



Controls on the chemical and isotopic composition of carbonate springs during evolution to saturation with respect to calcite



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ABSTRACT

We investigated the stable carbon isotopic composition ($\delta^{13}\text{C}$) of dissolved inorganic carbon (DIC) in carbonate springs that evolve chemically to supersaturation with respect to calcite and to isotopic equilibrium with atmospheric $\text{CO}_{2(\text{g})}$. The $\delta^{13}\text{C}$ of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) will track isotopic fractionation accompanying carbon loss to the atmosphere, precipitation of calcite or carbon exchange with atmospheric $\text{CO}_{2(\text{g})}$. We assessed the DIC and $\delta^{13}\text{C}_{\text{DIC}}$ evolution along the flow paths of springs in the field. Since chemical equilibrium is a precondition for isotopic equilibrium, and because it is difficult to follow the evolution of carbonate springs to isotopic equilibrium with atmospheric $\text{CO}_{2(\text{g})}$ in field settings, three sets of spring samples were exposed to laboratory atmospheric $\text{CO}_{2(\text{g})}$ and allowed to evolve to isotopic equilibrium. One subset of the experimental sample was agitated to simulate mixing in the field. The physical, chemical and carbon isotopic changes in the field and laboratory experiments were complex and varied. Chemical speciation and isotopic mass balance modeling showed that the evolution to calcite supersaturation can be conceptualized in 4 discrete steps, each characterized either by kinetic fractionation, equilibrium fractionation or carbon isotopic exchange with atmospheric $\text{CO}_{2(\text{g})}$. These steps sequentially are (1) undersaturation to supersaturation where DIC decreases from $\text{CO}_{2(\text{g})}$ loss from solution and small increases in the $\delta^{13}\text{C}_{\text{DIC}}$ (1–2‰) are from kinetic fractionation, (2) saturation to supersaturation where relatively no DIC is lost and small increases in the $\delta^{13}\text{C}_{\text{DIC}}$ (~1‰) are likely due to isotopic exchange of carbon between DIC and atmospheric $\text{CO}_{2(\text{g})}$, (3) decreasing supersaturation where DIC concentration decreases and larger increases in the $\delta^{13}\text{C}_{\text{DIC}}$ (~5‰) are from equilibrium isotopic fractionation and (4) increasing saturation where the previous decreasing supersaturation and DIC concentration decreases reverse and increase because of evaporation, and the continued increase in the $\delta^{13}\text{C}_{\text{DIC}}$ (~2‰) is from isotopic exchange of carbon between DIC and atmospheric $\text{CO}_{2(\text{g})}$. The unmixed laboratory samples evolved through steps 1, 2 and 3, while the mixed laboratory sample evolved through steps 1, 2, 3 and 4 because agitation of the solution increased the reaction rates and enhanced DIC–atmospheric $\text{CO}_{2(\text{g})}$ interaction. The chemical and isotopic evolution of the field samples were limited to steps 1 and 2 because of the relatively short length of flowing springs which limit carbonate evolution to calcite saturation. Our findings suggest that for carbonate springs in contact with atmospheric $\text{CO}_{2(\text{g})}$, significant $\delta^{13}\text{C}_{\text{DIC}}$ enrichment that occurs after calcite supersaturation is dominated by equilibrium isotopic effect, despite conditions conducive for calcite precipitation. We hypothesize that the chemical and isotopic behavior observed for the field and laboratory experiments may characterize other carbonate-rich waters (e.g., streams and lakes) evolving in contact with the atmosphere.

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1. Introduction

Springs issuing from a carbonate aquifer (carbonate springs) with high concentrations of dissolved inorganic carbon (DIC) and high partial pressure of CO_2 ($p\text{CO}_2$) will lose $\text{CO}_{2(\text{g})}$ as they evolve towards chemical equilibrium with atmospheric $\text{CO}_{2(\text{g})}$. As $\text{CO}_{2(\text{g})}$ is lost from solution, the equilibrium solubility of calcite (CaCO_3) decreases to the point of calcite

saturation and CaCO_3 can precipitate from solution (e.g., Jacobson and Uzdowski, 1975; Herman and Lorah, 1986; 1987; Dreybrodt et al., 1992; Pentecost, 1995; Liu and Zhao, 2000). The carbonate spring–atmospheric $\text{CO}_{2(\text{g})}$ interaction is complex because both the saturation state with respect to calcite and the evolution to chemical equilibrium with respect to atmospheric $\text{CO}_{2(\text{g})}$ depend on carbon transformation between $\text{CO}_{2(\text{g})} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_{3(\text{s})}$ (Stumm and Morgan, 1981). The carbon isotopic composition of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) in the evolving carbonate spring will change because of isotopic fractionation accompanying carbon loss to the atmosphere, carbon loss from the precipitation of carbonate or carbon exchange with atmospheric

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$\text{CO}_{2(g)}$ (e.g., Clark and Fritz, 1997). Several studies have investigated the behavior of DIC and $\delta^{13}\text{C}_{\text{DIC}}$ of carbonate springs (e.g., Pentecost, 1995; Lu et al., 2000; Marfia et al., 2004; Li et al., 2010a,b). Moreover, measurements of $\delta^{13}\text{C}$ of calcite that precipitates during the evolution of carbonate-rich waters were conducted with the aim of determining the chemical and isotopic kinetics controlling calcite precipitation (e.g., Dandurand et al., 1982).

The DIC and $\delta^{13}\text{C}_{\text{DIC}}$ behavior in carbonate springs have not been examined in the context of (1) evolution of the carbonate system to saturation where carbon ($\text{CO}_{2(g)}$) is lost from the DIC pool, (2) chemical evolution at saturation with respect to calcite when carbon (CaCO_3) is removed from the DIC pool and (3) concomitant evolution of the DIC towards chemical equilibrium with atmospheric $\text{CO}_{2(g)}$. Chemical equilibrium is a precondition for isotopic equilibrium and in field settings, it is difficult to follow the chemical evolution of springs to isotopic equilibrium with atmospheric $\text{CO}_{2(g)}$. This is because over relatively short distances, springs flow into streams, are intercepted by tributaries or disappear underground, thus limiting the flow pathway along which carbonate evolution can be evaluated. Additionally, even if carbonate springs have long flow pathways that could be followed, assessing the chemical and isotopic evolution can be problematic due to the addition of carbon from organic matter decomposition (Wicks and Engeln, 1997). Furthermore, when the material lining the channels are carbonates, weathering may introduce DIC into the water column (e.g., Hess and White, 1988; Hoffer-French and Herman, 1989; Groves, 1992) thereby affecting the $\delta^{13}\text{C}_{\text{DIC}}$ (e.g., Doctor et al., 2008). Laboratory experiments provide a near ideal way to assess how the DIC and $\delta^{13}\text{C}_{\text{DIC}}$ for carbonate springs behave during the chemical evolution to calcite saturation and to chemical and isotopic equilibrium with atmospheric $\text{CO}_{2(g)}$. Results from the near-ideal behavior in laboratory experiments aid in the interpretation of processes that affect $\delta^{13}\text{C}_{\text{DIC}}$ behavior in carbonate springs in field settings.

In this study, we assessed the behavior of $\delta^{13}\text{C}_{\text{DIC}}$ associated with DIC evolution in field and laboratory experiments with waters from carbonate springs. We aimed to use the temporal and spatial DIC concentrations and the $\delta^{13}\text{C}_{\text{DIC}}$ to generate DIC- $\delta^{13}\text{C}_{\text{DIC}}$ models that characterize

carbonate springs that evolve to calcite saturation and to chemical and isotopic equilibrium with atmospheric $\text{CO}_{2(g)}$.

2. Study area

The springs used in this study are Antelope Spring (34°30'7.32"N, 96°56'29.05"W), Buffalo Spring (34°30'14.32"N, 96°56'16.05"W) and Byrds Mill Spring (34°35'40.47"N, 96°39'55.33"W) which issue from the Arbuckle–Simpson aquifer in Oklahoma, USA (Fig. 1). The rocks which make up the Arbuckle–Simpson aquifer crop out in south central Oklahoma and underlay parts of Carter, Coal, Johnston, Murray and Pontotoc Counties (Fig. 1). The Arbuckle–Simpson aquifer is highly folded, faulted and fractured and is made up of the Arbuckle and the Simpson Groups (Ham, 1955; Fairchild et al., 1990; Donovan, 1991; Campbell and Weber, 2006). The Arbuckle Group consists of Late Cambrian to Middle Ordovician limestones and dolomites (e.g., Ham, 1955; Donovan, 1991). The Simpson Group is Ordovician and consists of a basal sandstone, middle shale and an upper limestone (e.g., Fairchild et al., 1990). The Arbuckle–Simpson aquifer is overlain by Pennsylvanian limestones, conglomerates, shales and sandstones and underlain by Precambrian and Cambrian rhyolite and granite basement (Hanson and Cates, 1994).

The study area is a moist, sub-humid zone (Fairchild et al., 1990) where precipitation occurs mostly as rainfall, with occasional snow during the winter. The mean annual precipitation from 1960 to 2010 is ~1000 mm measured in Ada, Oklahoma (Fig. 1), ~40 km northeast of Antelope and Buffalo Springs and ~20 km north of Byrds Mill Spring (National Climatic Data Center, 2013). Antelope Spring discharges ~56 L/s and is located in the Chickasaw National Recreation Area (CNRA) near Sulfur, Oklahoma. Buffalo Spring discharges from several points into a rock-bound pool and flows from the pool at a discharge rate ~65 L/s. Buffalo Spring is located 270 m SE of Antelope Spring and flows for about 365 m before joining Antelope Spring 150 m downstream from its source. Byrds Mill Spring, which discharges ~527 L/s, is the largest spring in Oklahoma and is the drinking water source for the city of Ada (Christenson et al., 2009).

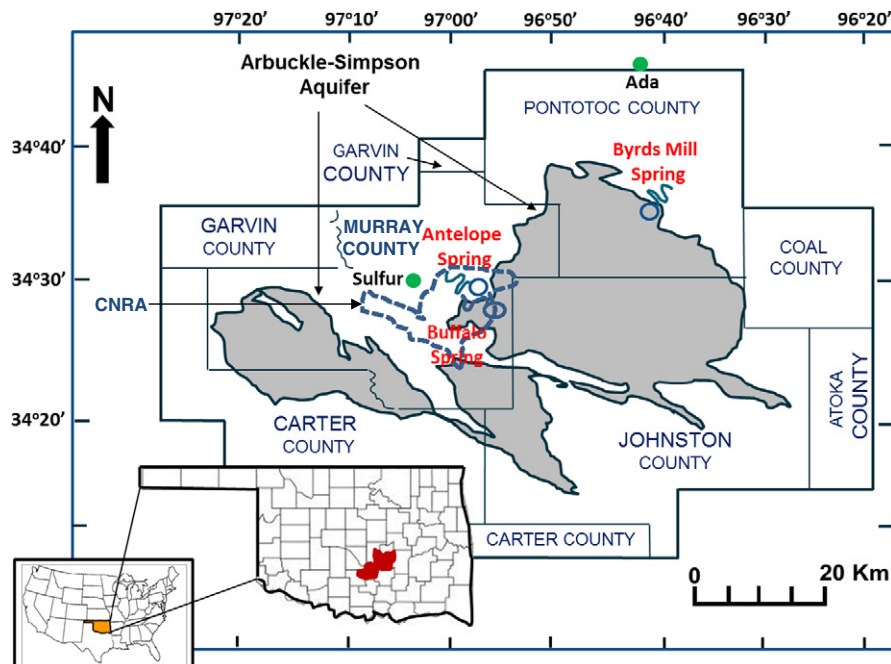


Fig. 1. Map showing the location of Antelope Spring, Byrds Mill Spring and Buffalo Spring and the aerial extent of the Arbuckle–Simpson Aquifer (Modified from Christenson et al., 2009). Insert shows location of Oklahoma in the USA and counties in south-central Oklahoma where Arbuckle–Simpson aquifer underlies. CNRA = Chickasaw National Recreation Area.

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