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Geochemical evolution of groundwater in a basaltic aquifer based on chemical and stable isotopic data: Case study from the Northeastern portion of Serra Geral Aquifer, São Paulo state (Brazil)

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SUMMARY

Groundwater from the fractured basalt Serra Geral Aquifer (SGA) represents an important source for water supply in Northeastern São Paulo state (Brazil). Groundwater flow conditions in fractured aquifers hosted in basaltic rocks are difficult to define because flow occurs through rock discontinuities. The evaluation of hydrodynamic information associated with hydrochemical data has identified geochemical processes related to groundwater evolution, observed in regional flowpaths. SGA groundwaters are characterized by low TDS with pH varying from neutral to alkaline. Two main hydrochemical facies are recognized: Ca–Mg–HCO_3, and Na–HCO_3 types. Primarily, the geochemical evolution of SGA groundwater occurs under CO_2 open conditions, and the continuous uptake of CO_2 is responsible for mineral dissolution, producing bicarbonate as the main anion, and calcium and magnesium in groundwater. Ion exchange between smectites (Na and Ca-beidelites) seems to be responsible for the occurrence of Na–HCO_3 groundwater. Toward the Rio Grande, in the northern portion of the study area, there is mixing between SGA groundwater and water from the sandstones of the Guarani Aquifer System, as evidenced by the chemical and isotopic composition of the groundwater. Inverse mass balance modeling performed using NETPATH XL produces results in agreement with the dissolution of minerals in basalt (feldspars and pyroxenes) associated with the uptake of atmospheric CO_2, as well as the dissolution of clay minerals present in the soil. Kaolinite precipitation occurs due to the incongruent dissolution of feldspars, while Si remains almost constant due to the precipitation of silica. The continuous uptake of CO_2 under open conditions leads to calcite precipitation, which in addition to ion exchange are responsible by Ca removal from groundwater and an increase in Na concentrations. Down the flow gradientCO_2 is subject to closed conditions where the basalts are covered by the sediments of Bauru Group or associated with deeper isolated discontinuities. A decrease in the amount of dissolution of labradorite and augite is observed, associated with precipitation of carbonates and kaolinite. Stable isotope ratios of SGA groundwater vary from −37.8‰ to −61.3‰ VSMOW for δ^2H VSMOW, and −5.7‰ to −8.9‰ VSMOW for $\delta^{18}O$, indicating temporal variations in climatic conditions during recharge.

1. Introduction

Basaltic rock aquifers represent an important groundwater resource, hosting water supply in several parts of the world. Basalts are good aquifers because they store water of excellent quality, generally characterized by low salinity, and the thickness and spatial extension of basaltic lava flows provide high storage capacity. Basaltic lava flows typically have geologic discontinuities responsible for groundwater storage and flow in these units (Deolankar, 1980; Léonardi et al., 1996; Domenico and Schwartz, 1998; Bourlier et al., 2005; Dafny et al., 2003, 2006; Lastoria et al., 2006; among others). Basaltic provinces around the world constitute excellent aquifer units including: Deccan Plateau in India (Deolankar, 1980; Kulkarni et al., 2000), Columbia River Plateau in USA (Deutsch et al., 1982), Golan Heights in Israel (Dafny

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et al., 2006), and the Atherton Tabelands in North Queensland, Australia (Locsey and Cox, 2003), among others.

Evaluation of groundwater hydrochemistry and isotopic composition is being increasingly used to complement studies focused on understanding the flow condition and origin of groundwater in fractured and heterogeneous aquifers units, such as basaltic aquifers. Hydrochemistry can be an aid to define chemical reactions produced by water–rock interaction and stable isotope data ($\delta^{18}O$ and $\delta^{2}H$) can be used as tracer of groundwater origin, mixing of waters of different origins, as well as to interpret paleoclimate recharge conditions for groundwater (Aggarwal et al., 2005). Combining these analytical data allows the construction of geochemical models, which can be used to determine the evolution of groundwater along flow paths in aquifers, based on the interpreted reactions and processes related to water–rock interactions or anthropogenic sources (Plummer et al., 1990; Rosenthal et al., 1998; Bouhlassa and Aiachi, 2002; Bretzler et al., 2011; among others).

Located in the Southeastern portion of South America, the Paraná Sedimentary Basin is comprised of a vulcano-sedimentary sequence up to 8000 m thick, with a generally elliptical shape that has the major axis trending NE–SW. Among several sedimentary units, the Serra Geral Aquifer (SGA) is an important Cretaceous volcanic stratigraphic unit that can reach up to 1500 m thick in the center of the sedimentary basin, and is one of the most important aquifers located in the region (Fig. 1). The SGA represents an important water source for public supply, irrigation and industrial purposes, largely in the states of Paraná, Santa Catarina, Rio Grande do Sul and Mato Grosso do Sul, Brazil, as well as in Argentina, Paraguay and Uruguay. Hydrochemical studies of groundwater in the SGA have been conducted in the southern portion of Brazil, allowing groundwater chemical characterization and the establishment of the hydraulic relationship with the underlying unit, the Guarani Aquifer (Bittencourt, 1996; Bittencourt et al., 2003; Boff et al., 2006; Buchmann Filho et al., 2002; Lastoria, 2002; Lastoria et al., 2006; Machado et al., 2002; Nanni, 2008, among others). Aquifers in Mesozoic rocks of the Paraná Sedimentary Basin (Bauru, Serra Geral and Guarani Aquifers) provide public water supply in the West portion of São Paulo state. Due to the importance of these units in the region, the hydrodynamics and hydrochemistry of the Guarani and Bauru aquifers have been studied since the 1970s, and several conceptual models for groundwater flow and hydrochemical evolution have been formulated (eg. Gallo and Sinelli, 1980; da Silva, 1983; Kimmelmann e Silva et al., 1986; Rebouças, 1994; Campos, 1987, 1993; Meng and Maynard, 2001; Sracek and Hirata, 2002; Barison, 2003; Paula e Silva et al., 2005; Gastmans et al., 2010; among others). However, the hydrochemical and hydrogeological characteristics of the SGA have not been studied extensively.

This study has three main objectives. First, to recognize and characterize the water types that exist in the basaltic aquifer, based on their chemical composition. Second, to examine the geochemical evolution and stable isotope composition of SGA groundwater along selected flow paths, thereby defining a set of possible reactions based on changes in groundwater composition and related to the observed mineralogy of the aquifer. Based on these possible reactions, using NETPATH XL (Plummer et al., 1994; Parkhurst and Charlton, 2008), mass transfer along a number of flow paths is tested, as well as the possibility of mixing with groundwater from the underlying unit (Guarani Aquifer System). The third objective is to evaluate the isotopic data to determine the effect of variations in climatic conditions over SGA groundwater stable isotope ratios.

2. Geological and hydrogeological settings

Basalts of the Serra Geral Formation are present in the Paraná Magmatic Province (PMP), which constitutes one of the largest volcanic manifestations of basic rocks in a continental area. This magmatic province includes lava flows and intrusive basic rocks (sills and dykes) representing, according to Milani et al. (1994), an important contribution to generation of continental crust during the Mesozoic. The radiometric ages indicate that volcanic activity began between 133 and 132 Ma, starting in the South and moved towards the North in a relatively short interval of approximately 3 Ma (Renne et al., 1992, 1996; Ernesto et al., 1999). This vast volume of basaltic lavas reaches thicknesses up to 2000 m toward the center of the Paraná Sedimentary Basin, and was deposited over the aeolian sandstones of the Botucatu Formation, which constitutes one of the stratigraphic units of the Guarani Aquifer System.

The greatest part of the magmatic volume of the Serra Geral Formation (up to 97%) is represented by basalts and andesites, while in the southern region of Brazil rhyodacites and rhyolites (Palmas (ATP) and rhyodacites and quartz latitites Chapecó (ATC)) are recognized (Bellieni et al., 1986; Nardy et al., 2002). In São Paulo state there are mainly basalts of mafic to intermediate composition, consisting of plagioclase (mainly labradorite), pyroxene (augite and piegonite), and olivine, mainly as pseudomorphs (Machado et al., 2007). Vesicular zones of variable thickness are recognized at the boundary between basaltic lava flow events. Secondary minerals forming amygdales fill these vesicles, including quartz, calcite, zeolites, fluorite and commonly greenish clays, probably of the celadonite group (Machado, 2007). The occurrence of mordenite and other minerals of the zeolite group has been described by Shinzato et al. (2008) and Frank (2008). The intense weathering of basaltic rocks is responsible for the very deep soils observed in the southern portion of Brazil, and the weathering of plagioclase produces gibbsite and amorphous silica, while pyroxenes weather to smectite, goethite, and gibbsite (Clemente and Azevedo, 2007).

Rebouças and Fraga (1988) present a generic hydrogeological model for groundwater flow conditions in the basalts of the Serra Geral Formation. They recognize permeable and impermeable zones for each lava flow event. At the top and bottom of each sequence, a highly permeable zone is observed, associated with basalt weathering, and groundwater flow is associated with the occurrence of a vesicular basaltic layer that has extensive horizontal fractures. The central portion of each sequence represents an aquitard, where minor vertical movement of water is associated with vertical discontinuities (joints and fractures). A groundwater flow conceptual model for the basaltic aquifer in the region of Ribeirão Preto (SP-BR), including possible recharge toward the underlying unit, the Guarani Aquifer, was proposed by Wahnfried (2010) and Fernandes et al. (2010). They suggested groundwater flow predominantly along horizontal discontinuities in the basaltic rocks and a lack of vertical flow through the geological lineaments, identified by aerial surveys, that limits recharge of the underlying Guarani Aquifer by water from the Serra Geral basalts.

Groundwater flow in the study area for the SGA is driven by the topography, with flow from elevated areas, located in the East, westward towards the main rivers that cross the basalt outcrop areas (Fig. 2). This suggests that the SGA in the study area is an unconfined aquifer, at least in the outcrop zone, and the main rivers represent local discharge zones. Gastmans and Chang (2012) recognized the existence of an artesian zone in the Guarani Aquifer along the rivers Pardo, Sapucaí, Mogi Mirim and Grande, and some groundwater contribution coming from groundwater flow from the underlying Guarani Aquifer toward basaltic discontinuities might be expected, leading to the potential for mixing with SGA.

Groundwater from the SGA has low electrical conductivities (EC), due to low total dissolved solids (TDS), and a wide range of pH values, from acid to alkaline. The chemical composition shows the groundwater to be mainly $Ca–HCO_3$ and $Ca–Mg–HCO_3$ type (DAEE, 1974, 1976; Campos, 1993). In the Northwestern region