Application of brine differentiation and Langelier–Ludwig plots to fresh-to-brine waters from sedimentary basins: Diagnostic potentials and limits

Tiziano Boschetti

Department of Earth Sciences, University of Parma, 157a Parco Area delle Scienze, 43100 Parma, Italy

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ABSTRACT

Classical chemical classification plots that use major anions and cations can discern between different water facies but they do not offer sufficient discriminatory power for salt waters from sedimentary basins, whose origin is therefore frequently misunderstood.

The Brine Differentiation Plot (BDP) was proposed by Hounslow (1995) in order to investigate the brine genesis, principally evaporite dissolution, alkali lakes and oilfield brines. However, its diagnostic potential has been undervalued so far.

In this paper, the potential of BDP was tested and compared with the classical Langelier–Ludwig plot using concentration of major dissolved constituents of fresh to brine waters from different sedimentary basins (Northern Apennine Foredeep, Italy; Provence Basin, Western Mediterranean; Caucasus; Trinidad). Mixing processes between different water types as evaluated by these diagrams would seem to be constrained by the boron–chloride plot.

1. Introduction

Chemical classification of subsurface waters from sedimentary basins aids in interpreting the complex processes involved in producing their dissolved solids, to better understand their origin and evolution, and the origin of water that is more likely to be associated with hydrocarbon accumulation (Collins, 1975). From a general point of view, hydrocarbon accumulations are primarily related to Ca-chloride and secondarily to Na-bicarbonate waters (Sulin, 1946). The relative arrangement of the major constituents on a square plot was first proposed by Tolstikhine at the end of 1930, and was applied to distinguish between hydrocarbon-bearing Ca-chloride and Na-bicarbonate waters (Chilingar, 1957; Chilingar et al., 2003). A similar plot but with inversion of the axis was proposed by Langelier and Ludwig (1942), and is nowadays universally employed in water classification (hereafter LLP). However, classification plots that use major dissolved constituents are unsuccessful to distinguish between salinization mechanisms like seawater evaporation and salt dissolution because waters of different origin fall in the same Na-chloride field; therefore other elements like Br and I coupled with Cl in binary diagrams should be used (e.g. Richter and Kreitler, 1993). Recently, a Brine Differentiation Plot (hereafter BDP) was proposed as a tool to discriminate between different brine origins (Hounslow, 1995). The plot uses molar $Ca/(Ca+SO_4)$ and $Na/(Na+Cl)$ on the vertical and horizontal axes, respectively. On this diagram, field characteristic of

oilfield brines, evaporite solutions and seawater is separate and distinct. Despite its clarity, it is still practically neglected by geochemists.

2. Distinction between seawater-derived Ca-chloride brines and Na-chloride waters from evaporite dissolution
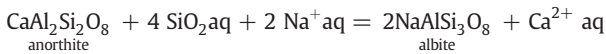
Ca-chloride waters were first defined as waters with qNa/qCl<1 and q(Cl-Na)/qMg<1, where q is the equivalent % (Sulin, 1946); most recently, the definition of this water class was revised as rNa/rCl<0.86 ± 0.05 (seawater ratio) and $rCa/r(SO_4+HCO_3)>1$, where r is the mEq/L concentrations (Rosenthal, 1997). In the brine waters from Northern Apennine Foredeep (NAF) sodium and chloride are the most abundant ions. Therefore these waters should be classified as Na-chloride. However, they are also definable as Ca-chloride waters using the above ratios (Boschetti et al., 2011). Chemical and isotope composition revealed that Ca-chloride brines derive from a Miocene seawater evaporated up to a stage between gypsum and halite saturation, then diluted by Miocene or present-day waters of meteoric origin and modified by water–rock interaction (Boschetti et al., 2011). Contrary, Picotti et al. (2007) concluded for a meteoric origin of these waters followed by interaction with rocks. In Fig. 1B, major chemistry of Ca-chloride brines from NAF is plotted on LLP along with waters of meteoric origin dissolving evaporite minerals (Poiano springs, ~6 g/L; Forti et al., 1988 and our unpublished data). All of them are displaced in the Na-chloride area and no genetical distinction is possible because waters from evaporite could be interpreted as diluted Ca-chloride waters.
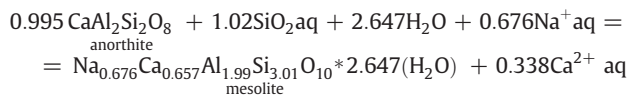
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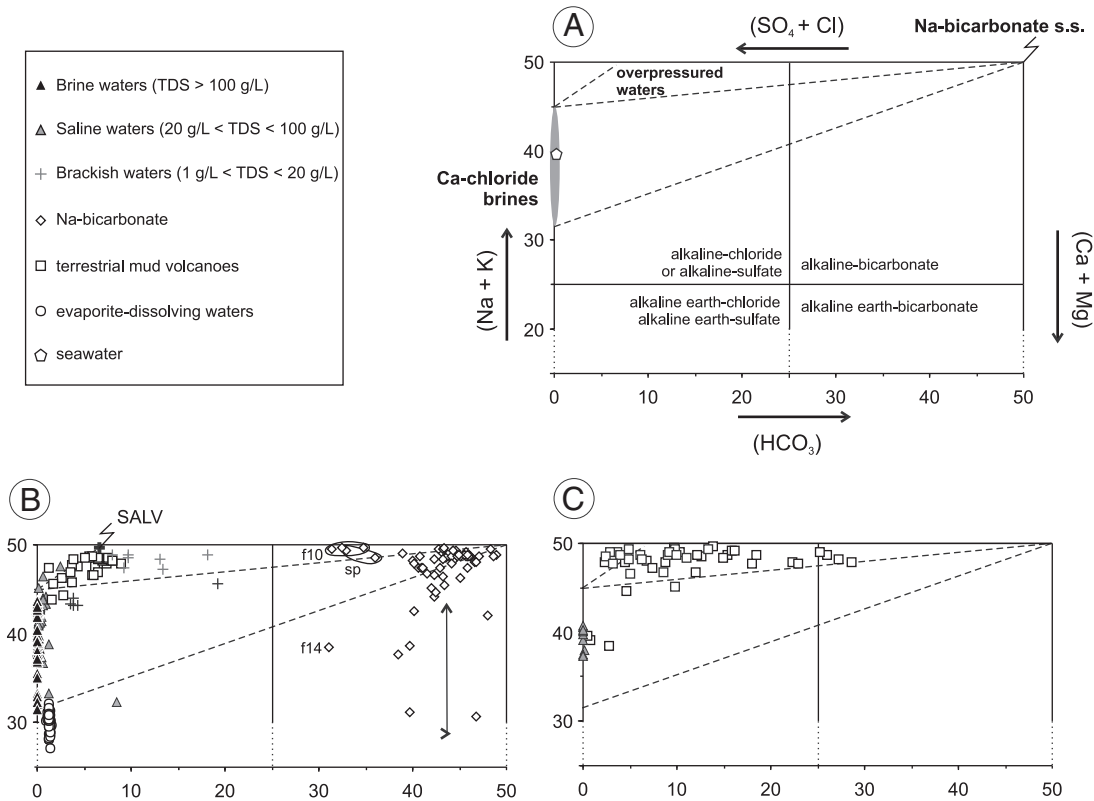
Fig. 1. Langelier–Ludwig plot, where $(Na+K) = (\Sigma r_{Na+K}/\Sigma r_{cations}) \times 50$ and $(HCO_3) = r_{HCO3}/\Sigma r_{anions} \times 50$, where r is the mEq/L concentration of the constituents. The $(Ca+Mg)$ and (SO_4+Cl) are complementary values. (A) Reading key; dashed lines represent binary mixings. (B) Waters from Northern Apennine Foredeep (NAF); brine, saline and brackish waters from mud volcanoes: Boschetti et al. (2011); Martinelli and Ferrari (1991). Bold cross: brackish groundwater enriched in Na and depleted in Ca due to overpressure (SALV, Boschetti et al., 2011); black crosses (Lesignano waters, Boschetti et al., 2011) and grey crosses (Porretta waters; Bencini and Duchi, 1980; Ciancabilla et al., 2007): Ca-chloride and overpressured waters mixed with Na-bicarbonate waters, respectively. Fresh Na-bicarbonate waters (*sp, f10* and *f14* are brackish samples mixed with hydrocarbon-bearing waters): Duchi et al. (2005); Venturelli et al. (2003); our unpublished data. Water of meteoric origin dissolving evaporites: Forti et al., 1988; our unpublished data. Double arrow in the alkali-bicarbonate field represents mixing with or evolution from Ca-bicarbonate fresh waters. (C) Saline to brine interstitial waters from Provence Basin (site 372, Western Mediterranean; McDuff et al., 1978); mud volcanoes from Caucasus (Lavrushin et al., 2003) and Trinidad (Dia et al., 1999).

In Fig. 2 waters are shown on BDP. In this type of diagram, seawater has $Na/(Na+Cl) = 0.46$ and $Ca/(Ca+SO_4) = 0.26$, whereas Na-chloride waters from evaporite dissolution arrange exactly in the center of the plot because dissolution of gypsum-anhydrite and halite is the main source of dissolved constituents. In the same diagram, Ca-chloride brine waters have $0.38 < Na/(Na+Cl) \leq 0.46$ and $0.9 < Ca/(Ca+SO_4) \leq 1$, thus falling in the oil-field brine space (Fig. 2B). However, in spite of the original BDP representation in which the oil-field waters are connected with the area of evaporite dissolution and their great distance from seawater point, no contribution from evaporite dissolution is manifest in Ca-chloride brines from NAF. In fact, they derive from evaporated seawater up to gypsum precipitation followed by variations in the cationic concentration due to deep burial diagenetic processes (Boschetti et al., 2011; Davisson and Criss, 1996). In particular, plagioclase albitization

$$\underset{\text{anorthite}}{CaAl_2Si_2O_8} + 4\,SiO_2aq + 2\,Na^+aq = \underset{\text{albite}}{2NaAlSi_3O_8} + Ca^{2+}\,aq$$

and/or zeolitization

$$0.995\,CaAl_2Si_2O_8 + 1.02SiO_2aq + 2.647H_2O + 0.676Na^+aq =$$
$$= \underset{\text{mesolite}}{Na_{0.676}Ca_{0.657}Al_{1.99}Si_{3.01}O_{10}*2.647(H_2O)} + 0.338Ca^{2+}\,aq$$

involve a 2:1 exchange of Na for Ca, whereas sulfate drop is ascribed to sulfate reduction. Therefore, seawater-derived brines may be well represented by a reversed triangle having Ca-chloride waters as base and seawater as vertex (Fig. 2A). In fact, its worthy of note that

seawater and evaporated seawater solutions up to gypsum precipitation have an almost constant $Na/(Na+Cl)$ ratio of about 0.46, that is similar to the maximum ratio revealed in the NAF Ca-chloride brines (Fig. 2B).

In order to confirm the potentiality of the BDP to describe the seawater origin and the diagenetic processes, interstitial waters from Provence Basin have been added to the plot (grey triangles in Fig. 2C; site 372, Western Mediterranean; McDuff et al., 1978). Similar to NAF waters, they were misinterpreted as evaporite-dissolving waters (McDuff et al., 1978), but most recently their evaporated-seawater origin has been confirmed by chemical and boron isotope investigations (Vengosh et al., 1994, 2000). In fact these waters, classifiable as Ca-chloride brines $[1 < rCa/r(SO_4+HCO_3) < 16]$, are displaced in the reversed triangle field of the BDP, and have $Na/(Na+Cl) < 0.46$ and $0.55 < Ca/(Ca+SO_4) < 0.95$, that is they evolve from seawater towards typical oil-field brines because of sulfate loss (reduction) and Ca increase (albitization and/or zeolitization) related to an early burial diagenesis (eogenesis).

3. Na-bicarbonate waters and terrestrial mud volcanoes

Fresh Ca-bicarbonate is the dominant facies of the shallow groundwaters and its origin, i.e. shallow meteoric water interacting with calcite-bearing sediments, is well known and common also in other places of the world, therefore it is not discussed further. Na-bicarbonate waters are less common than Ca-bicarbonate but they are considered as a favourable, shallow indicator for the presence of hydrocarbons (e.g. Chilingar et al., 2003; Collins, 1975). In the NAF and elsewhere, these waters have fresh to brackish salinity, are