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The major ion, $^{87}Sr/^{86}Sr$, and $\delta^{11}B$ geochemistry of groundwater in the Wyodak-Anderson coal bed aquifer (Powder River Basin, Wyoming, USA)

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ABSTRACT

We developed a multicomponent, 1D advective transport model that describes the downgradient evolution of solute concentrations, $^{87}Sr/^{86}Sr$ ratios, and $\delta^{11}B$ values in the Wyodak-Anderson Coal Bed (WACB) aquifer located in the Powder River Basin, Wyoming, USA. The purpose of the study was to evaluate the chemical vulnerability of groundwater to potential environmental change stemming from the extraction of coal bed methane and shale gas. Model calculations demonstrate that coupling between microbial activity and the dissolved carbonate system controls major ion transport in the WACB aquifer. The analysis of $^{87}Sr/^{86}Sr$ ratios further reveals the importance of ion-exchange reactions. Similarly, $\delta^{11}B$ data emphasize the significance of pH-dependent surface reactions and demonstrate the vulnerability of the aquifer to the long-term acidification of recharge water.

1. Introduction

The Powder River Basin (Wyoming, USA) is one of the most active areas for coal bed methane production (EIA, 2007). Major ion mass balances and radiogenic isotope measurements (e.g., Sr, Nd, U, Th) are powerful tools for analyzing the rates and mechanisms of water–rock interaction during groundwater transport. Numerous studies have utilized these techniques to develop comprehensive models that describe the origin and compositional evolution of groundwater in silicate and carbonate aquifers (e.g., Banner and Hanson, 1990; Bullen et al., 1996; Jacobson and Wasserburg, 2005; Johnson and DePaolo, 1997; Lucas et al., 2010; Maher et al., 2006; Négrel and Petelet-Giraud, 2010). By comparison, only a few studies have examined water/rock interactions in coal bed aquifers (Bartos and Ogle, 2002; Bates et al., 2011; Brinck et al., 2008; Frost et al., 2002; Rice et al., 2000) and at present, models describing the geochemistry of these unique aquifer systems are relatively scarce (Bartos and Ogle, 2002).

To address this problem, we analyzed the downgradient evolution of dissolved major ions, $^{87}Sr/^{86}Sr$ ratios and $^{11}B/^{10}B$ ratios (expressed below as $\delta^{11}B$ in ‰) along a 102 km flow path in the Wyodak-Anderson coal bed (WACB) aquifer in the Powder River Basin (PRB). The opportunity to sample groundwater in the WACB aquifer has increased, owing to the expansion of wells for extracting microbially-produced methane (e.g., Frost et al., 2002; Rice et al., 2000). Importantly, microbial

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methanogenesis is known to concurrently modify carbonate equilibria conditions and major ion concentrations in organic-rich aquifers (e.g., McIntosh et al., 2004). By analogy to the methanogenic Antrim Shale in the Michigan Basin, microbial methanogenesis is expected to greatly influence the compositional evolution of WACB groundwater (McIntosh et al., 2004), but the lack of major ion characterizations has hindered consensus on the overall reaction pathway occurring within the aquifer (Bartos and Ogle, 2002). Other factors affecting the transport of major ions may include sulfate reduction, ion-exchange, and cross-formational mixing (Bartos and Ogle, 2002; Frost et al., 2002; Rice et al., 2000). However, the interrelationships between these various processes, as well as their rates and relative controls on solute geochemistry, are presently unknown.

In this paper, we use a 1D multicomponent advective transport model to determine reaction pathways and rates required to produce the observed water chemistry in the WACB aquifer. The model incorporates new geochemical data for both groundwater and coal samples. To evaluate the downgradient evolution of Sr^{2+}, we treat dissolved ^{87}Sr/^{86}Sr ratios as dynamic tracers of progressive water–rock interaction (Johnson and DePaolo, 1997; Maher et al., 2006). That is, dissolved ^{87}Sr/^{86}Sr ratios measured at a given distance downgradient reflect the physical properties of fluid transport (e.g., velocity, cross-formational mixing, etc.) as well as the chemical properties of the dissolving, precipitating, or exchanging solid phases (e.g., Sr concentration, ^{87}Sr/^{86}Sr ratio, rate of reaction, etc.). Importantly, because the Sr isotope model is linked to the major element data through mass-balance relationships, we are able to present an integrative and self-consistent interpretation of the factors controlling groundwater geochemistry in the WACB aquifer. We further couple this information with the behavior of B isotopes, which can elucidate the nature of water–rock interactions, in particular pH-dependent processes, as well as those resulting from water-mass mixing (e.g., Cividini et al., 2010; Gonfiantini and Pennisi, 2006; Lemarchand and Gaillardet, 2006; Vengosh et al., 1994; Zhao et al., 2011).

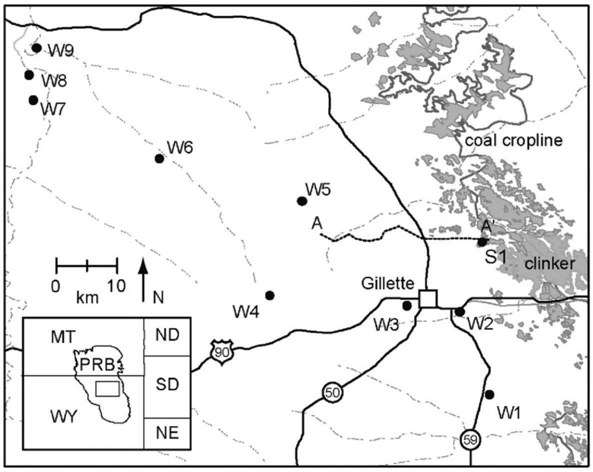

Fig. 1. Map showing sample locations (S1, W1–W9) and the generalized geology of the study area. Groundwater flow is to the northwest. Inset shows the location of the Powder River Basin (PRB) within the geographic context of the USA. Small box within the inset shows the approximate location of the study site within the PRB.

2. Sampling site

2.1. Geological characteristics

The study region is located in north-eastern Wyoming near the eastern margin of the $\sim$35,000-km^2 Powder River Basin (Fig. 1). The Paleocene Fort Union Formation, which is subdivided into the Tullock, Lebo, and Tongue River Members, contains sandstone, siltstone, mudstone, claystone, carbonaceous shale, limestone, and coal (Ellis, 2002; Warwick and Stanton, 1988). The thickest and most laterally continuous coal beds in the PRB belong to the Wyodak-Anderson Coal Zone (WACZ) in the Tongue River Member (Bartos and Ogle, 2002; Ellis et al., 1999; Flores and Bader, 1999; Flores et al., 1999). At least eleven individual coal beds compose the WACZ (Flores et al., 1999). The beds developed from raised peat mires that were dissected or overrun by meandering fluvial systems fed by ancestral alluvial fans at the margin of the PRB (Ellis, 2002; Flores and Bader, 1999; Warwick and Stanton, 1988). Between the top of the uppermost bed and the bottom of the lowermost one, the entire WACZ is $\sim$180 m thick (Ellis, 1999). Individual beds ranging in thickness from a few centimeters to $>$ 60 m (Frost et al., 2002) are separated by clastic sedimentary rocks ranging in thickness from a few centimeters to $\sim$45 m (Ellis, 1999).

The coal is non-marine, low-sulfur, and subbituminous in rank (Ellis, 2002; Ellis et al., 1999; Flores and Bader, 1999; Van Voast, 2003). Small amounts of silicate, carbonate, phosphate, sulfate, sulfide, and metal oxide minerals are present in WACZ coal (Brownfield et al., 2005; Crowley et al., 1993; Palmer et al., 2000). Mineral sources include volcanic ash fall, Eolian deposition, and fluvial delivery during peat formation; in situ alteration of primary minerals during diagenesis, coalification, and groundwater flow; and direct precipitation from solution (Brownfield et al., 2005; Crowley et al., 1993; Palmer et al., 2000). Of these minerals, quartz and kaolinite are the most prevalent (Brownfield et al., 2005). Trace carbonates include calcite and dolomite (Brownfield et al., 2005). No studies have reported halite. The WACZ outcrops along the eastern margin of the PRB. In this region, natural burning of coal has baked overlying sediments to form clinker, which has a distinct orange to red color (Heffern and Coates, 1999; Warwick and Stanton, 1988). The Tongue River Member is overlain by the Eocene Formation, which has a similar depositional history and lithology as the Fort Union Formation (Flores and Bader, 1999). The Wasatch Formation is aerially exposed in much of the PRB (Bartos and Ogle, 2002).

2.2. Hydrological characteristics

The aquifer recharges through infiltration of precipitation and stream-flow loss in the clinker zone. The clinker is