Regional geochemical and isotopic variations in badwaters of the Edwards aquifer

Gregg C. Oetting, Jay L. Banner, John M. Sharp, Jr.
Department of Geological Sciences, University of Texas, Austin, TX 78712

Abstract

A range of geochemical and isotopic parameters were determined for saline groundwaters on a regional scale in the Edwards aquifer in order to evaluate groundwater evolution models. These saline groundwaters, termed badwaters, have a range in salinity from 1,000 to 8,000 ppm total dissolved solids (TDS). The 'badwater line' defines the down-dip limit of potable waters in the aquifer. The evaluation of models for badwater evolution is complicated by: 1) the range in compositions of saline basinal fluids that may migrate into the Edwards aquifer from its deeper down-dip section and from underlying hydrostratigraphic units; 2) the range of depositional, diagenetic, and mineralogic variations in the host aquifer rocks; and 3) extensive faulting of the aquifer, which in places juxtaposes aquifer units with confining units.

Major element variations in badwaters define six hydrochemical facies ($Ca\text{-}SO_4$, $Ca\text{-}Mg\text{-}SO_4$ [low Na-Cl], $Ca\text{-}Mg\text{-}SO_4$ [high Na-Cl], Na-Cl, $Na\text{-}SO_4\text{-}Cl$, and $Na\text{-}Cl\text{-}SO_4\text{-}HCO_3$). Transitions between these hydrochemical facies are in some locations coincident with changes in depositional settings in the Edwards and associated limestones (Kea), and with broad structural features. Sr isotopic compositions in badwaters ($^{87}Sr/^{86}Sr = 0.7075$ to 0.7094), Edwards Formation brines (0.7078 to 0.7097), and saline groundwaters from underlying hydrostratigraphic units (0.7088 to 0.7097) are nearly all higher than values for Edwards carbonate and evaporite rocks (0.7074 to 0.7076).

Geochemical and isotopic variations in badwaters from the western part of the aquifer can be accounted for by incongruent dissolution/precipitation reactions between carbonate and evaporite minerals. In the extensively faulted eastern part of the aquifer, badwater compositions appear to be additionally modified by fluid mixing processes involving Edwards Formation brines and saline groundwaters from underlying hydrostratigraphic units.

Introduction

The badwater line is the surface expression of the down-dip limit of freshwaters in the Edwards aquifer. At this limit, groundwater salinities rise rapidly to >1000 ppm TDS. Geochemical studies of groundwaters in the Edwards aquifer (Sharp and Clement, 1988; Clement, 1989) have delineated a Ca-HCO_3 freshwater zone and six distinct hydrochemical facies in a 'badwater' zone. These badwater facies are as follows: Ca-SO_4 (facies A), Ca-Mg-SO_4 (low Na-Cl; facies B), Ca-Mg-SO_4 (high Na-Cl; facies C), Na-Cl (facies D), Na-SO_4-Cl (facies E), and Na-Cl-SO_4-HCO_3 (facies E'). Multiple processes have been proposed for the origin of each water type, including: 1) fluid-rock interaction involving carbonates, evaporites, siliciclastics, and volcanics within or adjacent to the Edwards aquifer, 2) fluid mixing between local meteoric recharge, water from aquifers and confining units adjacent to the Edwards, and oil-field brines migrating up-dip from the Gulf of Mexico sedimentary basin.

Previous studies of groundwaters and carbonate rocks of the Edwards aquifer include detailed studies of structural, depositional, and geomorphic controls on aquifer development, hydrodynamics, carbonate rock compositions, and groundwater geochemistry (Abbott, 1973, 1974, 1975; Mueller, 1975; Rightmire et al., 1974; Longman and Mench, 1978; Woodruff and Abbott, 1979; Land and Prezbendowski, 1981; Woodruff and Slade, 1984; Ellis, 1985; Woodruff et al., 1985; Maclay et al., 1985; Maclay and Small, 1983, 1986; Senger and Kreitler, 1984; Maclay and Land, 1988; Deike, 1987, 1990; Pavlicek et al., 1987; Groschen, 1988; Clement, 1989; Clement and Sharp, 1987, 1988; Sharp and Clement, 1988; Ogden and Collar, 1990; Sharp, 1990). Geochemical studies of groundwaters in the Edwards aquifer provide analyses of major and trace elements, and O, H, C, N, S, and U isotopes (Browning, 1977; Rightmire et al., 1974; Pearson and Rettman, 1976; Osmond and Cowart, 1982; Land and Prezbendowski, 1981; Ellis, 1985; Clement, 1989; Senger, 1990; Ogden and Coller, 1990). These previous investigations provide this study with an opportunity to integrate major and trace element concentrations, and stable O, H, and S isotopic data from previous studies with major and trace element concentrations, and O, H, and Sr isotopic data collected for this study.

Sr isotopes have recently been utilized in studies of regional fluid flow, and have provided significant insight into the origin and evolution of groundwaters and basinal brines (Banner et al., 1989; Land and Macpherson, 1992; Musgrove and Banner, 1993). Specific geochemical processes can be effectively traced through the integration of geochemical, stable isotopic, and Sr isotopic variations. A summary of the major results of this study will follow. A more complete discussion of these results will be presented elsewhere (Oetting et al., in prep.).

Regional hydrogeology of the Edwards aquifer

The Edwards aquifer developed from karstification of uplifted Mid-Cretaceous platform carbonates on the northwestern margin of the Gulf of Mexico sedimentary basin. The carbonate rocks that comprise this aquifer, the Edwards and associated limestones (Kea) and the Georgetown Formation, extend from outcrops in central Texas down-dip to the subsurface Stuart City Reef Trend, which formed the Cretaceous shelf margin (Figs. 1, 2, 3). The Del Rio Clay and Glen Rose Limestone are low-permeability units that confine the Edwards aquifer and form local barriers to flow where faulting juxtaposes these units with permeable Edwards aquifer rocks (Figs. 1, 2, 3).

The badwater line represents a narrow transition zone from a rapidly circulating freshwater system up-dip to slowly migrating sedimentary basin fluids down-dip (Fig. 1a). Estimated rates of flow up-dip and down-dip of the badwater line range from 90 to 900 cm/d and 1 to 2 cm/d respectively (Maclay et al., 1985; Maclay and Land, 1988). The estimated rates of freshwater and badwater flow reflect a sharp decline in the permeability of the Kea across the badwater line (Maclay and Land, 1988). Freshwater flow in the confined freshwater aquifer is parallel to the badwater line, indicating that only diffuse flow from the freshwater zone may cross the badwater line. The geochemistry of Edwards Formation brines reflects fluid-rock interaction with evaporites and siliciclastics (Land and Prezbendowski, 1981; Land and Macpherson, 1992). Previous studies of Edwards Formation brines suggest that highly saline fluids migrate along faults into the Kea, and up-dip after entering the Kea (Land and Prezbendowski, 1981; Fig. 3).

Regional groundwater hydrochemistry

The freshwater aquifer is characterized by Ca-HCO_3 waters having salinities generally less than 500 ppm TDS. Major element variations in badwaters vary regionally (Fig. 1b, c). Characteristic major element variations of badwaters from specific regions define hydrochemical facies, or groups (Figs. 1b, c, 4; Clement, 1989). Geochemical variations between badwater hydrochemical facies demonstrate regional correlations with broad structural features and depositional settings in the Kea (Figs. 1b, c; Clement, 1989).

Previous work suggests that each hydrochemical facies evolved from a set of geochemical processes specific to a badwater facies region (Clement, 1989). Several processes are common to more than one badwater hydrochemical facies, but each facies reflects a unique combination of geochemical processes. Table 1 summarizes the important geochemical processes proposed by previous investigators to describe the evolution of the six badwater hydrochemical facies.

Facies A badwaters:

The Facies A region lies on the northern margin of the Maverick Basin, west of the Balcones Fault Zone where the Kea reaches its greatest thickness (Fig. 1b). The scarcity of large faults and lack of volcanic and intrusive igneous rocks in the facies A region simplify hydrogeologic relationships in this facies region. Major element variations in facies A badwaters suggest an evolution involving dilute groundwater dissolution of carbonate and evaporite rocks (Fig. 1c). O and H isotopic variations in facies A badwaters bear a meteoric signature (Fig. 5a, b). $^{87}Sr/^{86}Sr$ variations in facies A badwaters suggest that nearly all Sr in these badwaters is derived from Edwards carbonate and evaporite rocks (Fig. 6). Major element geochemical and isotopic evidence cited above supports conclusions of previous investigators based on major element variations (Clement, 1989).

Trace element and $^{87}Sr/^{86}Sr$ variations in facies A badwaters indicate significant geochemical evolution involving incongruent reaction between Edwards carbonate and evaporite minerals. Major element geochemical variations show little or no evidence for these geochemical processes. Sulfur isotopic variations in badwaters (Pearson and Rettman, 1976) suggest that bacterial sulfate reduction of evaporite derived SO_4 mediates incongruent reactions between carbonate and evaporite minerals. Na and Cl variations in facies A badwaters suggest a non-evaporite source of Na (Fig. 4). Clement (1989) identified two sources that could elevate Na/Cl ratios in Facies A badwaters: 1) Ca/Na exchange with clay minerals in the Kea or in adjacent confining units; and 2) fluid mixing with saline groundwaters from underlying units. Both ion exchange with clays and fluid mixing would contribute dissolved Sr with high $^{87}Sr/^{86}Sr$ to facies A badwaters. The low $^{87}Sr/^{86}Sr$ values observed in these groundwaters (Fig. 6), however, requires that the Sr derived from ion exchange or fluid mixing constitutes an insignificant fraction of the dissolved Sr budget of facies A badwaters.

Facies B badwaters:

The Kea in the facies B region was deposited in shelf margin and basinal depositional settings (Fig. 1b). The Kea in this region is predominantly composed of calcite, dolomite, gypsum and anhydrite. The hydrochemical facies boundary between facies A and B generally corresponds to the geographic location of westernmost faulting in the Balcones Fault Zone. Ca, SO_4, and HCO_3 variations in facies B badwaters are similar to facies A badwaters, but concentrations of Na, Mg, and Cl are higher in facies B badwaters. The similarity of Kea carbonate and evaporite rock compositions in the facies A and B regions suggests a similar origin of Ca, SO_4, and HCO_3 in the two facies. It has been proposed by previous investigators that significant Na and Mg in facies B badwaters may be derived from volcanic and intrusive igneous rocks that crosscut the Kea in the Uvalde area (Fig. 1a, b). $^{87}Sr/^{86}Sr$ variations in facies B badwaters suggest a source of Sr with $^{87}Sr/^{86}Sr$ values much higher than values for both Late Cretaceous [illegible] rocks in the Uvalde area and Kea carbonate and evaporite rocks (Fig. 6). $^{87}Sr/^{86}Sr$ variations in facies B badwaters suggest an extraformational source of Sr that may be derived from underlying units, Edwards Formation brines migrating out of the Gulf of Mexico sedimentary basin, or some contribution from both extraformational sources (Fig. 6). Na and Cl variations in facies B badwaters suggest an Edwards Formation brine source of Na and Cl (Fig. 4).

Facies C and D badwaters:

The Kea in the facies C and D regions was deposited in tidal flat environments proximal to the San Marcos Arch (Rose, 1972; Fig. 1b). The Kea in the facies C and D regions is predominantly composed of calcite, dolomite, gypsum, and anhydrite. Dolomitized tidal flat environments in the Kea extend from the eastern edge of the Devils River Reef to the northeastern edge of the San Marcos Arch (Fig. 1b). Carbonate rocks in the Kea are increasingly dolomitic along a west to east transect from the Devils River Reef to the axis of the San Marcos Arch (Abbott, 1973; 1974; Longman and Mench, 1978; Ellis, 1985; Deike, 1987; Fig. 1b). The more dolomitic character of the Kea toward the axis of the San Marcos Arch is regionally coincident with increased faulting intensity, and displacement along faults in the Balcones Fault Zone. Mg and Ca concentrations in badwaters along a transect from the facies B to the facies D region vary consistently with the greater abundance of dolomite along the axis of the San Marcos Arch (Fig. 1c). Facies C and D badwater Na and Cl variations are intermediate between pathways for halite dissolution and mixing of Edwards freshwaters and formation brines (Fig. 4). The lack of halite in the Kea in this region and the intermediate $^{87}Sr/^{86}Sr$ values in facies C and D badwaters suggest a brine source of Na and Cl (Figs. 4a, 6). Water-rock interaction with clay minerals or fluid mixing with saline groundwaters from underlying units followed by mixing with Edwards Formation brines can account for Na and Cl variations in Facies C and D badwaters. Variations in Mg, Ca, SO_4, and HCO_3 in facies C and D badwaters suggest that groundwaters undergo significant fluid-rock interaction with Kea carbonate and evaporite rocks prior to mixing with Edwards Formation brines (Fig. 1c).

The facies D region extends over an area that lies up-dip of oil fields in the Luling Fault Zone (Fig. 1). Facies D badwaters have a limited range of $^{87}Sr/^{86}Sr$ values relative to facies B and C badwaters with similar TDS ranges (Fig. 6). The relatively narrow range of facies D badwater $^{87}Sr/^{86}Sr$ values is similar to the narrow range of $^{87}Sr/^{86}Sr$ values for Luling Fault Zone brines relative to Stuart City Reef brines (Fig. 6). Mixing between endmember brines during up-dip migration can explain the narrower ranges of $^{87}Sr/^{86}Sr$ values in both Luling Fault Zone brines and facies D badwaters.

Facies E and E' badwaters:

The Kea of the facies E/E' region was deposited in open shallow marine environments, and is predominantly composed of calcite and dolomite (Rose, 1972). Although the displacement along faults in the Balcones Fault Zone is relatively small in this region, the Kea thins and pinches out at the aquifer's northernmost extent, suggesting that stratigraphic displacement in this region may in places be similar to that of the facies D region (Clement, 1989; Baker et al., 1986; Senger, 1990). Facies E and E' badwater Ca, SO_4, and HCO_3 concentrations are dissimilar to facies A badwaters, suggesting different origins of these elements in the three facies (Fig. 1c). Unlike facies B, C, and D badwaters, facies E and E' badwaters show very similar geochemical variations to saline groundwaters from underlying hydrostratigraphic units (Fig. 1c; Clement, 1989). $^{87}Sr/^{86}Sr$ values of saline groundwaters from underlying hydrostratigraphic units are similar to those of facies E and E' badwaters, which supports evidence from major element variations for fluid mixing.

Discussion and conclusions

Geochemical evolution of badwaters in the Edwards aquifer has been ascribed to two fundamental processes: fluid mixing and fluid-rock interaction. Variations in major and trace element concentrations, and S, O, H, and Sr isotopic values reflect a groundwater evolution model that involves varying roles of 1) fluid mixing between groundwaters within the aquifer and more saline fluids from down-dip sections of the Edwards and from underlying hydrostratigraphic units; and 2) fluid-rock interaction between groundwaters and rocks of the Edwards aquifer and its confining units. The unique structural and stratigraphic setting of each badwater hydrochemical facies region appears to result in facies-specific fluid evolution pathways that give rise to distinctive geochemical and $^{87}Sr/^{86}Sr$ variations.

Major and trace element concentrations, stable isotopic, and Sr isotopic variations suggest that facies A badwaters evolve from dilute meteoric water interaction with Kea carbonate and evaporite rocks. Trace element and $^{87}Sr/^{86}Sr$ variations in facies A badwaters are indicative of significant incongruent reaction between carbonate and evaporite minerals. Both the geochemistry and a number of structural and depositional characteristics in the aquifer change from the facies A region to other badwater facies regions. The geochemical effects of faulting and changes in depositional environment on badwater compositions can be evaluated by comparing the geochemistry and isotopic composition of facies A badwaters to badwaters in other hydrochemical facies regions.

Similarities in facies A, B, C, and D badwater Ca, SO_4, and HCO_3 variations indicate fluid-rock interaction processes that are common to facies A-D. The increase in Mg/Ca ratios in facies B, C, and D badwaters along a transect from the Devils River Reef to the axis of the San Marcos Arch suggests that the geochemistry of these badwaters reflect the more dolomitic character of the Kea along this transect. $^{87}Sr/^{86}Sr$ values in facies B badwaters do not support a volcanic or intrusive igneous source of Na and Mg, but indicate some extraformational source of Sr with $^{87}Sr/^{86}Sr$ values higher than both volcanic rocks in the Uvalde area and Kea carbonate and evaporite rocks (Table 1).

O and H isotopic variations in facies B, C, D, E, and E' badwaters bear a meteoric signature similar to freshwaters in the aquifer. The absence of significant halite in the Kea, however, indicates an extraformational source of Na and Cl in all of these badwaters. Na, Cl, and $^{87}Sr/^{86}Sr$ variations suggest that facies B, C, and D badwaters evolve from fluid-rock interaction with Edwards carbonate and evaporite rocks followed by fluid mixing with Edwards Formation brines

(Figs. 4, 6). Na, Cl, and $^{87}Sr/^{86}Sr$ variations in facies E and E' badwaters suggest fluid mixing processes between groundwaters in the Edwards aquifer and saline groundwaters from underlying hydrostratigraphic units.

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