

Water Geochemistry of Oil Field Brines

Water geochemistry provides a series of powerful tools for solving various oil field development and production problems. Specifically, naturally occurring chemical "tracers" in water can be used to identify the origin and track the movement of water in oil fields, as well as predict the precipitation of scales. These naturally occurring tracers include the absolute and relative abundance of the various dissolved salts (anions and cations) as well as the isotopic composition of certain cations (e.g., $^{86}\text{Sr}/^{87}\text{Sr}$) and the hydrogen and oxygen stable isotopic composition of the water itself.

Which formation is responsible for water [moving behind casing](#) can be determined by comparing formation water geochemistry data with data from produced waters. Similarly, the [progression of water floods](#) can be monitored, as can the relative progression of water that is flooding a group of discrete sands. Additionally, water geochemistry can be used to diagnose the cause of precipitation of mineral scales (e.g., barite, calcite, silica, iron oxide, halite) in flow-lines, valves, gauges and other surface equipment by identifying the mixing of [geochemically incompatible formation fluids](#) at surface facilities.

The rest of this article describes why water geochemistry is able to distinguish different waters from one another. The types of processes described below provide the geochemical signals that we monitor to track the origin and movement of oil field waters and brines. Although this article gives particular emphasis to Gulf of Mexico water geochemistry, the concepts and tools described here can be applied in any basin to any oil field.

Aqueous Fluid Chemistry - Formation and Evolution

Figures 1 through 6 are cross-plots of water geochemistry data for various cation and anion constituents. Common to each of these figures are: the seawater evaporation trajectory showing seawater composition, and the gypsum and halite precipitation points (McCaffrey et al., 1987; Carpenter, 1978). Each figure also highlights regions showing the range of compositions of formation water produced from US Gulf Coast Cenozoic and Mesozoic reservoirs (from published and unpublished data: Graf et al., 1966; Carpenter et al., 1974; Carpenter and Trout, 1978; Land and Prezbindowski, 1981; Stoessel and Moore, 1983; Grossman et al., 1986; Kharaka et al., 1987; Morton and Land, 1987; Land et al., 1988; Land and Macpherson, 1989; Land and Macpherson, 1992; Moldovanyi and Walter, 1992; Moldovanyi et al., 1993; Macpherson, 1992; A. B. Carpenter personal communication to M. A. Beeunas, 1996).

Figure 1: Chloride versus Sodium Evaporation Trajectory

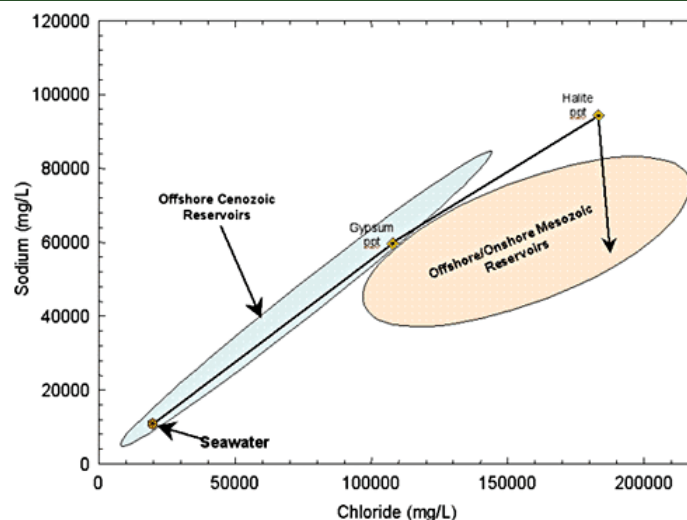


Figure 1: On this cross plot (and the following) of chloride versus sodium concentration (mg/L) are shown the composition of normal seawater with an evaporation trajectory through the gypsum and halite precipitation points (McCaffrey et al., 1987; Carpenter, 1978). Also are highlighted regions showing the compositional ranges of formation water from Gulf of Mexico offshore Cenozoic reservoirs, and offshore/onshore Mesozoic reservoirs (from published and unpublished data: see References). A significant number of the formation brines from Mesozoic reservoirs have both sodium and chloride concentrations less than that defined by the evaporation trajectory and are most likely the result of dilution with fresher waters during the initial evaporation stage or shortly after burial.

Figure 2: Chloride versus Calcium Evaporation Trajectory

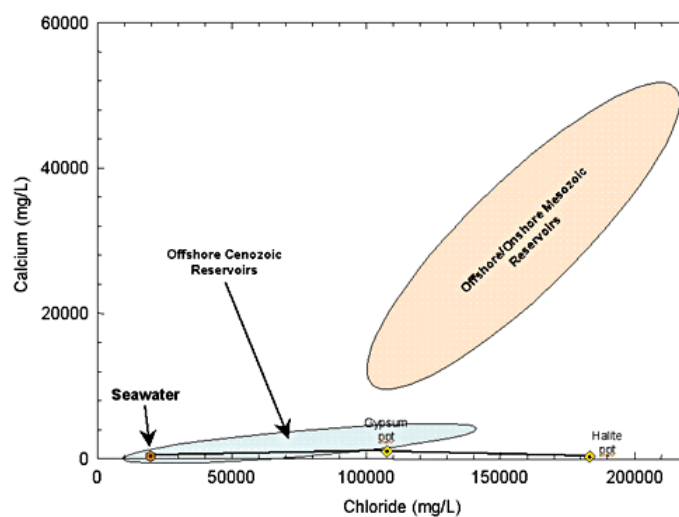


Figure 2: Cross plot of chloride versus calcium concentration (mg/L). The affects of sulfate lost due to bacterially mediated sulfate reduction during early burial, the greater association of calcium carbonate containing lithologies during the Mesozoic and the generally greater reservoir temperatures result in the calcium concentration of Mesozoic age formation water to depart from the evaporation trajectory to higher concentrations.

Figure 3: Chloride versus Magnesium Evaporation Trajectory

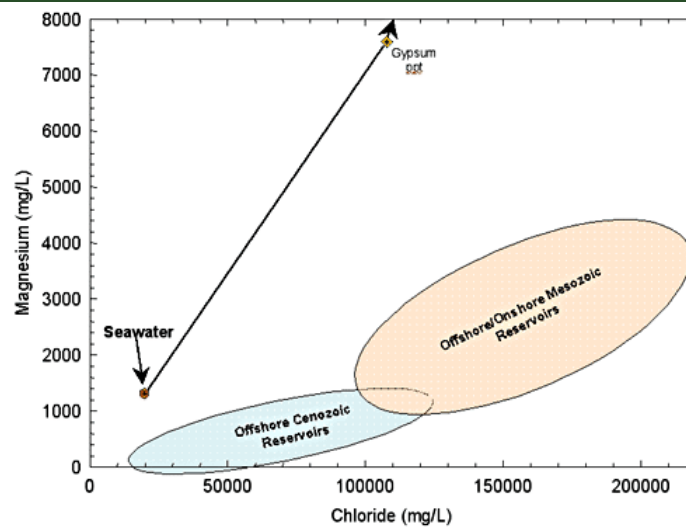


Figure 3: Cross plot of chloride versus magnesium concentration (mg/L). The range of magnesium concentrations of formation water from Gulf Coast Cenozoic and Mesozoic reservoirs plot well below the evaporation trajectory due to magnesium removal during the formation of dolomite.

Figure 4: Chloride versus Potassium

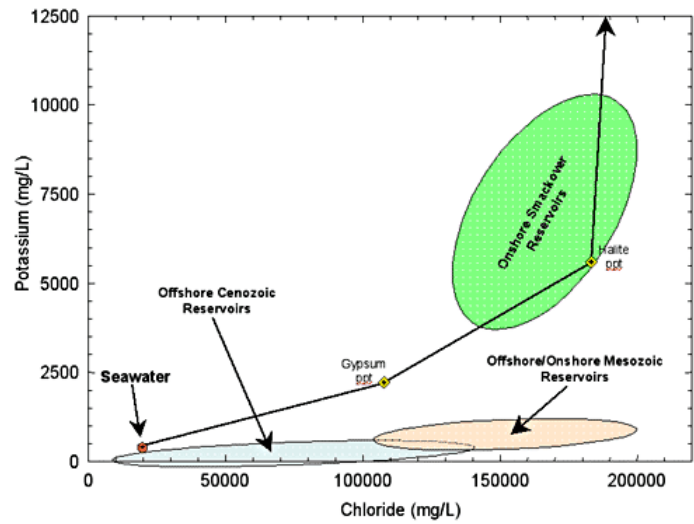


Figure 4: Cross plot of chloride versus potassium concentration (mg/L). The range of potassium concentrations of formation water from Gulf Coast Cenozoic and Mesozoic reservoirs plots below the evaporation trajectory due to potassium removal during the formation of kaolinite and or illite. The greater concentration of potassium in formation water from Smackover reservoirs is due to the greater degree to which the Smackover brines were evaporated and from the albitization of K-feldspar.

Figure 5: Chloride versus Specific Gravity

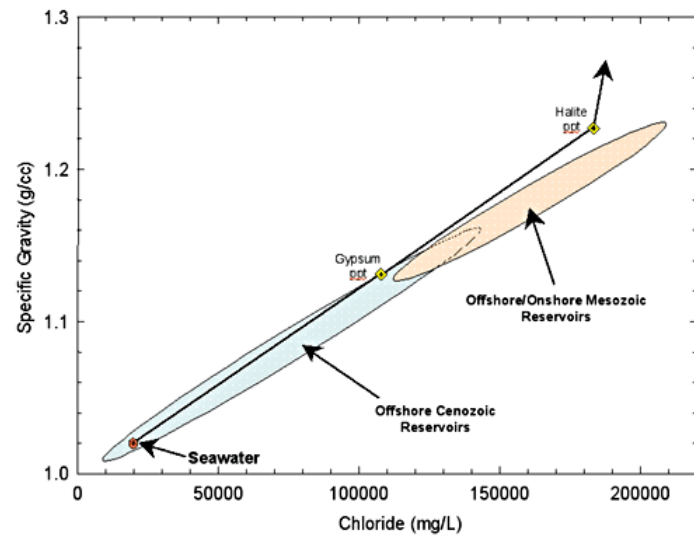


Figure 5: Cross plot of chloride (mg/L) versus specific gravity (g/cc).

Figure 6: Bromide versus Sodium Evaporation Trajectory

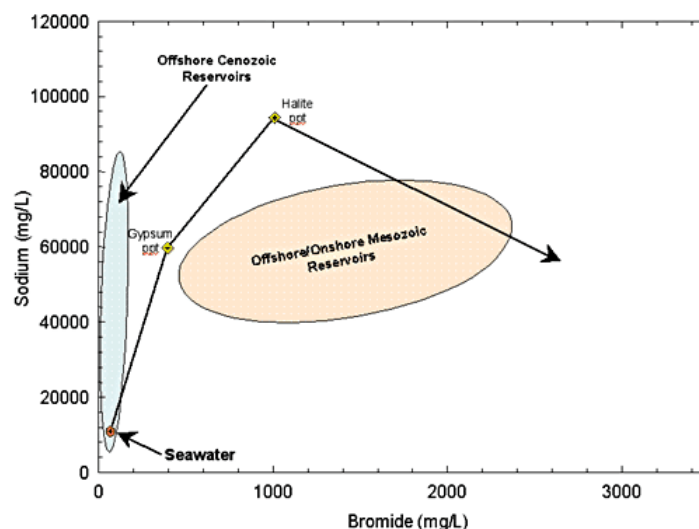


Figure 6: Cross plot of bromide versus sodium concentration (mg/L). A significant number of the formation brines from Gulf Coast Mesozoic reservoirs have both sodium and bromide concentrations less than that defined by the evaporation trajectory and are most likely the result of dilution with fresher water during the initial evaporation stage or shortly after burial.

In nearly all cases, the water in a formation fluid was derived from the earth's surface, either buried with the sediments or later flowing into and displacing preexisting fluids. Formation fluids range from fresh potable water to highly concentrated brines. From the time these fluids leave the surface of the earth (either during burial with the sediments or during later flow into the sediments), the water geochemistry continues to evolve. For example, beginning at depths ranging from the sediment-water interface to several meters of burial, one of the main anion constituents of seawater, sulfate, is profoundly affected by bacterial processes. Dissolved sulfate is reduced to sulfide by sulfate-reducing bacteria (Goldhaber and Kaplan, 1974, 1975; Orr, 1974; Ivanov, 1981), and this sulfide then either reacts with iron to form sedimentary pyrite or reacts with organic matter to form organically bound sulfur.

At greater burial depths, the water itself as well as the dissolved constituents it contains, can react with the surrounding rock. These reactions are primarily controlled by the type and concentration of the dissolved constituents, the mineralogy of the surrounding rock, the relative volumes of water and rock that interact, the pressure, and the temperature. For example: the concentration of magnesium can be lowered by reaction with calcite to form dolomite; potassium concentration can be reduced by the formation of kaolinite and illite or increased by the albitization of K-feldspar; sodium and chloride can increase from the dissolution of bedded halite.

In the greater **Gulf of Mexico**, there are two broad water geochemistry families of formation fluids produced from Mesozoic and Cenozoic oil and gas reservoirs. One water geochemistry family is derived from seawater deposited with the clastic sediments (NaCl-Type; Land and Macpherson, 1992). The other water geochemistry family is derived from evaporated seawater associated with the deposition of evaporites (Ca-Type; Land and Macpherson, 1992). During the Mesozoic, principally starting in the late Middle Jurassic (Callovian) with the deposition of the Louann Salt, a series of bedded evaporites was deposited (Salvador, 1987). These evaporites were precipitated by evaporation of seawater in restricted basins, concentrating the seawater to the point of saturation. These fluids typically have higher concentrations of calcium: 10,000 to 70,000 mg/L; magnesium: 1,000 to 4,500 mg/L; and bromide: 400 to 2,400 mg/L as compared to formation water from younger Cenozoic reservoirs (Carpenter et al., 1974; Carpenter and Trout, 1978; Kharaka et al., 1987).

The formation water produced from Gulf of Mexico Cenozoic reservoirs is predominantly a sodium chloride brine derived from seawater which is little modified by evaporation and has lower concentrations of calcium: <4,000 mg/L; magnesium: <1,400 mg/L; and bromide: <200 mg/L (Posey et al., 1985; Grossman et al., 1986; Land et al., 1988; Land and Macpherson, 1992). The chloride concentration of formation water produced from Cenozoic reservoirs varies widely from about 10,000 mg/L (half that of normal seawater) to over 140,000 mg/L. Formation water less saline than seawater were diluted by mixing with fresh surface/ground water at zones of mixing landward of the delta front along the delta plain (Suchecky and Land, 1983) or from fresh water derived from de-watering of clay minerals during compaction (Burst, 1969; Bruce, 1984). Formation water produced from Cenozoic reservoirs more saline than seawater and with calcium concentrations <4,000 mg/L have derived their increased salinity from the dissolution of allochthonous halite (tongues, domes, dikes and sills; Land and Prezbindowski, 1981; Hanor, 1987). Although the vast majority of formation water produced from Cenozoic reservoirs is of the NaCl-Type, there are occurrences of Ca-Type that represent fluids expelled from the underlying Mesozoic section (Morton and Land, 1987).

The water geochemistry of evaporating seawater at modern man-made salt works is similar to the water geochemistry of brines that existed during deposition of ancient evaporites (McCaffrey et al., 1987). Therefore water geochemistry data from modern salt works can be used to identify when hypersaline depositional environments are the source of connate brines produced from oil fields. Additionally, connate evaporate brines are found as fluid inclusions trapped in evaporite minerals that precipitated from the evaporating brine (Holser, 1979; Roedder, 1982; Knauth et al., 1986). These trapped fluids provide a snap-shot of the chemical composition of the evaporating brines in ancient sabkhas.

For more information on the water geochemistry techniques described here, or to discuss a specific project, e-mail us at info@oiltracers.com, or call us at (214) 584-9169.

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