tarim basin, China) have carried to reservoirs together with hydrocarbons thermally generated in Cretaceous from Caohu graben.
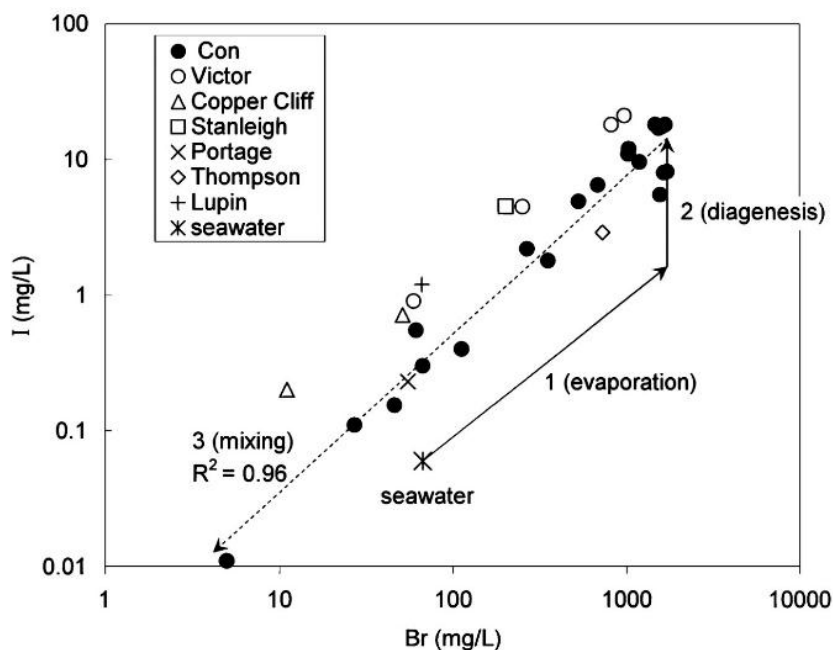

Figure 14. I vs. Br concentration relationships for Con mine (solid circles) and other Canadian Shield mine waters (see legend). Line 1 is the concentration trend for seawater. Line 2 is hypothetical iodine enrichment trend due to diagenesis of organic sediments during brine infiltration. Line 3 is mixing (dilution) trend between Con brine and recent infiltration (Bottomley et al., 2002)

Compression in deeply buried marine sediments pushes the iodine-rich porewaters towards sands which are more conductive from clays and muds. Decomposition of organic matter releases iodine to porewaters, the though slowly conditions of such process. Diagenesis of marine muds to shales causes a decline approximately 40% to 10% in the porosity from less and from 50 to 8 ppm in iodine content (solid phase). This process is a function of the pace of release, the age of sediment, depth and mineralogy, formation temperature and nature of bound iodine (Figs., 15 and 16; Fabryka-Martin, 1984). While organic matter turns into petroleum, most of the iodine is released to related waters (Fehn et al., 1990). In halogen systematics of marine porewaters are seen that gas hydrates and most of the organic bromine are merged whereas maturing hydrocarbons, H_2S, CH_4, and iodine together are migrated the basin (Figure 17; Kendrick et al., 2011; Fehn et al., 2003; Gieskes and Mahn, 2007; Muramatsu et al., 2007). Therefore, the potential of hydrocarbons to influence iodine and bromine contents of formation waters is high. High saline formation waters ensure organic Br contribution. Combined noble gas and halogen analyses provide an intriguing new method for investigating hydrocarbon-groundwater interactions because hydrocarbons have elevated Br and I contents and noble gases and halogens are both fractionated between hydrocarbons and groundwater (Kendrick et al., 2011).
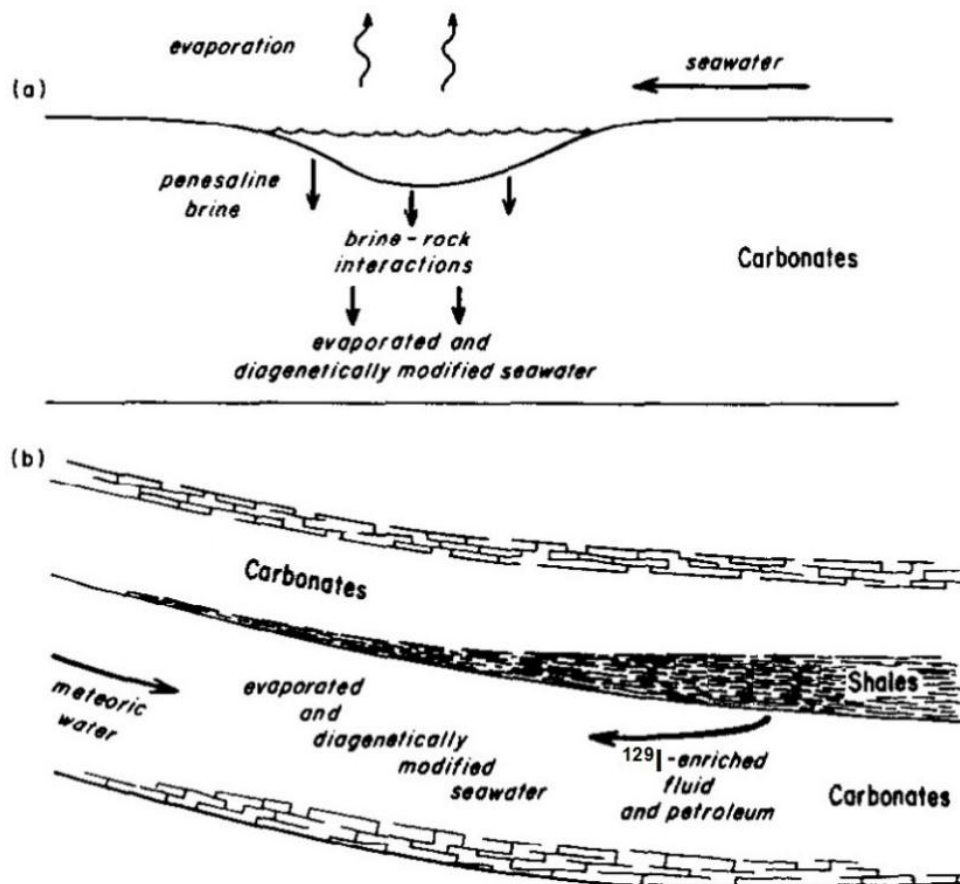

Figure 15. (a) The schematic diagram showing subaerial evaporation of seawater, followed by chemical modification of penesaline brine in the subsurface. (b) Schematic diagram showing subsequent mixing of remnant brine with an I-enriched fluid from shales and with meteoric water from recharge areas (modified from Stueber and Walter, 1991)
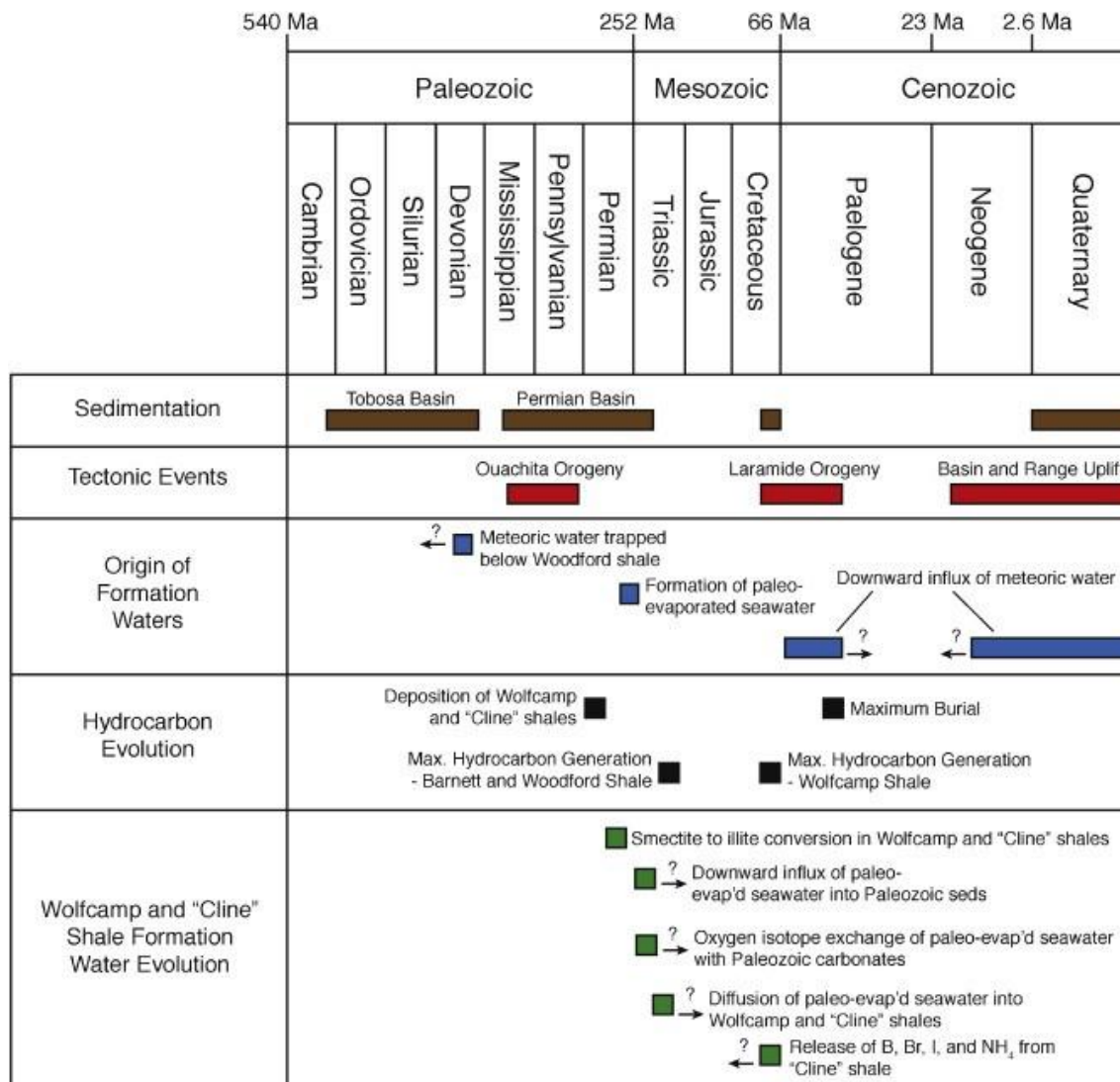
Figure 16. The relative timing of events related to sedimentation, tectonic events, hydrogeology, water-rock interaction, and hydrocarbon evolution in the Permian Basin (Engle et al., 2016)

Buried organic matter, which turn into petroleum after maturing and which cause to increase of iodine concentration in surrounding waters and which is the source of iodine in waters of sedimentary basins having vast amounts of hydrocarbon accumulation have dominant control over total iodine concentration. Chen et al. (2016) have stated that these iodine-rich waters mediate the hydrocarbon migration. Therefore, iodine concentrations of basin fluids can be used as a first approach to tracer the interaction between fluids and organic-rich sediments (Osborn et al., 2012). Land (1991) and Stueber et al. (1993) studies have proved that to be a flow mechanism from depths towards the Earth's surface of fluids in sedimentary basins. Harrison and Summa (1991) has calculated vertical velocities of fluids in sedimentary basins and suggested the iodine releasing model from thermal alteration of organic matter in solution (Mani et al., 2011). Synder and Fabryka-Martin (2007) stated that formation water has same ^{129}I/I age with on the environment it derives and the organic matter it interacts. Moran et al. (1995) submitted the long distance vertical

migration model for hydrocarbons and waters related with iodine, in the study made on fluid movements in sedimentary basins and age of source. Problems in these models are whether or not the iodine is bound to organic molecules for millions of years. It is an important subject. Because, iodine concentration of crude oil is very low (< 1 ppm) (Özdemir, 2018; Fehn et al., 1990; Tullai et al., 1987). Therefore, iodine has preserved its relation with organic C throughout the decomposition of organic matter and sedimentation process and has released in water during thermal maturing. As the iodine protects its close relation with organic C systems, the age of the iodine will be the age of the organic matter with which the iodine is in relation (Moran et al., 1998).
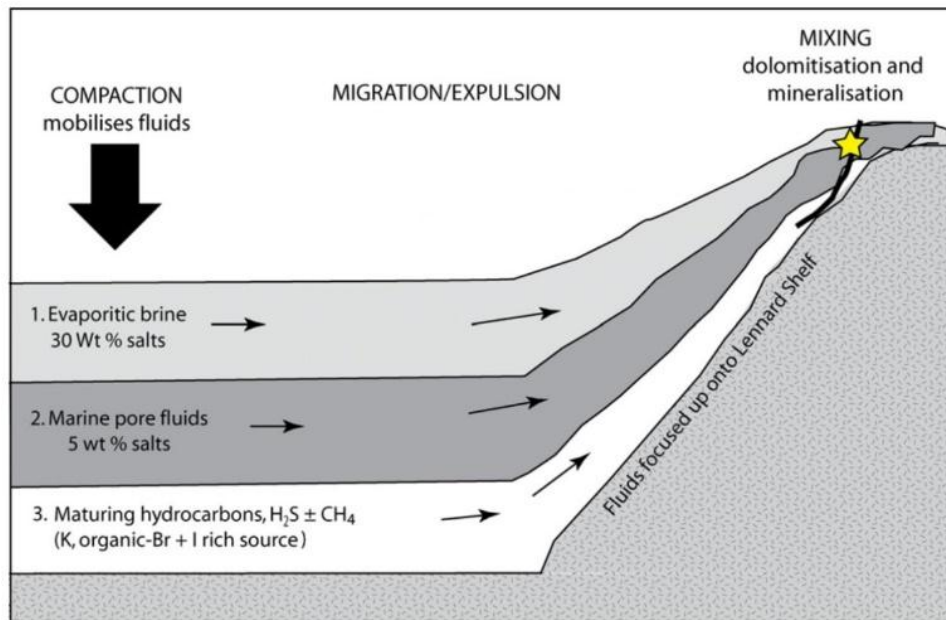
(a)
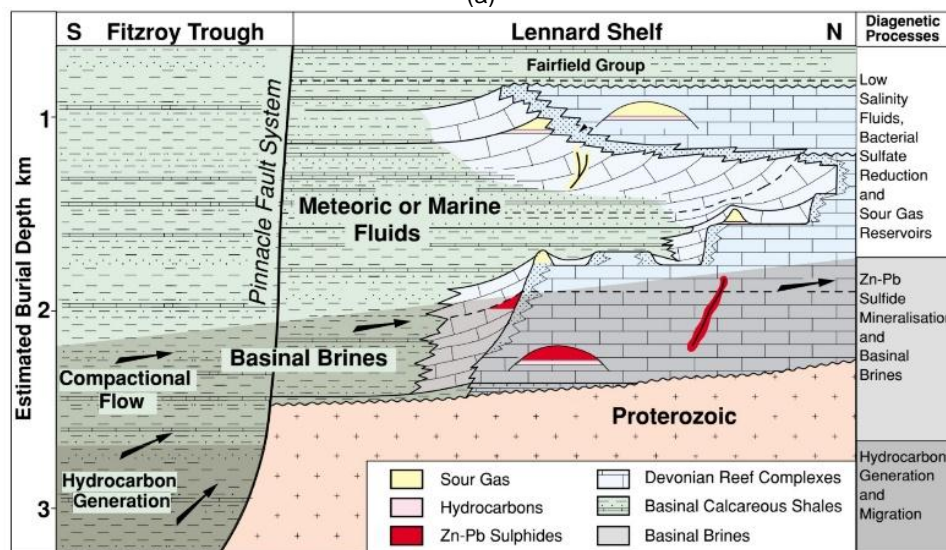
(b)

Figure 17. In the Lernard shelve of maturing hydrocarbons with iodine, (a) migration (from Kendrick et al., 2011), (b) trapping models (Wallace et al., 2002)

The decomposition of Type-II kerogen is the primary source of the iodine found in formation waters (Engle et al., 2016; Worden, 1996). Worden (1996) sub-categorized the formation waters according to the type of source rock (kerogen) as; Type-II (Algal or other marine material, oil-prone) or Type-III (Terrestrial plant material, gas-prone) (Figure 18). Also, he also stated that iodine concentrations are not affected by the type of kerogen in the basin, and the basins having Type-II source rocks might have higher bromine concentrations and lower Cl/Br ratios compared to basins having Type-III source rocks because the salt form in basins where it has the strong marine effect. The relation between the type of basin and bromine concentrations is a function of the dominance of the marine sedimentation in a basin. Iodine concentrations in formation waters are independent of the type of kerogen (Worden, 1996; Collins et al., 1971). In other geological factors do not have any impact on formation waters halogen concentrations. Processes controlling halogen concentrations are independent of occurrence style of the sedimentary basin. There is no impact of reservoir lithology on halogen concentrations because sandstones and carbonates do not contain much halogen minerals. Therefore, they do not affect halogen concentrations in formation waters. Besides, heat does not affect halogen concentrations in formation waters. The depth of burial has probably no influence on halogen concentrations because halogens do not expose to water-rock interaction caused by depth or heat (Worden, 1996). Therefore, the most reliable method to evaluate the presence or potential of oil and gas in a basin is to examine halogen contents (I, Br and CI) of basin waters.
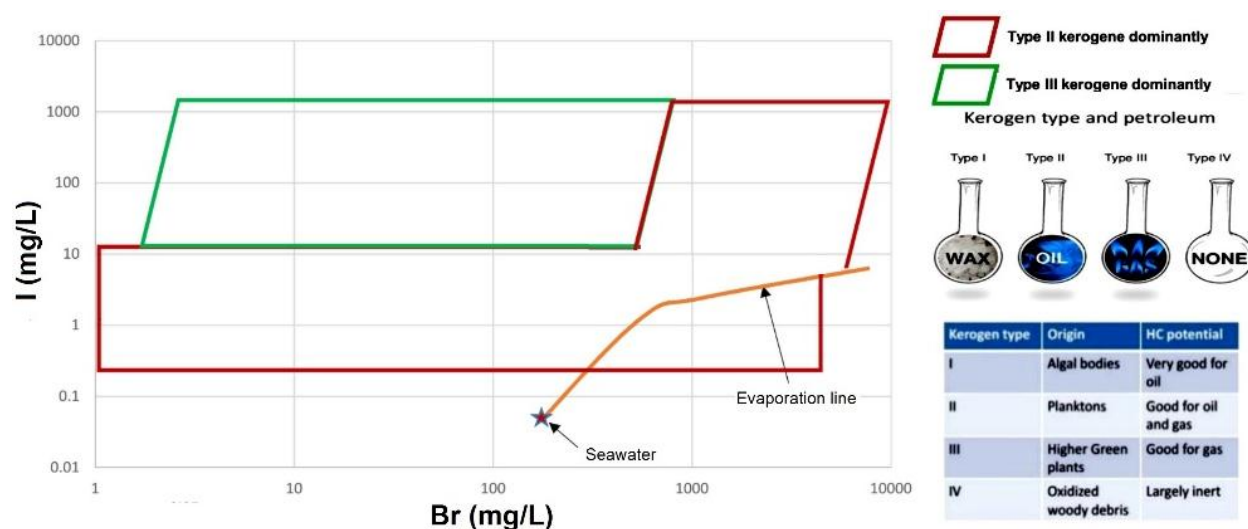

Figure 18. Relationship between I/Br ratios of formation waters and the kerogen type. Iodine concentrations are independent of kerogen type despite the relationship between marine organic matter and iodine. Basins containing type II kerogen (marine algal dominant) can have higher bromine concentrations than basins containing type III kerogen (terrestrial dominant) (Özdemir, 2018)

Iodine acts conservatively concerning being available in waters. However, its close relation with organic matter makes its geochemical character different from other isotopic tracers. Iodine generally migrates together with organic matters due to its proximity to organic matters and is a good tracer for hydrocarbon migration and movement history of related waters. Iodine generally enters source rocks with ^{129}I/I surface ratio together with the hydrocarbon generating organic matter

(Fehn et al., 1990). This surface $^{129}I/I$ ratio is 1500 x 10^{-15}. Tissiogenic and cosmogenic compounds, make iodine contribution at a ratio close to the pre-anthropogenic $^{129}I/I$ ratio, similar to the surface iodine reservoir ratios (Approximately 1500 x 10^{-15}). Although ^{129}I contribution to subsurface is insignificant for systems younger than 10 million years, the source for high ^{129}I contribution in such systems is petroleum source rocks as dominant (Fabryka-Martin, 1984; Moran et al., 1995). When fissiogenic production reaches the balance of approximately 100 million years, ^{129}I concentration remains as stable in the system and reflects uranium concentration of formation (Liu et al., 1997).

Iodine, which is a stable biophilic element, is found in highly enriched amounts in fluids associated with hydrocarbons such as oilfield waters (Hummel, 2011; Moran et al., 1995) or coal-bearing methane (CBM) reservoirs (Snyder et al., 2003). Due to its nature, iodine isotope (^{129}I) has been recently used in determining the hydrocarbon sources in various structures and the age and migration process of the formation waters related to those hydrocarbon sources (e.g. Fehn et al., 1987; Fehn et al., 1990; Martin et al., 1993; Moran et al., 1995; Liu et al., 1997; Fehn et al., 2000; Birkle, 2006; Fehn et al., 2007; Muramatsu et al., 2007; Lu et al., 2008; Tomaru et al., 2009a,b; Togo et al., 2014; Alvarez et al., 2015 and 2016; Santschi et al., 2016; Chen et al., 2016). The amounts, types, and ages (129I) of iodine in waters determine by spectrophotometer, gas chromatograms (GC-MS) and mass spectrometry (AMS) devices. Age of iodine (the age of hydrocarbons at the same time) can be determined by using below-mentioned formula (Fehn et al., 2007) or $^{129}I/I$ isotope graphics (Figs.,19 and 20).

$T = \ln (^{129}I/I_{sample}/^{129}I/I_{cosmogenic\ (marine)})/(-Λ_{129})$

$T = Age\ (My)$

$^{129}I/I_{cosmogenic\ (marine)} = 1500\ x\ 10^{-15}$

$Λ_{129} = Decay\ constant = 4.41\ x\ 10^{-8}\ year$

Iodine half-life, $T_{1/2} = 17$ million years
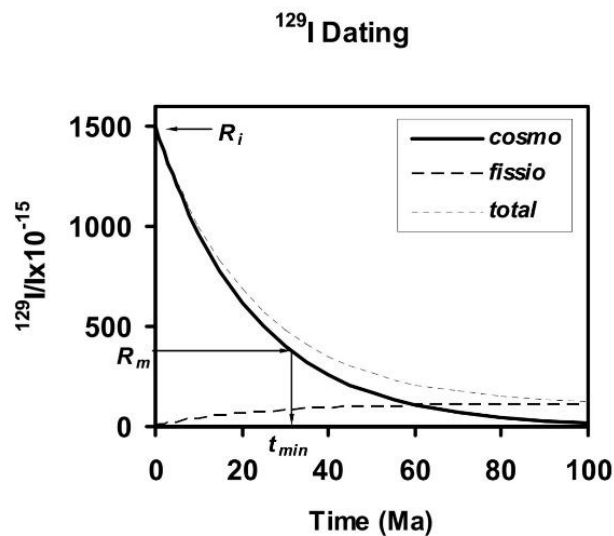

Figure 19. Iodine dating: systematics of the decrease of cosmogenic and build-up of fissiogenic $^{129}I/I$ ratios. The cosmogenic (marine) $^{129}I/I$ ratio decays from the input ratio $R_i = (1500 \pm 150) \times 10^{-15}$. Arrows indicate the determination of the minimum age tmin from the measured ratio R_m using the decay curve of cosmogenic $^{129}I/I$ (Fehn et al., 2007)
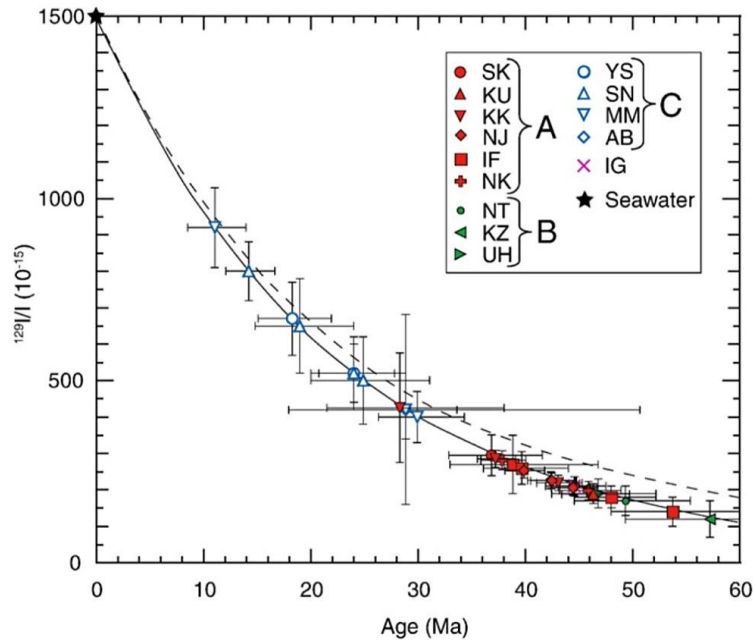
Figure 20. Iodine ages of 3 different types of water samples. Wells containing A type water - SK: oil, KU: gas, KK: gas, NJ: gas and iodine, IJ: oil and gas, NK: gas and iodine. B type geothermal wells - NT, KZ, UH. C type gas and geothermal wells - YS: gas, SN: geothermal, MM: geothermal, AB: geothermal, IG: geothermal. Iodine ages plotted on the standard decay curve (solid line) and maximum fissiogenic ^{129}I-corrected curve (dashed line). Iodine ages for Type A and B samples are as old as ~50 Ma, those for Type C samples are < 30 Ma (Tomaru et al., 2009a)

In hydrological studies, ^{129}I concentrations have usually reported as the ratio of ^{129}I to the total I, i.e., ^{129}I/I. Due to the very small of this ratio, it is multiplied by a coefficient, i.e., ^{129}I/I × 10 x. However, the coefficient is not well established as yet, whether it is 10^{12} or 10^{14}. Here, in the calculations, we have chosen 10^{12}. Iodine-129 analysis results can be reported in atoms/L as well. ^{129}I/I value is converted to atoms/L using below-mentioned formula (Kazemi et al., 2006).

^{129}I (in atoms per liter) = 4700 x B x R

where B is the concentration of iodine in the sample in µg/L and R is ^{129}I/I × 10^{12}. Example: If the ^{129}I/I × 10^{12} in a water sample is 41 and the concentration of I⁻ is 14 µg/L, what would be the concentration of ^{129}I in the sample?

^{129}I (in atoms per liter) = 4700 x B x R = 4700 x 14 x 41 = 2,697,800 atoms/L

For dating groundwater, the initial ^{129}I/I value of $1.1 ± 0.4 × 10^{-12}$, corresponding to $2 × 10^4$ atoms/L, is adapted. For dating pore waters, the initial ^{129}I/I value of $1.5 × 10^{-12}$, which is that of the recent sediments below the zone of bioturbation (Moran et al., 1998), is used (Kazemi et al., 2006).

Example: If the concentration of ^{129}I in a groundwater sample is 14,000 atoms/liter, what is the age of this sample?

$$t = -\ln \frac{^{129}I}{^{129}I_0} \Big/ \lambda = -\ln \frac{14000}{20000} \Big/ 4.41 \times 10^{-8} = 8,080,514 \, \text{years}$$

When ^{129}I enters the hydrosphere (more specifically to the marine system), it probably follows the stable iodine ^{127}I isotope. Iodine, which is a geochemically mobile element, has long staying periods in oceans (> 300000 years). Due to the relatively long half-life of ^{129}I and the close relation of iodine and organic matter, it has been suggested using the ^{129}I system, to determine the age of the buried organic matter or derivatives (such as hydrocarbons). This implementation is dependent on the fate of iodine in reactions related to the maturing process. Comparison of iodine concentrations of marine organic matter (iodine content > 50 ppm) and crude oil (iodine content $<$ 1 ppm), shows that there is iodine loss from the organic matter during maturation. Nevertheless, it is not clear the answer to question whether iodine is lost only from organic matter or whether iodine exchange to be at the same time with maturing. In the first case, ^{129}I isotope can be directly used to approximately determine the burial age of oil-generating organic matter. The second case is more complicated. ^{129}I concentration in crude oil will reflect isotopic compound of source rock. ^{129}I production of source rock depends on uranium content of source rock. If uranium contents of source rock and reservoir rocks are different from each other (typically uranium content of source rocks is higher than reservoir rocks due to relation uranium with organic matter), and iodine exchange is limited with maturing process. Iodine compound in petroleum will be related to the release time of oil from source rock (Figure 21; Fehn et al., 1987).
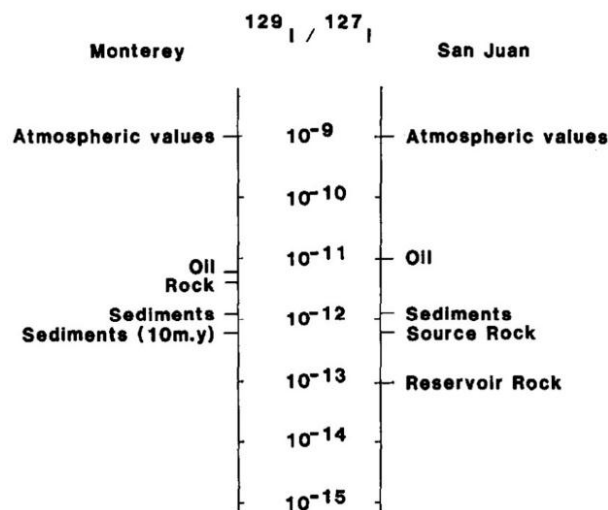

$^{129}I / ^{127}I$

Monterey		San Juan
Atmospheric values	10^{-9}	Atmospheric values
	10^{-10}	
Oil / Rock	10^{-11}	Oil
Sediments / Sediments (10m.y)	10^{-12}	Sediments / Source Rock
	10^{-13}	Reservoir Rock
	10^{-14}	
	10^{-15}	

Figure 21. The relationship between $^{129}I/^{127}I$ ratios measured in two crude oils and those estimated values for associated source and reservoir rocks. Values for post-bomb iodine in the atmosphere, pre-bomb iodine in recent and in 10 Ma old marine sediments, respectively, are also indicated (Fehn et al., 1987)

The occurrence of hydrocarbons, maturing time and start of migration are the critical questions in understanding the formation process of petroleum reservoirs. Liu et al. (1997) have been used the ^{129}I isotope system to answer these questions. The study has made on the samples gathered from various hot springs and oilfield waters (Eagle springs and Kate spring fields) most of which are related to geothermal systems in Railroad Valley (Nevada). The water and oils in the region are the close relation and have a common background. The reason why this region is chosen

is that the current waters in the area are not of meteoric origin and that occurrence of the oilfield is associated with the geothermal system (Figure 22). Besides, there are many geological, geochemical, geophysical, and structural studies on the occurrence of these oilfields. The residence times on reservoir rocks of oilfield waters found with the oil in Railroad Valley has been calculated as 6-24 million years by using [129]I isotope system (Figure 23). When tissiogenic/fissiogenic impacts stemming from reservoir rocks are taken into consideration, the age range is 7-28 million years. This case indicates that brines coexisting with oil were separated from source regions at different times during the evolution of fluid migration system. The longest residence time has considered as the starting of the fluid cycle in that region. The age of the structural activity in Railroad Valley is considerably compatible with geothermal activity process in the region (Liu et al., 1997).
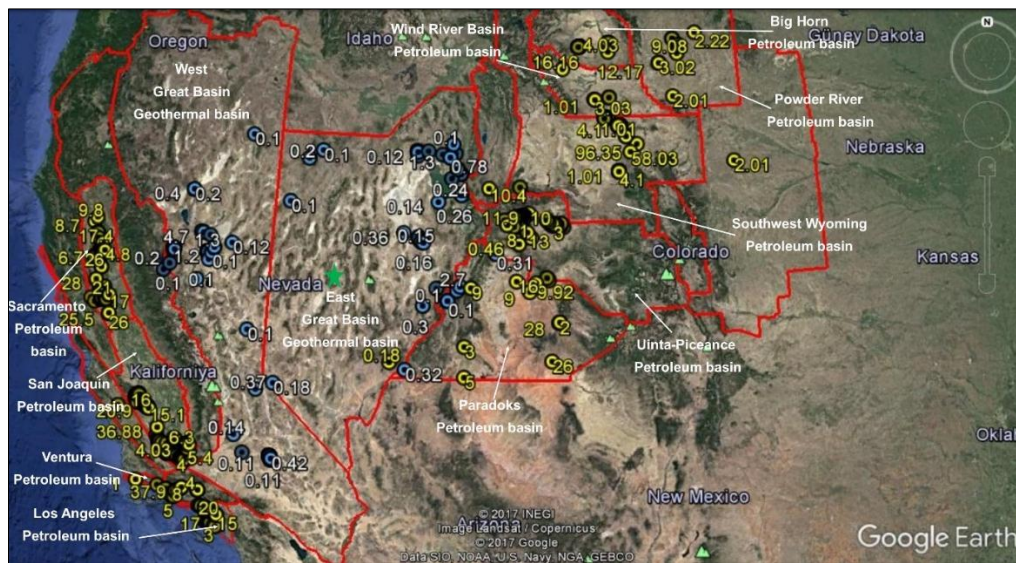
Basin	Well depth (m)	Average depth (m)	Average iodine (mg/L)	Max. iodine (mg/L)	Min. iodine (mg/L)	Sample Number
Great Basin (geothermal basin)	0 - 1830	140	0.07	4.7	0.001	756*
Kate Springs oilfields **	-	-	5.65	7.1	4.2	2
Eagle Spring oilfields **	-	-	4.84	7.1	2	5
Ventura	1280 - 4220	2640	66.55	294	5	24
Los Angelas	720 - 3450	1430	74.66	190	1.02	163
San Joaquin	320 - 4040	2120	26.39	148	0.1	155
Sacramento	540 - 3390	1750	28.62	73.8	4	61
Paradox	770 - 2870	2015	17.09	53	2	11
Uinta-Piceance	1370 - 5750	3385	15.27	48.6	0.46	55
Southwest Wyoming / Green River	180 - 3150	1990	26.90	519	1	37
Powder River	1180 - 2650	2015	19.98	53.58	2.01	12
Big Horn	705 - 3200	1735	8.44	23.37	1.01	17
Wind River	486 - 2635	1552	19.33	57.57	1	8

* The iodine contents of 9 geothermal fluids are bigger than 1 mg/L, 93 is between 0.1-1 mg/L, and the other 654 is smaller than 0.1 mg/L.
** Data: Liu et al. (1997)

Figure 22. The relationship between oilfields (green star) in Railroad Valley (Nevada) in East Great Basin (USA) with West America petroleum systems (Data: USGS Produced Water Database)

When the age of source rocks in Railroad Valley has taken into consideration, the original [129]I (surface) in this source has reduced to an insignificant level, and the proportion of [129]I/I has balanced in time. In the study, it has assumed that iodine has migrated together with mature

hydrocarbons and related water until it has trapped in the reservoir. Due to the relationship between oilfields and geothermal activity in Railroad Valley is thought that oil and water are carried upwards together. However, after then separated at the top of the convecting system due to their densities are different, have become part of a bigger convecting system. The 129I value of reservoir rock where carried oil and water is generally lower than the source rock. However, the porosity of reservoir rock is higher than source rock. Difference between the 129I value of two rock groups (source and reservoir) is used in calculating residence time of petroleum and water in the reservoir (Figure 22). When low iodine concentration in meteoric waters is taken into consideration (< 200 ppb), the ^{129}I contribution from meteoric sources can be ignored. In results of the study is seen that the residence time in the reservoir is in a range (7-28 million years). This observation is compatible with typical occurrence mode of oilfields. Petroleum usually separates from thermal convecting system during the batch mode. Upflowing fluid transports hydrocarbons to top of upwelling zones where they accumulated until saturation occurs and then separated from the convecting system. Longest residence time can be interpreted as the onset of convection in the region or arrival of the first batch.The estimated onset time of oldest batch in these oilfields is worth mentioning that compatible with the mechanism which reason for hydrothermal convection, and formed as a result of structural activity in the region (Figure 23; Liu et al., 1997).

The study made in Tahe oilfield in the Tarim basin of China by Li et al. (2011) has the same results with the study of Liu et al. (1997). Li et al. (2011) determined that oil emplacement to Ordovician aged carbonate reservoirs realize as a result of upwelling and mixing of partially freshwater and substantially hydrothermal fluids (Figure 24). According to this result, oil is separated from the thermal convecting system during the batch mode. The hydrocarbon-containing and upflowing fluid accumulate on top zones until saturating and continue upwelling after separated from the convecting system. Both chemical and isotopic data shows that waters, especially geothermal fluids play an important role in oil emplacement to the reservoir. The reason of high iodine content in such fluids is hydrocarbon accumulations found in the same basin with the geothermal fluids (e.g. Liu et al., 1997; Synder and Fehn, 2002; Fehn and Synder, 2002; Muramatsu et al., 2004; Birkle, 2005; Tomaru et al., 2009a; Li et al., 2011; Togo et al., 2014).
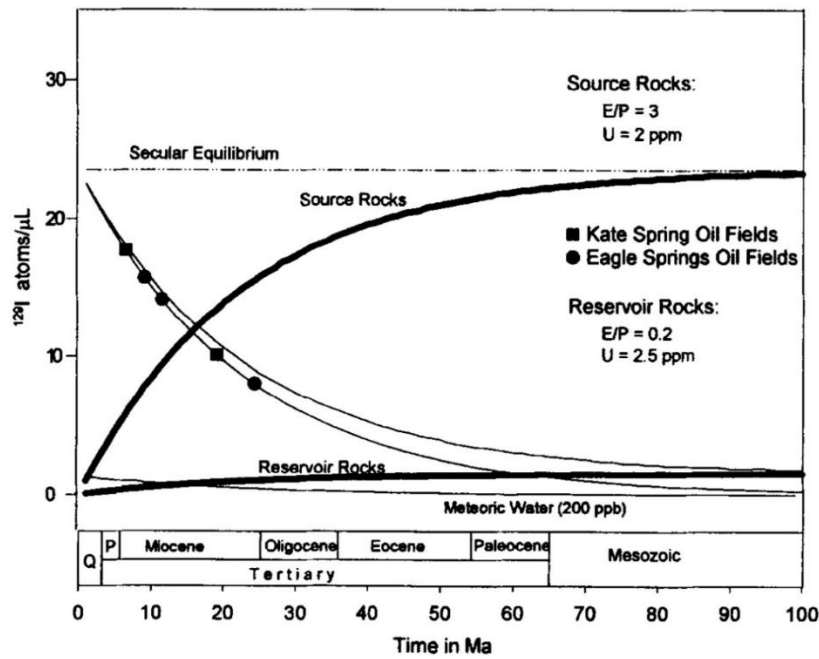
Figure 23. The evolution of ^{129}I concentrations in source rocks and reservoir rocks (heavy lines) and the decrease of ^{129}I concentrations after the separation from the source rocks (thin lines). The numerical time scale refers to residence times associated with the decay curves (thin lines), the geological time scale to the age of formations and the buildup curves (heavy lines). Data points are plotted on the uncorrected decay curve, the line above it indicates the decay corrected for the contribution from the production in the reservoir rock (see text). Potential contribution from pre-anthropogenic meteoric water is also shown in the diagram (Liu et al., 1997)
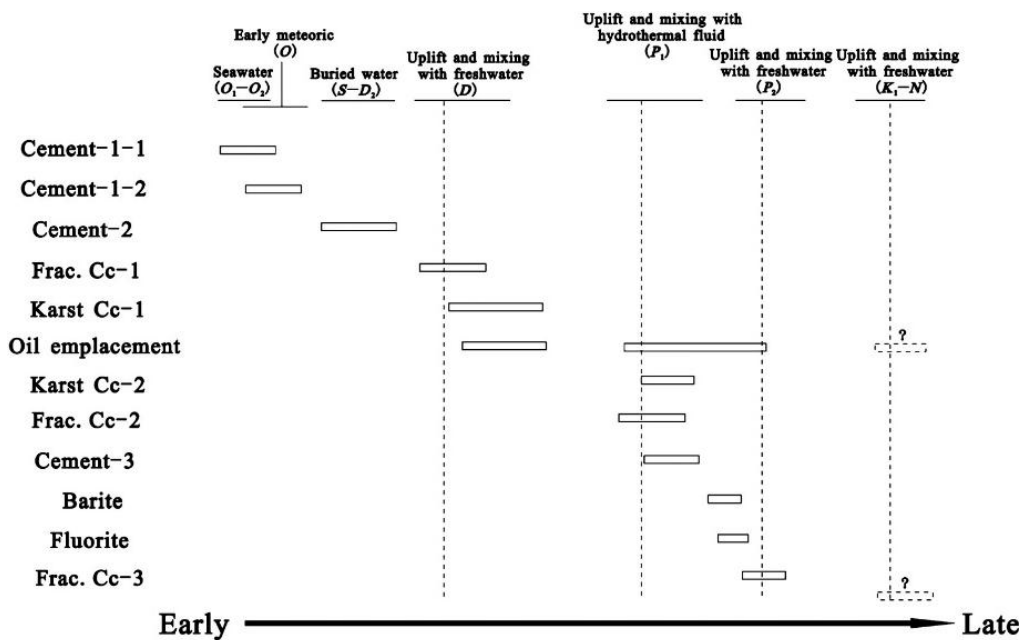

Figure 24. The synthetic paragenetic sequence shows the main stages in diagenetic evolution of Ordovician carbonates in Tahe oilfield (China) (Li et al., 2011)

Chen et al. (2016) used iodine concentrations and [129]I/I ratios to examine the relationship between hydrocarbons and waters in Lunnan oilfield (Tarim basin, China). Iodine concentrations of the waters in oilfield (3.70 - 31.2 mg/L) and [129]I/I ratios (189 - 897 x 10^{-15}) show that iodine in the paleo-seawater and meteoric water has different origins and [129]I specifications. Previous studies and the results of this study showed that water of the Ordovician paleokarst reservoir in Lunnan oilfield is a product of the mixing of evaporated paleo-seawater in the east and the paleo-meteoric waters in the west. The high iodine content in paleo-seawater (~ 31 mg/L), shows that the iodine enters into the reservoir in Cretaceous together with the thermally generated hydrocarbons when the source rocks of Caohu sag in the east reach the maximum oil generation level. When all possible sources of iodine and [129]I taken into consideration, it is seen that meteoric water preserves its first iodine content (0.01 mg/lt) and [129]I/I ratio (1500 x 10^{-15}). Besides, iodine-rich paleo-seawater (IPSW) demonstrates a [129]I value (265 x 10^{-15}) where fissiogenic [129]I contribution is balanced in time. The reservoir water evolution model developed through these data shows that the meteoric water entered the reservoir in the Miocene (approximately 10 million years) and mixing with iodine-rich paleo-seawater (IPSW). Faults occurred during Himalayan orogenesis has facilitated movement of meteoric water. Later, meteoric water concentrated after the dissolution of Paleogene halite and had leaked into the reservoir at high pressure (Figure 25). Iodine and [129]I concentrations of water provide information about the history of fluid in the reservoir and the migration path.
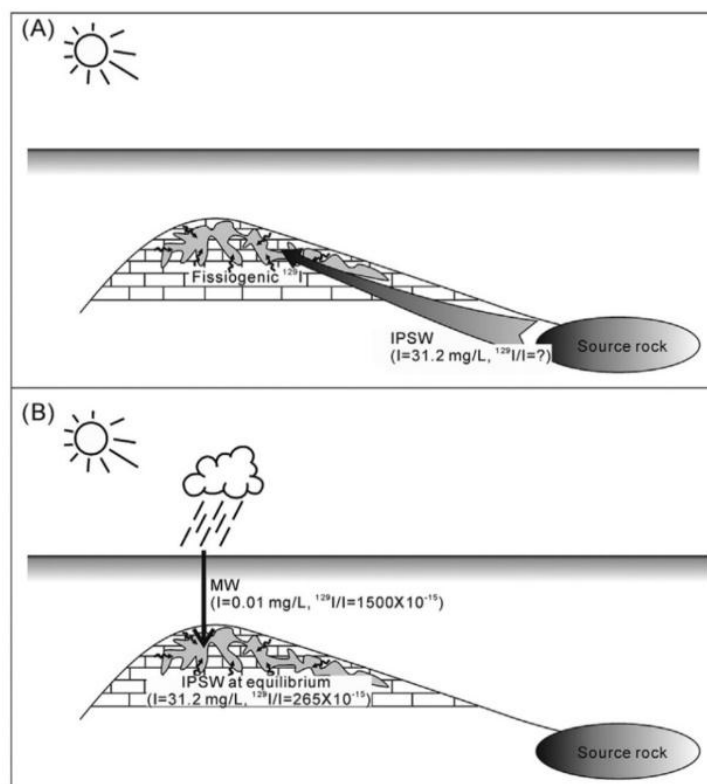

Figure 25. The schematic diagram of brine evolution. (A) During the Cretaceous, iodine enriched paleo-seawater (IPSW) has expelled into the reservoir. (B) During the Miocene, meteoric water (MW) infiltrated downward to mix incompletely with paleo-seawater at secular equilibrium (Chen et al., 2016)

The highest and lowest iodine concentrations in Lunnan oilfield has found in the deep LG351C well (31.2 mg/L) on the east part and in shallow LN101C well (3.70 mg/L) on the west part of the basin. The source of high iodine concentrations in water samples on the east part in the basin is paleo-seawater derived from source rocks in Caohu sag on the east of Lunnan oilfield (Chen et al., 2013). This paleo-seawater had absorbed iodine from organic matter, then migrated into the reservoir together with maturing hydrocarbons released from source rock. The reason for low iodine concentrations in the water samples taken from the west of the basin is diluted by meteoric waters containing-low iodine of the iodine-rich paleo-seawater (IPSW). This information can be beneficial for petroleum exploration because hydrocarbon migration is related to water movement. In this study, it is seen that can provide useful information to reduce the costs and to increase the efficiency of petroleum exploration activities of 129I isotope system (Figure 26; Chen et al., 2016).
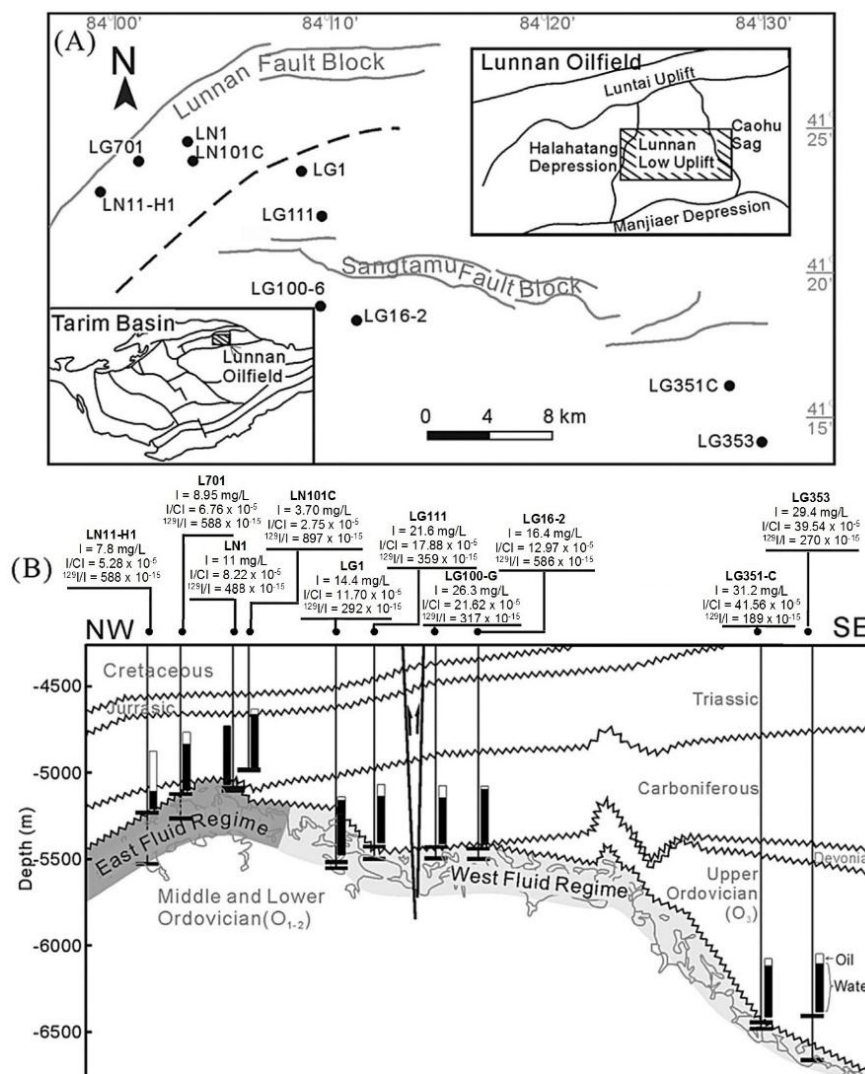

Figure 26. (A) Location of sampling wells in Lunnan oilfield, Tarim Basin, China. (A) The structural maps of Tarim Basin and Lunnan oilfield. (B) Strata profile from Well LN11-H1 to Well LG353. Note: the oil/water volume ratios show in the short columns. Two fluid regimes divide by dashed line in A and by different colors in B (from Chen et al., 2016)

Iodine Availability in Petroliferous Sedimentary Basins

In abundance in formation waters in a sedimentary basin, chlorine is the first and bromine is the second halogen (Figure 27). Chlorine and bromine have a strong systematic which gives rise to the thought that they have the same control mechanism. Fluorine is in relatively high concentrations only in high chlorine and bromine concentrations. This case shows that concentrations of fluorine, chlorine, and bromine are controlled most probably by the same processes. Iodine is not related to any other halogens and indicates that the concentration of iodine in water is controlled by distinctive processes (Worden, 1996).
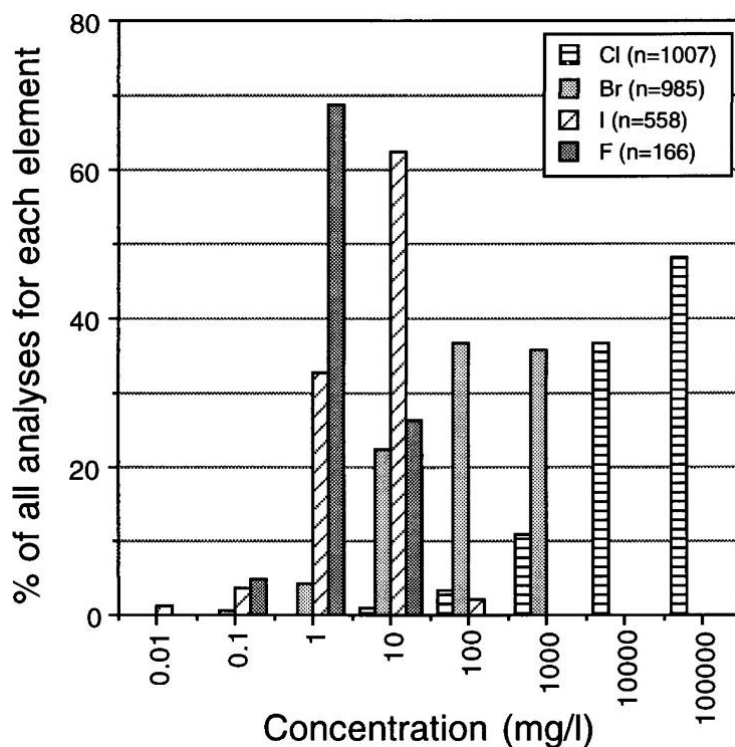

Figure 27. Compare of halogen concentrations of formation waters in sedimentary basins. Chlorine is the most abundant halogen followed by bromine, then iodine and finally fluorine (Worden, 1996)

Harkness et al. (2015) stated that the I/Cl ratios of flowback fluids of shale oil and gas produced from Marcellus and Fayetteville shales in Appalachian basin (USA) and produced water from conventional oil and gas fields is higher than I/Cl ratio of seawater evaporation. Because the iodine in the oilfield waters is derived from a secondary source (iodine release from the organic-rich formation) rather than seawater evaporation. The different iodine concentrations observed in different formation waters in this study and previous studies reflects the primary iodine contribution made by the organic matters in the formations where water exists. At the same time, the data show that I/IC ratios are related with Br/CI. At this case, it is seen that the primary source of waters (in other words evaporation level of the original saline water or halite dissolution) also has a contribution on iodine concentration (Figure 28).
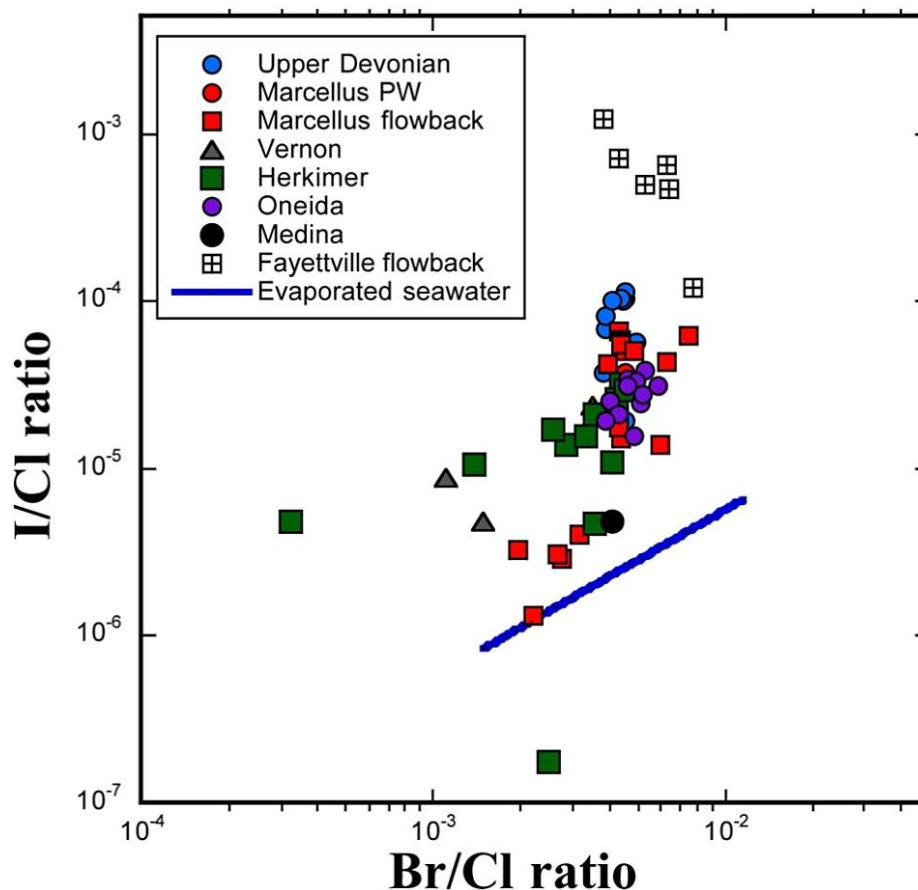
Figure 28. I/Cl versus Br/Cl (molar, log scale) ratios of flowback and produced waters. I/Cl ratios of most flowback and produced waters are several orders of magnitude higher than projected I/Cl in evaporated seawater for a given Br/Cl ratio, reflecting net enrichment of iodide in formation waters due to release of I- from organic matter in formations. Diluted Marcellus flowback waters are lower Br/Cl, and I/Cl ratios, reflecting dilution of Marcellus brines with Br, and I free freshwater. Produced waters from Upper Silurian Vernon and Herkimer formations also is lower Br/Cl and I/Cl ratios that could be derived from the contribution of salts originating from the dissolution of halite minerals (Harkness et al., 2015)

Compliance of iodine with evaporite minerals is lower than that of bromine (Holser, 1979). This case means that iodine concentration within organic matter in sedimentary rocks has dominant control on the iodine content of formation water and I/CI ratio (Collins, 1969; Worden, 1996). On the other hand, it has been argued that generally amount of organic matter has little effect on Br/Cl ratio of formation waters (Carpenter, 1978; Walter et al., 1990; Fontes and Matray, 1993; Hanor, 1994; Kendrick et al., 2005). Level of impress by organic matter of Br/Cl ratio of any fluid be evaluated by using Br/Cl and I/Cl mixing diagram (Figure 29; Kendrick et al., 2005). Kendrick et al. (2011) have submitted a diagram for sedimentary marine porewaters (Figure 30). Seawater border lines were added to the graph to show that sedimentary porewaters are the marine origin. The slope of data defines the Br/I ratio of the halogens generating form organic matter. Most of the marine porewaters have similar organic Br/I ratios (~ 0.5-2.5) with seaweeds and corals (Kendrick et al., 2011; Collins, 1969). Iodine is more mobile than bromine in oxidized porewaters (Martin et

al., 1993). In sedimentary basins, it is probable that Br/I ratios of some fluids interacting with organic matter will increase. For instance, Br/I ratio of Brazilian coal is 4 (Flores et al., 2008) and Br/I ratios of peat bog are 11 ± 4 (Biester et al., 2004).
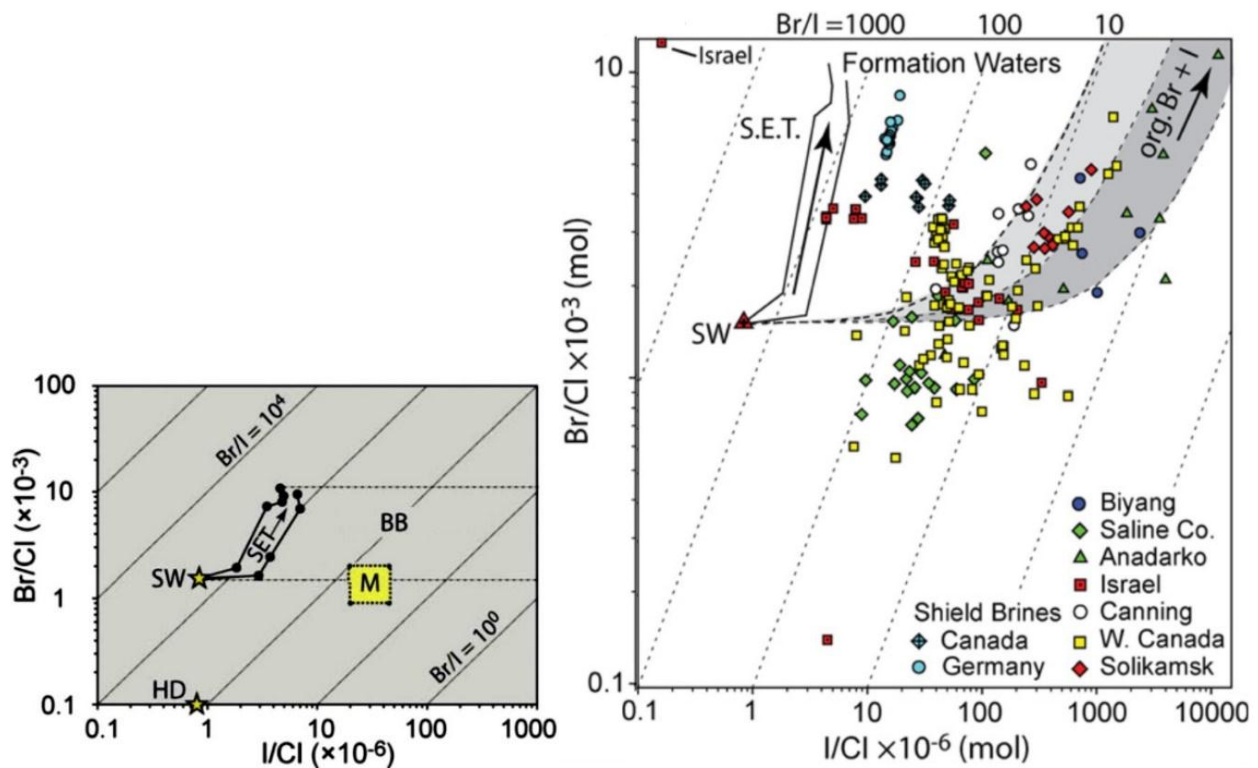

Figure 29. (a) Molar I/Cl and Br/Cl diagram. M: magmatic fluids, SW: seawater, SET: seawater evaporation trajectory, HD: halite dissolution water and BB: sedimentary formation waters relatively enriched with iodine compared to SET. (b) Halogen systematics of sedimentary formation waters and shield brines. Dark grey wedge based on pore-fluid trend has organic Br/I of 0.5-2.5; light grey wedge has an organic Br/I ratio of 8.5 and is based on halogen compositions reported for peat bogs (from Kendrick et al., 2011; Kendrick and Phillips, 2009)

Source of low iodine concentration in sediments and organic matters in the terrestrial environment usually are rainwater (Fuge and Johnson, 1986). Waters associated with hydrocarbons are derived from organic-rich sediments, and they have higher iodine content than the waters derived from sediments not containing organic matters (Worden, 1996; Fuge and Johnson, 1986). Potentially iodine is related with organic-rich rocks independently of marine and terrestrial environment and is used as a good tracer for sedimentary basin brines. As Br/I ratios of organic matters derived from marine and terrestrial are not the same, it is appropriate to use Br/I ratios to differentiate between marine source rocks and terrestrial source rocks in organic-rich environments (Fuge and Johnson, 1986). Iodine and bromine released during decomposition of organic matter are used to identify the origin of fluid. Iodine concentration is high in the marine environment. A terrestrial environment probably is higher Br/I ratios whereas marine organic-rich environment will have high iodine content and lower Br/I ratios (Hummel, 2011; Worden, 1996). Hummel (2011) observed that organic-rich rocks in Junggar basin (China) represent different geological environments according to their Br/I ratios (Figs., 31 and 32). Therefore, iodine is a sensitive tracer

for identifying oil and gas fields in sedimentary basins where organic-rich formations accumulating in marine environments (Hummel, 2011). Lu et al. (2015) made a detailed study proving that iodine is a good tracer to determine the effect of organic-rich shales on shallow groundwaters.
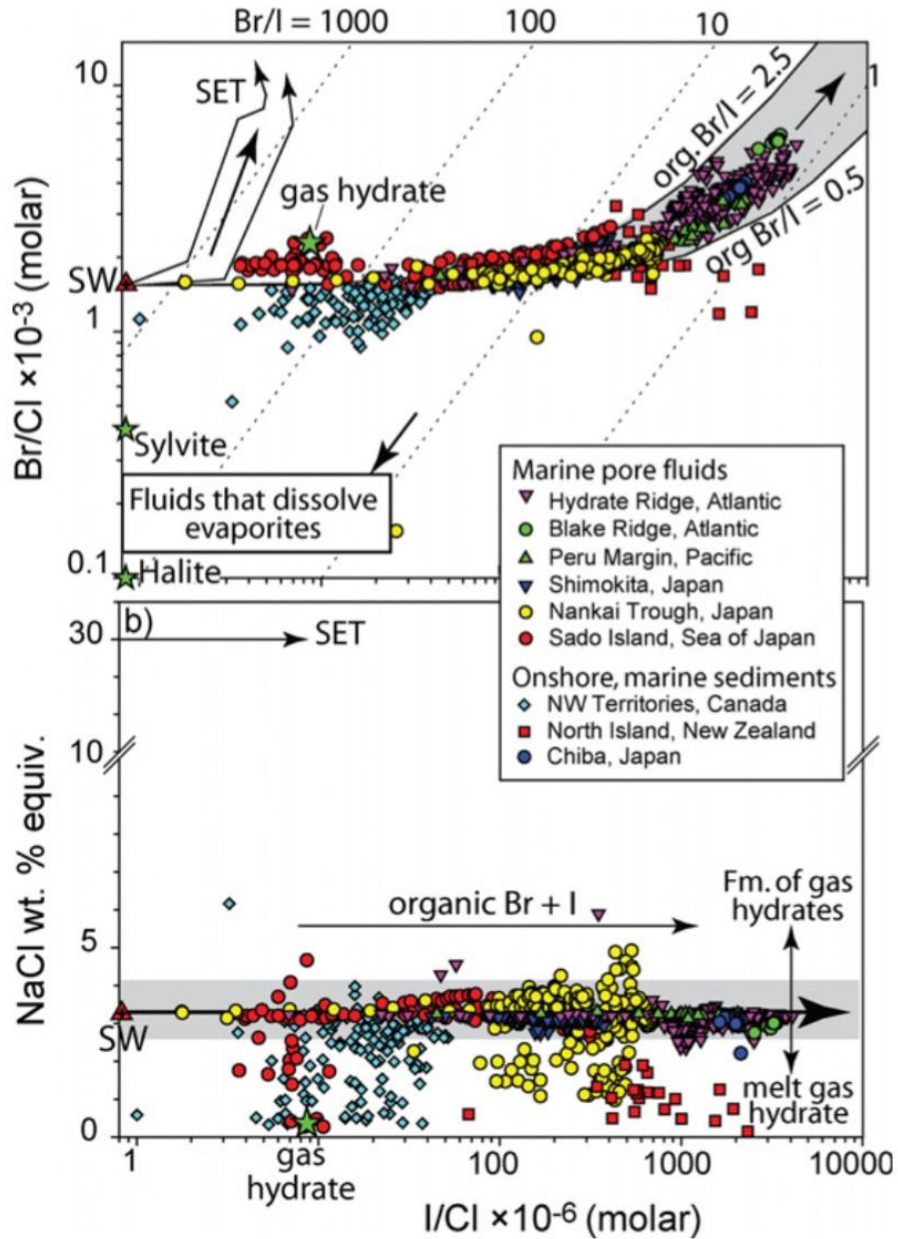
Figure 30. Halogen systematics of sedimentary formation waters and pore fluids: (a) log-log I/Cl versus Br/Cl showing seawater (SW), the seawater evaporation trajectory (SET); the compositions of halite, sylvite, gas hydrate (green stars) and pore fluids in modern marine sediments. Assuming an initial seawater Br/Cl value, most pore fluids acquire organic Br and I in a ratio of 0.5-2.5. (b) I/Cl versus salinity plot showing interaction with organic matter increases the I/Cl value of the fluid but has little effect on salinity which is influenced by the formation of gas hydrate (Kendrick et al., 2011).
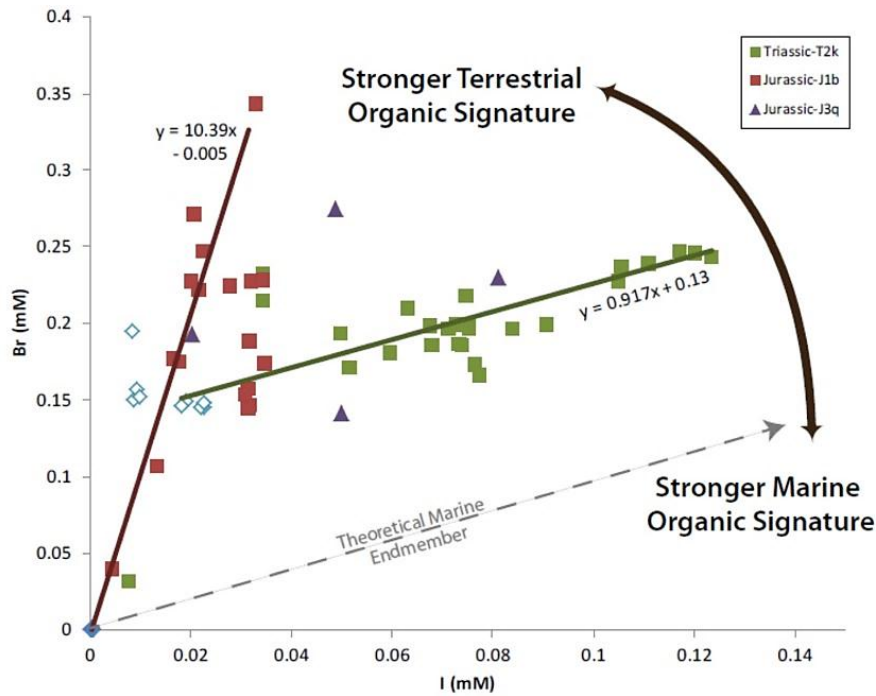
Figure 31. The plot of iodine and bromide concentrations. Theoretical marine end-member data comes from known iodine and bromide concentrations from organic-rich shale extractions. Blue diamonds represent injection waters (Hummel, 2011)

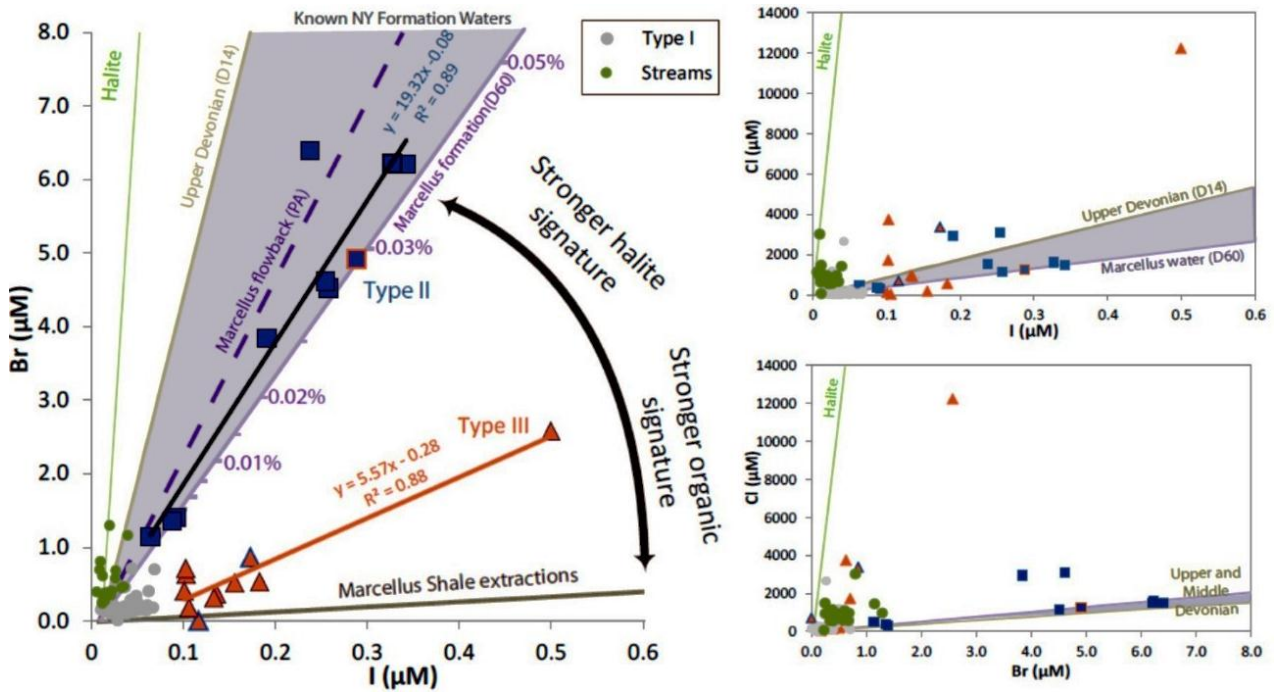Figure 32. I vs. Br, I vs. Cl and Br vs. Cl graphics of formation waters in Appalachian petroleum basin (New York, USA). Type I, II and III represent different types of waters (Lu et al., 2015; Hummel, 2011)

Relationship Between Iodine Soil Geochemistry and Seismic Survey

Iodine contents of soil are extremely different despite being 20-30 times more than of rocks. The soils generally contain more iodine than the rocks. Because soils usually contain a large amount of organic substance (Figure 33). The iodine content in soil is considerably variable, due to its relatively low absorption when compared to other ions, its washability and its ability to rapidly change, its high response to temperature, oxidation and precipitation. Besides, it is not possible to establish reliable relations with the iodine contents of the same plant types growing in the soil (Hosseini and Usta, 2000). Fuge (1990) stated that in soils formed on limestone as a result of iodine found on alkaline environments, iodate (IO_3) ions could not turn into I_2, therefore in waters running over such soil shall be iodine enrichment. Johnson (1980) analyzed 213 different soil samples to examine the relationship between organic matter and iodine contents. It showed that soils rich in organic matter are also rich in iodine ($r^2 = 0.57$). It has determined that such relation is dependent on the depth of soil. In surface soil samples (for soil thickness of 0-20 cm) it has been seen that there is a good relationship between organic matter and iodine contents ($r^2 = 0.70$). In soils with more than 20 cm thickness, no significant relation ($r^2 = 0.04$) was found between organic matter and iodine contents (Figure 34).
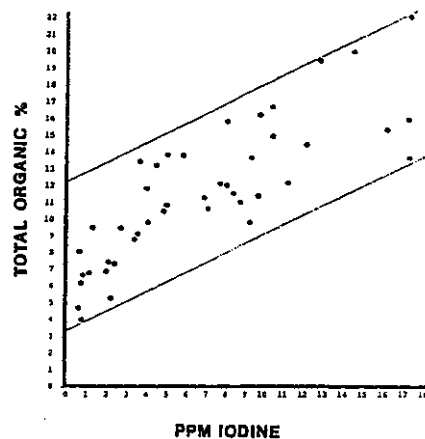

Figure 33. The relationship between total organic carbon (TOC) and iodine contents in soils (Allexan et al., 1986)
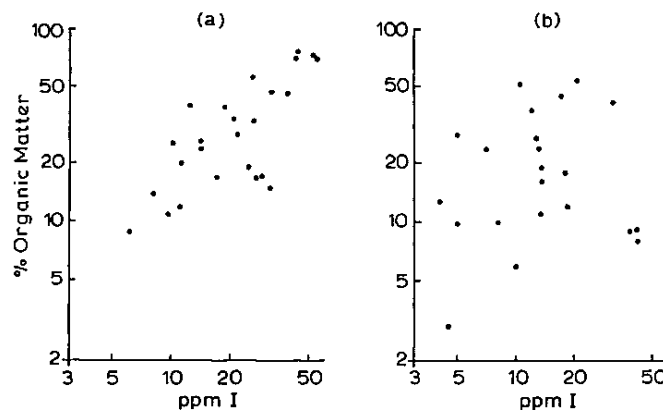

Figure 34. The relationship between organic matter vs. iodine contents in soils. (a) soils with 0-20 cm thickness (b) soil more than 20 cm thickness (Johnson, 1980)

To define specifics of iodine species found in soils and sediments and their geochemical behaviors, it is of critical importance to understand the transport mechanism of iodine in groundwaters. Li et al. (2017) stated that both iodine content and kf-iodate value are in a positive relationship with TOC (total organic carbon) and the potential source for iodine in soil/sediment samples is NOM (natural organic matter). NOMs in sediments find in organic-mineral complex forms, and NOMs in surface find in organic matter compounds embedded in levels near the surface. The decrease in the kf-iodate value in surface soils as a result of the chemical process of organic matter indicates that increased the iodate absorption in the surface soil of NOM. As a result of the chemical process of organic-mineral masses, the kf-iodate value in sediment samples increase. Lowest kf-iodate value for chemically processed surface soils and sediments, makes us think that organic-mineral masses have a dominant role in the geochemical behavior of iodate. Iodine when compared with iodate, displayed a lower predisposition towards chemical process in all soil/sediment samples.

As it is limited for iodine to turn into organic type in anoxic conditions, the source for the organic iodine in soil porewater is the dissolution of iodine in soil porewater as a result of the loss of organic matter in the soil. It is seen that the dissolution from organic iodine to iodide is a significant reaction to understand iodine behavior in sedimentary rocks containing organic matter and in reducing conditions such as soil-water and sediment-water systems (Shimamoto et al., 2011). The only reason for the increase of iodine in soil does not seem to be only methane. Standard decomposition of organic matter causes iodine increase in the soil, but it is never as high as iodine contribution by petroleum hydrocarbons to the soil. This situation is confirmed by taking as reference the biogenic gas and coal-bearing methane (CBM) production basins. Current thought on this subject is that iodine is related to one or more heavy hydrocarbons. The relationship between iodine with petroleum deposits in subsurface continues with hydrocarbon gasses on soil/air contact surface. Under the light of infrared and ultraviolet, hydrocarbons enter into reaction with iodine and forms iodoorganic (organic iodine) compounds. The release of hydrocarbon gases from soil causes physical and biological processes which gradually reduces the number of iodoorganic compounds (Tedesco, 1995). Besides, iodide amount must be higher than iodate content in soils over oil and gas deposits. It has been observed that iodine concentrations on soils over hydrocarbon accumulations increase a few times more of the average value (Kartsev et al., 1959; Gallagher, 1984; Allexan et al., 1986; Tedesco et al., 1987; Tedesco, 1995). The amount of hydrocarbon migrating or leakage from the subsurface to soil from depths is generally at ppm and sometimes ppb scale (Figure 35). The organic substance in soil corresponds to a percent in ppt level of the soil. Low amount of petroleum leakage may increase iodine content in the soil to 1.5-50 times (Tedesco, 1995). Kovda and Salvin (1951) showed that standard iodine content of the soil is $\% 10^{-4}$. However, iodine content in soils over oil and gas deposits increase until to $\% 10^3$ or $\% 10^2$.

Surface geochemistry aims to obtain various surface findings showing oil and gas deposits in the subsurface such as light gaseous hydrocarbons (from methane to butane) leaked from deep reservoirs to surface soils (Jones and Drozd, 1983; Xuejing and Binzhong, 1989; Klusman, 1993; Schumacher and Abrams, 1996). In many studies, iodine has used as a geochemical method for petroleum exploration (e.g., Kartsev et al., 1959; Allexan et al., 1986; Tedesco et al., 1987; Xuejing and Binzhong, 1989; Tedesco, 1995; Leaver and Thomasson, 2002; Mani et al., 2011). Current studies are showing that supporting geological and geophysical survey with iodine geochemistry increases the efficiency of hydrocarbon exploration. Use of iodine for the discovery of hydrocarbon fields has the advantage of both having reliable and consistent results and being simple and cost-

effective. Besides, as anomaly results are controllable and repeatable, risks and costs of exploration are mitigated to a great extent (Leaver and Thomasson, 2002).
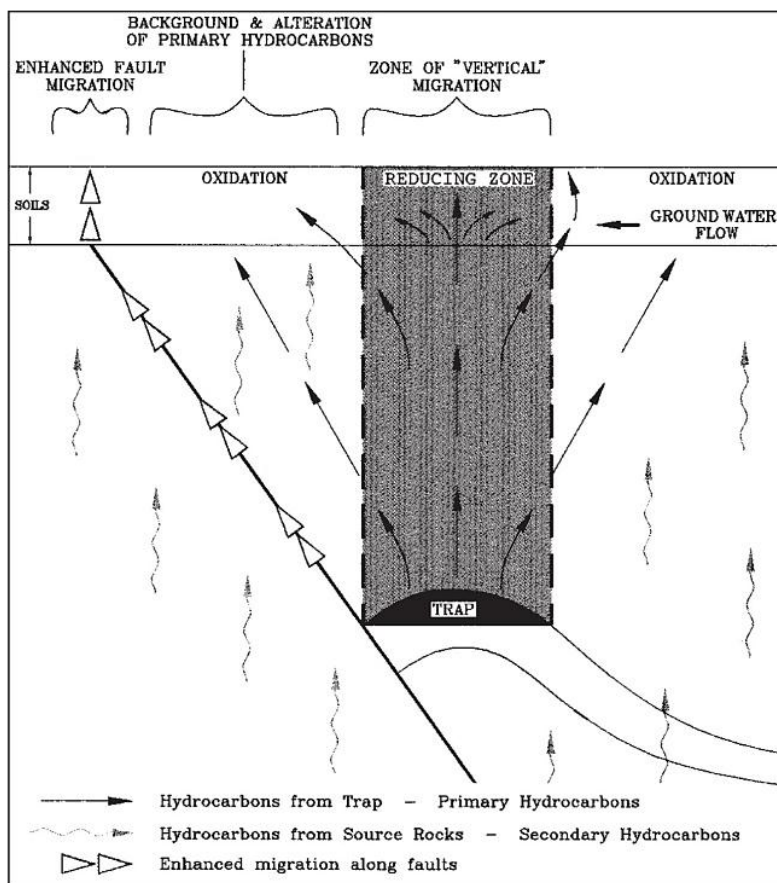

Figure 35. The schematic diagram of hydrocarbon leakage from a trap, showing the zone of vertical migration (Potter II et al., 1996)
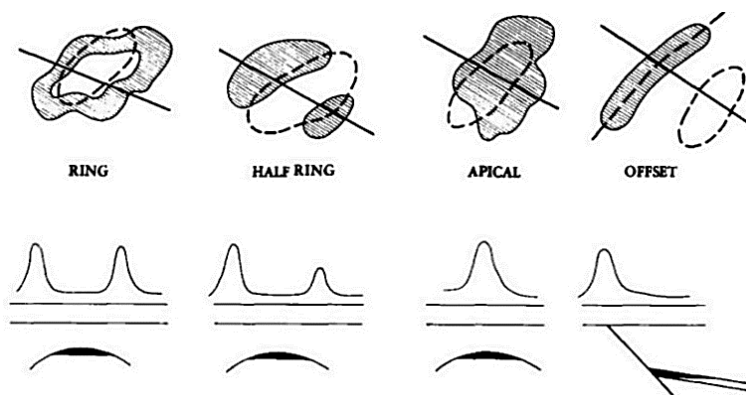
Figure 36. Different types of geochemical anomalies over oil and gas fields (Xuejing and Binzhong, 1989)

Surface geochemical anomalies of oil and gas deposits in the subsurface are very complex. These anomalies, whose type is controlled by faults and cracks (Figure 35) around oil and gas fields, can be the ring, half ring, apical or offset type (Figure 36). These most cause uncertainty in interpretation. Experiences showed that even in the same field, any anomaly is not always in the type of ring, apical or offset. This situation makes it complicated even more to interpret (Barringer and Lovell, 1986). In Fig 37 is seen iodine anomaly types of soils over Osmancık and Umurcalı oil and gas fields in Thrace basin (Turkey).
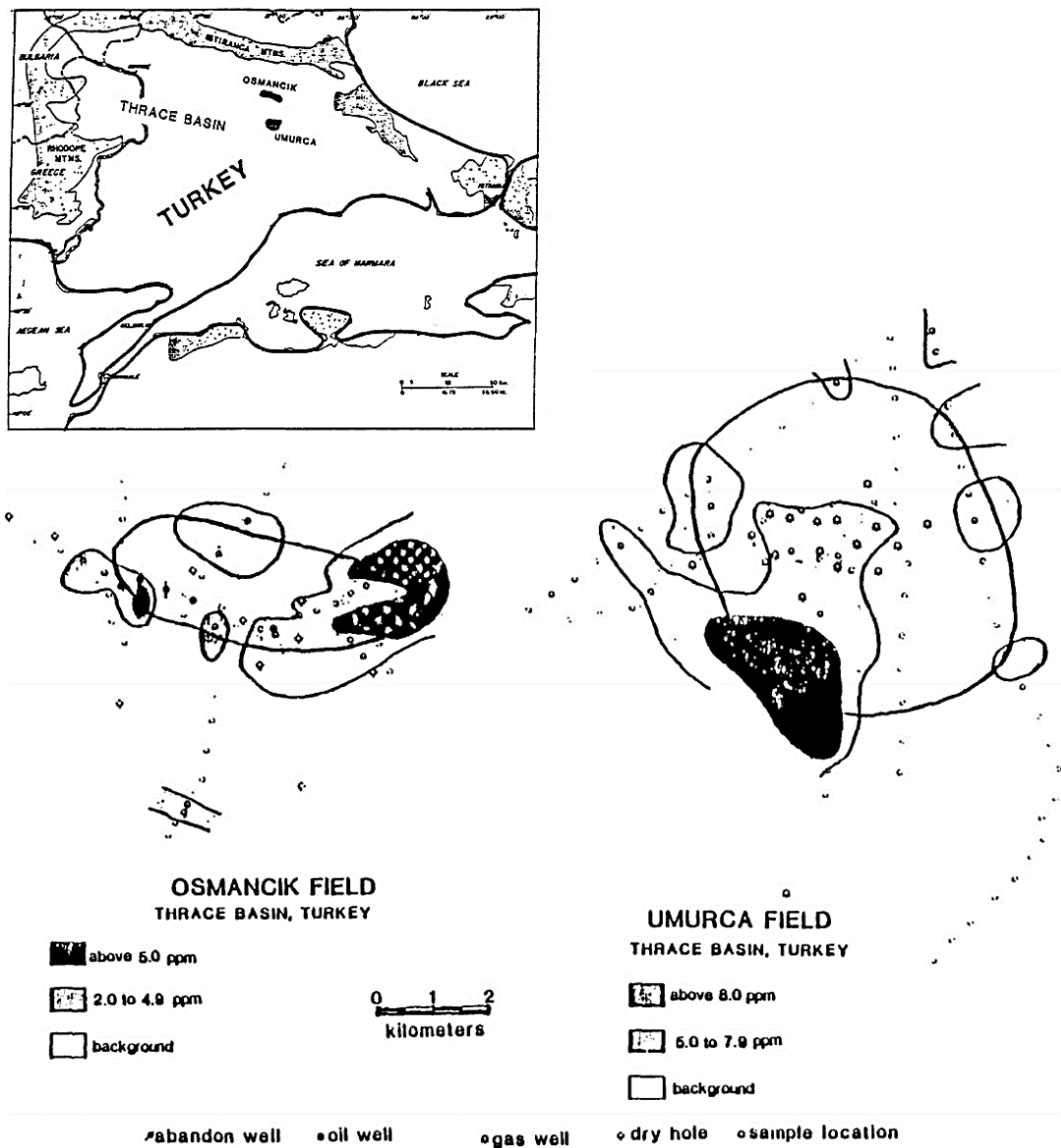
Figure 37. Distribution of iodine anomalies over Osmancık and Umurca oil and gas fields in Thrace basin, Turkey (Allexan et al., 1986)

Tedesco (1995) tested iodine geochemistry survey on soils over many oil and gas fields in which exploration studies completed, and production started. As a typical example, he has made a study on a transverse geological structure in Belize (Middle America) to examine the relationship

between iodine geochemistry and seismic measurements. The study area is the part of a basin where many giant oil and gas production fields located in northern Mexico. In the study is assumed that the geology of the field is similar to seismic interpretation data. The reservoir is probably highly fractured. Iodine samples have taken from the soils over seismic lines. It is seen that there is a significant association between the profile prepared according to analysis results of iodine samples and seismic line data (Figure 38). Presence of many faults in the field shows that the faults to be the migration pathways for hydrocarbons and they are the reason for large amounts of the leakages. Also, in the study made by Xuejing and Binzhong (1989), it is seen that there is a significant relation between iodine soil geochemistry and seismic profile data (Figure 39).
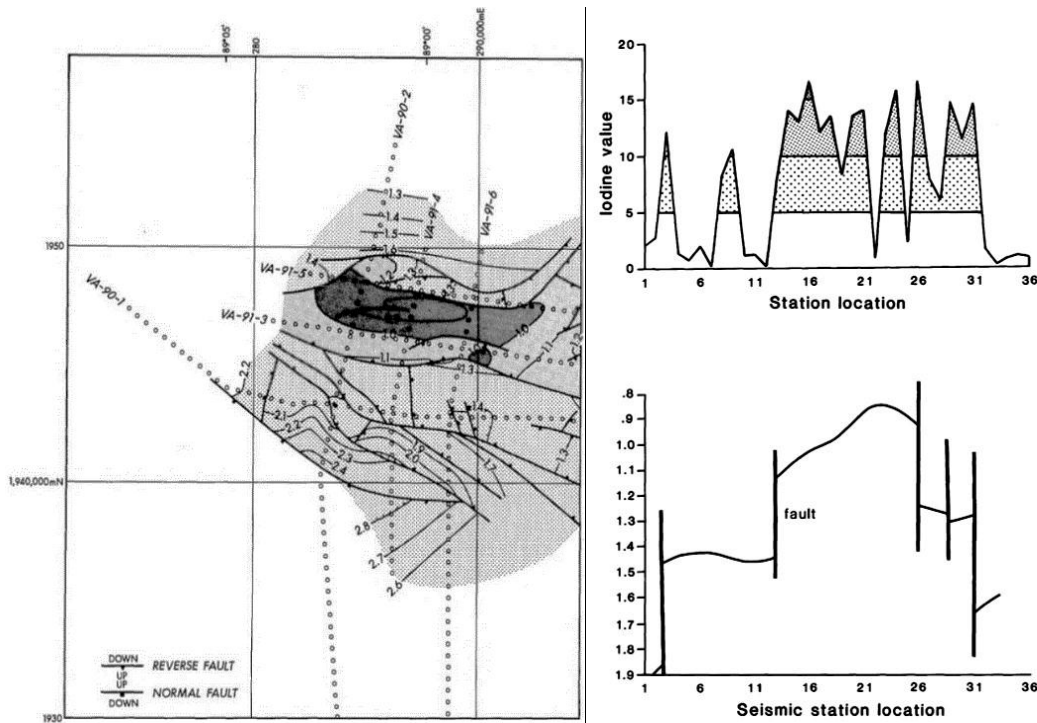
Figure 38. Iodine profile along seismic line VA-91-4 with associated geophysical interpretation below. Contour intervals are 5.0 to 9.9 ppm (light pattern), 10.0 to 14.9 ppm (medium pattern), and >15.0 ppm (dark pattern) of iodine. Seismic is in 0.1 s of time (Tedesco, 1995)
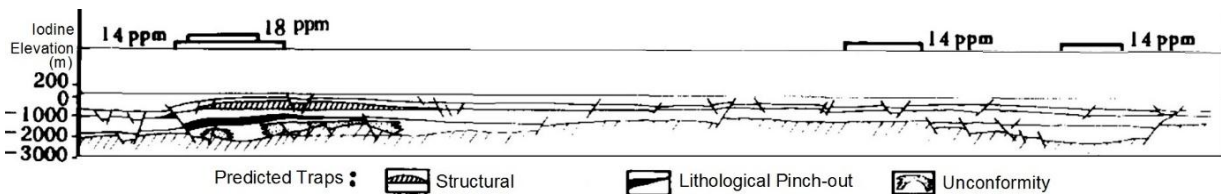
Figure 39. Idealized map showing the relation of iodine anomalies with probable oil traps predicted from analyzing seismic data along a profile in the southwest end of Qinggang structure (Xuejing ve Binzhong, 1989)

In soil geochemistry surveys, in order to describe present oil and gas fields and to find new fields, the only iodine from all halogens (Cl, Br, F, etc.) is used. The control of other factors on iodine increase or changes in soil is lower than petroleum. An iodine geochemistry survey requires numerous samples to set background values before considering the presence of anomalies. An iodine geochemistry survey requires numerous samples to set background values before considering the presence of anomalies. Sampling and analysis of iodine samples are much simpler than that of soil gas. If sufficient samples collected, interpretation is relatively easy. Unlike gases or liquids, organic iodine compounds are more stable. Iodine compounds in the soil are not easily affected by barometric pressure fluctuations, sudden changes in amounts of soil gas, soil wetting or drying or changes affecting evaporation of water in the soil. In case, the thickness of soil is maximum 50 cm, features of soil have not as a factor which may influence the results of the survey. An essential advantage of iodine geochemistry surveys is repeatability of measurements. Also, the simplicity of sampling and analysis reduces error probability. The disadvantage of iodine geochemistry survey is the requirement of numerous samples for an accurate interpretation and a model for comparison (Tedesco, 1995).

Conclusion

Iodine scarcely finds on Earth's crust. 99.6 % of Earth's crust is composed of 32 main elements. Remaining 0.4 % shared among 64 trace elements. Ranking 61 among these 64 elements concerning abundance, iodine is one of scarcest non-metal elements within the composition of Earth's crust. Biological connection between iodine and carbon systems well established. There is a strong relation between organic C and iodine concentrations in marine sediments. Iodine founds in low concentration in sedimentary rocks. Compliance of iodine with evaporite minerals is lower than that of bromine. Shales generally contain high iodine concentrations like 1-20 ppm. Iodine amount found in sedimentary rocks cannot be found in any rock-forming mineral and cannot be absorbed in clay. It is more related to preserved organic C. There is a strong relation between organic C and I concentrations in marine sediments. High amounts of iodine concentrations have measured in shales containing kerogen, the primary organic matter. As the iodine content increases in shales, the oil and organic carbon content also increase. Therefore, iodine has preserved its relation with organic C throughout decomposition of organic matter and sedimentation process and has released in water during thermal maturing. As iodine protects its close relation with organic C, the age of iodine will be the age of the organic matter with which iodine is in relation.

The source of iodine in sedimentary basin brines, which is a large amount of hydrocarbon accumulation, is the organic-rich dehydrated sediments in the buried basin. It is known that oilfield waters contain iodine with higher concentrations compared to seawater. Therefore, in the early stages of diagenesis, iodine in petroleum source rocks is preserved to a great extent, and this is most probably an indicator of anoxic conditions on the surface of the original sediment. The primary reservoir of iodine in actual marine environments is organic matters. Organic-rich sediments or their volatile derivatives (hydrocarbons) are primary sources of iodine in many sedimentary basins. Organic-rich marine sediments and halite are the primary sources for iodine in the terrestrial environment. Their I/Br ratios differentiate these sources. Salt lakes either contain a little iodine or no iodine at all. It is known that algae and foraminifera muds contain high amounts of iodine. Amount of decomposed organic matter during generating of hydrocarbon in the marine environment affects the amount of released iodine. The reason for such a significant amount of iodine enrichment in waters cannot be seawater evaporation, halite dissolution or any mineral

transition process (i.e., plagioclase albitization or dolomitization). Decomposition of Type-II kerogen is the primary source of the iodine found in formation waters. Such concentration is an indicator of the presence of organic matter related to the biophilic character of iodine.

In halogen systematics of marine porewaters are seen that gas hydrates and most of the organic bromine are merged whereas maturing hydrocarbons, H_2S, CH_4, and iodine together are migrated the basin. Therefore, the potential of hydrocarbons to influence iodine and bromine contents of formation waters is high. Combined noble gas and halogen analyses provide an intriguing new method for investigating hydrocarbon-groundwater interactions because hydrocarbons have elevated Br and I contents and noble gases and halogens are both fractionated between hydrocarbons and groundwater. Buried organic matter, which turn into petroleum after maturing and is the source of iodine in waters of sedimentary basins having vast amounts of hydrocarbon accumulation have dominant control over the total iodine concentration of formation waters. Besides, such iodine-rich waters mediate hydrocarbon migration.

Iodine concentrations in formation waters are independent of the type of kerogen. In other geological factors do not have any impact on formation waters halogen concentrations. Processes controlling halogen concentrations are independent of occurrence style of the sedimentary basin. There is no impact of reservoir lithology on halogen concentrations because sandstones and carbonates do not contain much halogen minerals. Therefore, they do not affect halogen concentrations in formation waters. Besides, heat does not affect halogen concentrations in formation waters. The depth of burial has probably no influence on halogen concentrations because halogens do not expose to water-rock interaction caused by depth or heat. Therefore, the most reliable method to evaluate the presence or potential of oil and gas in a basin is to examine halogen contents (I, Br and CI) of basin waters. Russians have asserted iodine as a hydrogeochemical indicator for petroleum. Due to the petroliferous basins contain the waters with high iodine concentrations, examination of iodine concentrations of waters in the basin can be used as the first method for petroleum exploration activities in the explored basin. Iodine enrichment in waters increases with proximity to petroleum reservoirs and depth of burial.

Iodine, which is a stable biophilic element, is found in highly enriched amounts in fluids related to hydrocarbons such as oilfield waters. Due to its nature, iodine isotope (^{129}I) has been recently used in determining the hydrocarbon sources in various structures and the age and migration process of the formation waters related to those hydrocarbon sources. Iodine and ^{129}I concentrations of water provide information about the history of fluid in the reservoir and the migration path.

In soil geochemistry surveys, in order to describe present oil and gas fields and to find new fields, the only iodine from all halogens (Cl, Br, F, etc.) is used. The control of other factors on iodine increase or changes in soil is lower than petroleum.

Iodine has been used in many studies to discover an oil and gas field. Current studies show that supporting geological and geophysical survey with iodine hydrogeochemistry and soil geochemistry increases the efficiency of hydrocarbon exploration. Use of iodine for the discovery of oil and gas fields has the advantages such reliability, consistency and simplicity and cost-effectiveness.

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