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Trace element geochemistry of groundwater in a karst subterranean estuary (Yucatan Peninsula, Mexico)

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Abstract

Trace element cycling within subterranean estuaries frequently alters the chemical signature of groundwater and may ultimately control the total chemical load to the coastal ocean associated with submarine groundwater discharge. Globally, karst landscapes occur over 12% of all coastlines. Subterranean estuaries in these regions are highly permeable, resulting in rapid infiltration of precipitation and transport of groundwater to the coast, and the predominant carbonate minerals are readily soluble. We studied the chemical cycling of barium (Ba), strontium (Sr), manganese (Mn), uranium (U), calcium (Ca) and radium (Ra) within the carbonate karst subterranean estuary of the Yucatan Peninsula, which is characterized by a terrestrial groundwater lens overlying marine groundwater intrusion with active submarine discharge through coastal springs. Terrestrial groundwater calcium (1–5 mmol kg^{-1}) and alkalinity (3–8 mmol kg^{-1}) are enriched over that predicted by equilibrium between recharging precipitation and calcite, which can be accounted for by groundwater organic matter respiration and subsequent dissolution of calcite, dolomite and gypsum. There is a close agreement between the observed terrestrial groundwater Sr/Ca, Mn/Ca, Ba/Ca and Ra/Ca and that predicted by equilibrium dissolution of calcite, thus the trace element content of terrestrial groundwater is largely determined by mineral dissolution. Subsequent mixing between terrestrial groundwater and the ocean within the actively discharging springs is characterized by conservative mixing of Sr, Mn, Ba and Ca, while U is variable and Ra displays a large enrichment (salinity: 1.9–34.9, Ba: 60–300 nmol kg^{-1}, Sr: 15–110 μmol kg^{-1}, U: 0.3–35 nmol kg^{-1}, Mn: 0.3–200 nmol kg^{-1}, Ca: 4.3–12.9 mmol kg^{-1}, ^{226}Ra: 18–2140 dpm 100 L^{-1}). The deep groundwater sampled through cenotes, local dissolution features, is typified by elevated Ba, Sr, Ca, Mn and Ra and the absence of U within marine groundwater, due to enhanced dissolution of the aquifer matrix following organic matter degradation and redox processes including sulfate reduction (salinity: 0.2–36.6, Ba: 7–1630 nmol kg^{-1}, Sr: 1.3–210 μmol kg^{-1}, U: 0.3–18 nmol kg^{-1}, Mn: 0.6–2600 nmol kg^{-1}, Ca: 2.1–15.2 mmol kg^{-1}, ^{226}Ra 20–5120 dpm 100 L^{-1}). However, there is no evidence in the spring geochemistry that deep marine groundwater within this reaction zone exchanges with the coastal ocean via spring discharge. Total submarine groundwater discharge rates calculated from radium tracers are 40–95 m^3 m^{-1} d^{-1}, with terrestrial discharge contributing 75 ± 25% of the total. Global estimates of chemical loading from karst subterranean estuaries suggest Sr and U fluxes are potentially 15–28% and 7–33% of total ocean inputs (8.2–15.3 mol y^{-1} and 4.0–7.7 mol y^{-1}), respectively. Radium-226 inputs from karst subterranean estuaries are 34–50 times river inputs (6.7–9.9 × 10^{16} dpm y^{-1}).

Abbreviations: SGD, submarine groundwater discharge; STE, subterranean estuary; SI, saturation index

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1. INTRODUCTION

Submarine groundwater discharge (SGD) is the transport of terrestrially sourced groundwater and groundwater of marine origin across the ocean-aquifer interface (Burnett et al., 2006). Many studies have shown that SGD is an important source of trace elements to the coastal ocean (Shaw et al., 1998; Basu et al., 2001; Moore et al., 2006; Beck et al., 2007; Bone et al., 2007; Moore, 2010; Santos et al., 2011; Beck et al., 2013; Gonneea et al., 2013). However, uncertainty remains concerning the total chemical flux via SGD, due in part to groundwater transit through the subterranean estuary (STE), the region of the coastal aquifer where sharp gradients in salinity, oxygen and redox state facilitate the biogeochemical cycling of trace elements (Moore, 1999; Charette and Sholkovitz, 2006; Kaleris, 2006; Beck et al., 2007; Gonneea et al., 2008; Santos et al., 2011). To fully understand the impact SGD has on the coastal ocean and the role SGD plays in global ocean element budgets, we need to quantify how chemical cycling within the subterranean estuary impacts transport of dissolved species to the ocean.

Geochemical transformations within the salinity-mixing zone of the subterranean estuary have been observed at many sites characterized by permeable sand and dominated by aluminosilicate minerals (Charette and Sholkovitz, 2006; Beck et al., 2007; Gonneea et al., 2008; Santos et al., 2011). Karst subterranean estuaries, however, have three unique characteristics: (1) the water to rock ratio is much higher and more variable due to multiple scales of permeability; (2) carbonate minerals are readily soluble; and (3) groundwater mixing occurs during channelized conduit flow of both terrestrial and marine groundwater, with springs being the primary route of water exchange with the coastal ocean (Perry et al., 2002; Beddows et al., 2007; Fleury et al., 2007; Charette et al., 2008; Garcia-Solsona et al., 2010; Einsiedl, 2012). The key processes that may alter dissolved trace element distributions in the subterranean estuary include mineral dissolution/precipitation, adsorption/desorption reactions, redox cycling, and mixing between water sources. In the case of radioactive trace elements such as the isotopes of radium, radioactive production or decay must also be considered.

Globally, 12% of submarine groundwater discharge flows through karst subterranean estuaries (as reported in Beck et al. (2013) calculated from aquifer lithologies presented in Gibbs and Kump (1994) and regional SGD estimates in Zekster et al. (2006)). This study evaluates geochemical cycling of barium (Ba), uranium (U), strontium (Sr), manganese (Mn), calcium (Ca) and radium (^{226}Ra, ^{228}Ra and ^{223}Ra) within the Yucatan Peninsula karst subterranean estuary. These elements are of interest given their utility as tracers of environmental processes. For example, past oceanic productivity can be reconstructed from $BaSO_4$ burial rates (Paytan et al., 1996) while the oceanic Sr isotope record serves as a proxy for various inputs to the ocean, including continental weathering and hydrothermal circulation (Hess et al., 1986; Palmer and Edmond, 1989). Variability in oceanic Ca may be related to changes in ocean carbon cycling on long time scales (Griffith et al., 2008). Ra is used extensively as a tracer of groundwater discharge (Moore, 1996). Uranium serves as a proxy of ocean redox state (Tribovillard et al., 2006). More recently, studies have shown SGD associated fluxes and chemical transformations within the subterranean estuary should be considered in oceanic element budgets (Dunk et al., 2002; Santos et al., 2011; Holmden et al., 2012; Beck et al., 2013). To this end, SGD-derived chemical fluxes are determined for the Yucatan Peninsula. We then extrapolate the karst end members reported here to calculate potential global SGD derived chemical fluxes through karst subterranean estuaries and compare them to ocean element budgets.

2. METHODS

2.1. Field site

The Yucatan Peninsula is a large karst platform (165,000 km^2) that is bordered by the Gulf of Mexico along the west and north coasts and by the Caribbean Sea on the east coast (Fig. 1). The peninsula is characterized by a humid tropical climate, with maximum daily temperatures ranging from 25 to 35 °C and average rainfall that varies spatially across the Peninsula from 555 to 1500 mm y^{-1}. Evapotranspiration rates are ~80% of total precipitation and invariant over the course of the year due to a low seasonal temperature difference and sustained vegetation growth (Bautista et al., 2009). The rainy season is from June through October with dry conditions prevailing from December through May, coinciding with cool temperatures (Giddings and Soto, 2003). From November through February temperatures are typically cool and north winds prevail. Tropical depressions, which frequently make landfall on the Yucatan Peninsula, result in large precipitation events (Boose, 2006).

The Yucatan Peninsula consists of limestone, dolomite and evaporite deposits, which can reach up to 1500 m thickness (Bauer-Gottwein et al., 2011). The permeability of the aquifer is so great that there are no streams or rivers. Preferential flow paths in the karst aquifer range in scale from large dissolution conduits (10–100's of meters) to smaller scale fractures (1–10 cm), thus aquifer permeability is largely scale dependent. The hydraulic gradient is very low (1–10 cm km^{-1}) and flow is generally perpendicular to the coast (Hanshaw and Back, 1980; Beddows et al., 2007; Gondwe et al., 2010). Marine groundwater lies beneath a freshwater lens across the entire northern Peninsula, with the depth to the saltwater interface increasing with hydraulic head elevation, as predicted by the Dupuit–Ghyben–Herzberg model. Close to the coast (<20 km), the halocline is at <40 m and it is possible to sample both terrestrial and marine groundwater through sinkholes, which are locally known as "cenotes" (Perry et al., 2009; Bauer-Gottwein et al., 2011). The freshwater portion of cenotes is typically oxic, with reducing conditions developing in the saline portions due to reduction of organic matter and presumably longer water residence times than terrestrial groundwater (Cervantes-Martinez et al., 2002; Perry et al., 2002; Schmitter-Soto et al., 2002; Torres-Talamante et al., 2011). A region of high permeability exists along the perimeter of the Cretaceous asteroid impact crater; known as the 'Ring of Cenotes', it bisects the coast at the Celestun and Bocas de Dzilam Lagoons (Perry et al., 1995).