**Isotopic and Geochemical Characterization of Fossil Brines of the Cambrian Mt. Simon Sandstone
and Ironton-Galesville Formation from the Illinois Basin, USA**

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Abstract

Geochemical and isotopic characteristics of deep-seated saline groundwater provide valuable insight into the origin and evolving composition, water-rock interaction, and mixing potential of fossil brines. Such information may yield insight into intra- and interbasinal brine movement and relationships between brine evolution and regional groundwater flow systems. This investigation reports on the $\delta^{18}\text{O}$ and δD composition and activity values, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations, and major ion concentrations of the Cambrian-hosted brines of the Mt. Simon Sandstone and Ironton-Galesville Formation and discusses the evolution of these brines as they relate to other intracontinental brines. Brines in the Illinois Basin are dominated by Na–Ca–Cl-type chemistry. The Mt. Simon and overlying Ironton-Galesville brines exhibit total dissolved solids concentrations of ~195,000 mg/L and ~66,270 mg/L, respectively. The δD of brine composition of the Mt. Simon ranges from -34‰ to -22‰ (V-SMOW), and the Ironton-Galesville is $\sim -53.2\text{‰}$ (V-SMOW). The $\delta^{18}\text{O}$ composition of the Mt. Simon brine ranges from -5.0‰ to -2.8‰ (V-SMOW), and the Ironton-Galesville brine is $\sim -6.9\text{‰}$ (V-SMOW). The $^{87}\text{Sr}/^{86}\text{Sr}$ values in the Mt. Simon brine range from 0.7110 to 0.7116. The less radiogenic Ironton-Galesville brine has an average $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7107. Evaluation of $\delta^{18}\text{O}$ and δD composition and activities and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios suggests that the Mt. Simon brine is likely connate seawater and recirculating deep-seated brines that have been diluted with meteoric water and influenced by the dissolution of evaporites with a minimal halite contribution based on Cl/Br ratios. The Ironton-Galesville brine is also likely originally connate seawater that mixed with other brines and meteoric waters, including possibly Pleistocene glacial recharge. The Ca- excess vs. Na-deficiency comparison with the Basinal Fluid Line suggests the Mt. Simon and Ironton-Galesville brines have been influenced by the effects of albitization and plot very close to the Basinal Fluid Line. These Cambrian-hosted brines appear to have a different albitization history than other regional basin brines and a strong component of seawater. The Ironton-Galesville brine appears more geochemically associated with other Illinois Basin brines than the Mt. Simon brine which appears more geochemically conservative. Comparisons with other extrabasinal North American brines suggest that the Michigan

basin brines are geochemically most similar to the Mt. Simon brines with the exception of the influence from carbonates in the Michigan Basin. Analyses of $^{87}\text{Sr}/^{86}\text{Sr}$ values in the Mt. Simon brine suggest that brine Sr has isotopically equilibrated with clay minerals in the Lower Mt. Simon and underlying bedrock formations and not with whole rock suggesting the influence of recirculating brines from the crystalline basement. Overall, the geochemistry of these Cambrian-hosted brines suggests an evolution from original seawater-like compositions. This investigation shows that intracratonic basins do not behave as closed systems but can be strongly affected by water-rock interaction and regional groundwater flow systems that circulate deep crystalline basement brines and brines from nearby basins.

Key words:

Mt. Simon Formation; brine geochemistry; Illinois Basin; Cambrian brines

1. INTRODUCTION

Much effort has focused on understanding the geochemical evolution of deep-seated brines (e.g., Frape et al., 1984; Davisson and Criss, 1996). These efforts include investigating the distinctions associated with brine environment (e.g., sedimentary or igneous host rock) involving processes related to water-rock interaction and brine isolation. Geochemical comparisons of deep-basinal brines also elucidate on mixing potential with groundwaters of different chemical and isotopic compositions and histories, original seawater signatures, and meteoric water influences. A recent geochemical investigation of brines in the Mt. Simon Sandstone and Ironton-Galesville Formation, part of the deepest and least accessible sedimentary units in the Illinois Basin, provides insight into the formation and evolution of deep-seated sedimentary brines. Geochemical comparisons between these Cambrian-hosted brines and other North American continental brines show a varied history of brine evolution and interaction.

Brines from Ordovician age and younger strata in the Illinois Basin (i.e., Stueber et al., 1987; Walter et al., 1990; Stueber and Walter, 1991, 1994; Stueber et al., 1993) and brines from Michigan, southwest Arkansas, eastern Ohio, the Alberta Basin and Canadian Shield (Frape et al., 1984; Lowry et al., 1988; Connolly et al., 1990; Wilson and Long, 1993a,b) have been studied extensively. These studies used various geochemical techniques such as ion concentration ratios, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, and δD values to understand groundwater evolution including mixing scenarios with evaporitic brines, glacial and non-glacial meteoric waters, signatures of original seawater, the influences of subaerial exposure and evaporation, and water-rock interaction. A previous study by Panno et al. (2013) used Cl/Br and Na/Br ratios of the Mt. Simon and Ironton-Galesville brines to postulate that brines of the Cambrian strata are a mixture of residual evaporitic brines, with dilution by seawater and fresh groundwater. This investigation focuses on the Mt. Simon Sandstone and Ironton-Galesville brine $\delta^{18}\text{O}$ and δD composition and activity values, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations, and major ion concentrations and discusses the evolution of these Cambrian-hosted brines as they relate to their origin and evolving composition, water-rock

interaction, and mixing potential with fresh and saline groundwaters from the Illinois Basin, adjacent intracratonic basins and crystalline basement brines.

2. CAMBRIAN FORMATIONS IN THE ILLINOIS BASIN

2.1 Location and geology of the Mt. Simon Sandstone and Ironton-Galesville Formation

The Mt. Simon Sandstone is part of the deepest, least accessible sedimentary unit in the Illinois Basin. Groundwater samples were collected through efforts from the Illinois Basin–Decatur Project (IBDP), a large carbon sequestration research effort being conducted by the Illinois State Geological Survey as the lead agency of the Midwest Geological Sequestration Consortium that is funded by the U.S. Department of Energy through its Carbon Storage Program. In 2009, a deep borehole was drilled on-site in Decatur, Illinois, to a depth of 2155 m. This site is located northwest of the Illinois Basin depocenter, where the Mt. Simon Sandstone is ~457 m thick. The depocenter of the Mt. Simon Sandstone in east-central Illinois does not correlate with the depocenter of the Illinois Basin in south-eastern Illinois and has been referred to as the proto-Illinois Basin (Kolata and Nelson, 2010; Freiburg et al., 2014). The maximum thickness of the Mt. Simon Sandstone is ~792 m and lies northeast of the IBDP site in east-central Illinois and west-central Indiana. The thickness of the Mt. Simon Sandstone is variable across the Illinois Basin and, in some cases, is absent, particularly in the western and southern flanks of the Illinois Basin (Leetaru and McBride, 2009). The Mt. Simon Sandstone is a Cambrian-age sedimentary unit consisting largely of fine- to coarse-grained, poorly sorted, and occasionally pebbly quartzose to arkosic sandstones with few interbedded shales (Fig. 1). The Mt. Simon Sandstone lies disconformably over the Argenta Formation; a Cambrian-age sandstone and conglomerate deposit (Freiburg et al., 2015). These pre-Mt. Simon rocks rest unconformably on Precambrian crystalline basement composed largely of granite, granodiorite, and rhyolite (Freiburg et al., 2014). The Mt. Simon is stratigraphically equivalent to the Lamotte Sandstone of Missouri (Workman and Bell, 1948) and possibly correlates to the Bayfield Sandstone of Wisconsin, the Jacobsville Sandstone of Michigan, and the Fond du Lac Sandstone of Minnesota (Buschbach, 1964). The sediment source for the Mt. Simon Sandstone is thought to be

predominantly from the Canadian Shield, with additional sediment sources from the St. Francois Mountains (Ojakangas, 1963; Houseknecht and Ethridge, 1978).

The Illinois Basin forms an elongated structure with the long axis trending north–south. The basin was formed during a rifting event in the early Paleozoic (Ervin and McGinnis, 1975). It is structurally bound on the northeast by the Kankakee Arch, on the northwest by the Mississippi River Arch, and on the south by the Cincinnati Arch, the Pascola Arch, and the Ozark Uplift. The La Salle Anticlinorium lies within the Illinois Basin and trends north–south just east of the long axis of the Illinois Basin. The Reelfoot Rift and Rough Creek Graben intersect in the southern part of the basin (Kolata and Nimz, 2010; Fig. 1). The proto-Illinois Basin is thought to have formed before the Illinois Basin in the same general area sometime between 1.48 billion and 500 million years ago (Kolata and Nelson, 2010). However, the depocenter of the Mt. Simon suggests the proto-Illinois Basin formed north of the Illinois Basin (Freiburg et al., 2014).

The paleogeographic location of the Illinois during the Late Precambrian was the tropics just south of the equator as part of the paleocontinent Laurentia (Scotese and McKerrow, 1990). The depositional environments for the Argenta Formation and Mt. Simon Sandstone consist of delta, fluvial, eolian, and shallow marine (Freiburg et al., 2014; Freiburg et al., 2015), where sediments were deposited unconformably on Precambrian basement crystalline rocks (Driese et al., 1981).

Porosity and permeability vary throughout the Mt. Simon Sandstone, affecting potential fluid migration, as described in detail by Freiburg et al. (2014). The Mt. Simon Sandstone is divided into three main depositional settings. The Lower Mt. Simon consists largely of fluvial braided river deposits. In the Lower Mt. Simon, feldspar dissolution and subsequent precipitation of clay minerals preserved abundant primary porosity and permeability (average 25% log porosity; 884 mD log permeability), creating high-quality reservoir rock.

The Middle Mt. Simon (1795 to 1951 m) is characterized by poor reservoir quality fluvial and eolian deposits. Primary porosity within the Middle Mt. Simon has largely been filled with diagenetic quartz cementation, resulting in poor porosity and permeability (average 12% log porosity; 44 mD log

permeability). The Middle Mt. Simon is referred to as the “tight zone” due to its characteristically low-quality reservoir properties, with porosities generally less than 10% (Freiburg et al., 2014). Because of its poorer hydraulic properties, the Middle Mt. Simon unit likely inhibits mixing of fluids between the Upper and Lower Mt. Simon brines.

The Upper Mt. Simon consists of intertidal sandstone and interbedded shale deposits (average 15% log porosity; 184 mD log permeability). The upper unit is conformably overlain by the Eau Claire Formation, which acts as a cap rock or primary seal for the IBDP and consists largely of shallow marine to intertidal sediments, including sandstone, dolomitic siltstone, mudstone, interbedded dolomite, and shale (Palkovic, 2015). Unconformably overlying the Eau Claire Formation are the Ironton-Galesville Sandstones, which are part to the Franconia Formation within the Sauk III sequence of the Late Cambrian (Kolata, 2010; Freiburg et al., 2014; Fig. 1).

The sandstones of the Ironton-Galesville Formation overlie the Eau Claire Formation and are comprised of Upper Cambrian sandstones that are part of the clastic sediments deposited on a broad, stable shelf. In central Illinois, these sandstones occur at a depth of ~1500 m. They are composed of mature, well-sorted orthoquartzites that exhibit a maximum thickness of ~75 m in northern Illinois and thin as the beds dip southward toward the study site and the deeper portion of the depositional basin. Grain size also decreases toward the depositional center of the Illinois Basin. In the southward extensions of the Ironton-Galesville Formation, dolomite becomes a significant lithologic component, both as a cement for the sandstone grains and as independent thin beds (Emrich, 1966).

2.2 Brine environment of the Mt. Simon Sandstone and Ironton-Galesville Formation

The Mt. Simon Sandstone is free of evaporites and contains relatively few shales. Panno et al. (2013) characterized the halide and halide/cation ratios of the brines of the Mt. Simon Sandstone and the overlying Ironton-Galesville Formation. They interpreted the brines of the Mt. Simon Sandstone as predominantly seawater that had evaporated beyond the point of halite precipitation, which subsequently mixed with seawater and dilute groundwater. The chloride/bromide (Cl/Br) ratios of the Mt. Simon Sandstone and Ironton-Galesville Formation brines are lower than those of any other sedimentary brines

within the Illinois Basin. Illinois Basin brines appear to be stratified with respect to Cl/Br and K/Cl ratios, suggesting various origins of the saline groundwater and brines. The brines of the Cambrian strata are postulated to have partially originated from outside the basin as residual evaporite brines. These brines are postulated to have migrated into the Cambrian strata during the Permian time through tectonic-induced migration pathways (Panno et al., 2013). The Mt. Simon Sandstone brine is believed to contain fluids influenced by ore-forming brines, possibly Mississippi Valley type ore fluids, and crystalline basement brines. These original Cambrian brines are thought to have mixed with or been replaced by extrabasinal brines, possibly from the Black Warrior Basin, Arkoma Basin, Michigan Basin, or their combination, or from saline fluids from evaporites that accumulated in the Reelfoot Rift during the Late Proterozoic (Leach et al., 1997; Chen et al., 2001; Panno et al., 2013).

The sandstones of the Ironton-Galesville form an important potable aquifer in northern Illinois and southern Wisconsin where the formation is closer to the surface. These sandstones are part of the Cambrian-Ordovician aquifer system where significant mixing between the Ironton-Galesville and younger aquifers is common. Transmissibility of the Cambrian-Ordovician aquifer system significantly decreases in the southward direction, and this is attributed to the increasing carbonate content of the sandstones (Emrich, 1966). Brine content also increases in the deeper portions of the basin. Within the study area, the total dissolved solids (TDS) of the Ironton-Galesville brine range from ~63,000 to 69,000 mg/L, a range well above the U.S. Environmental Protection Agency (USEPA) safe drinking water limits of 500 mg/L (USEPA, 2015) or the World Health Organization (WHO) limits of less than 1200 mg/L (WHO, 1996).

3. METHODOLOGY

3.1 Sampling strategy

The IBDP Monitoring, Verification, and Accounting Program includes a deep monitoring well, Verification Well #1 (VW1), drilled in 2010 to a depth of 2155 m and located 305 m north of the CO₂ injection well for this project. The well was perforated with 11 vertically isolated zones: 9 in the Mt.

Simon Sandstone and 2 in the Ironton-Galesville Formation. Zone 1 was in rhyolitic basement rock and was not sampled, so in 2010, samples were taken from zones 2 to 11. A standard swabbing technique was used at VW1 to produce water at the surface where the samples were collected. To ensure sample integrity, each perforated zone in the well was isolated using a packer and retrievable bridge plug during swabbing. For each zone, unit fluid was purged until field parameters measured at the wellhead had stabilized (i.e., density, pH, specific conductance) to ensure samples were representative (Table 1). In total, more than 289,000 L of fluid was purged from all zones sampled. Brine chemistry data used for this study were from the initial swab-sampling event, and further details on well construction and sampling methods are described by Locke et al. (2013). In general, samples were processed, preserved, and stored according to standard procedures and kept in cold storage at 4 °C until analyzed within prescribed holding times.

The Mt. Simon Sandstone included eight sampling zones. Zones 2 to 7 were in the Lower Mt. Simon and zones 8 and 9 were in the Upper Mt. Simon. The Lower Mt. Simon brine geochemistry samples were taken from depths of ~2116 to 1944 m. The Upper Mt. Simon brine samples were taken from depths of ~1770 to 1714 m below the surface. In general, all physical values except temperature were measured at the wellhead after field parameters stabilized and do not represent *in situ* conditions. Temperature values are from instruments deployed in each of the VW1 zones after swab sampling was completed. Brine environmental properties of the Mt. Simon reservoir are 46.0 to 51.3 °C, pH of 5.8 to 6.8, and alkalinity (as CaCO₃) of 62 to 108 mg/L. Zone 7, located near the base of the Middle Mt. Simon, is an abrupt transition zone between the lower and middle units in terms of porosity and permeability of the unit. Geochemically, zone 7 behaves most similarly to the Lower Mt. Simon and is discussed as part of this zone for the purposes of this study.

The overlying Ironton-Galesville Formation included two sampling zones (zones 10 and 11) at depths of 1515 and 1490 m, respectively. The younger Ironton-Galesville Formation is Upper Cambrian (Croixan) in age (Emrich, 1966). In the lower part of the Ironton-Galesville Formation, brine properties

are 42.6 to 43.8 °C, pH of 6.9 to 6.9, and alkalinity (as CaCO₃) of 114 to 129 mg/L. Brine isotope analyses included ratios of D/H, ¹⁸O/¹⁶O, and ⁸⁷Sr/⁸⁶Sr. Dissolved ion analyses were measured for Cl⁻, Ca²⁺, Na⁺, K⁺, and Sr²⁺ concentrations (Table 1).

Whole-rock samples were prepared for ⁸⁶Sr/⁸⁷Sr analysis. Sample powders were drilled from selected Mt. Simon, Argenta, and basement rock samples with a Dremel tool. Bulk samples, clay samples (illite/smectite), and individual feldspar grains were sampled. The selected sample depth and zone and a short description were noted (Table 2).

3.2 Analytical methodology

3.2.1 Brine $\delta^{18}\text{O}$ and δD composition analysis

The stable isotopes of oxygen and hydrogen ($\delta^{18}\text{O}$ and δD) of brines were analyzed for samples collected in the Mt. Simon Sandstone and Ironton-Galesville Formation. Isotopes are reported in delta notation:

$$\delta = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \times 10^3, \quad (1)$$

where R_{sample} is the molar ratio of the rare to abundant isotope of the unknown sample and R_{standard} is the molar ratio of the rare to abundant isotope of a known standard. Values are reported in per mill (‰) or parts per thousand.

Brine isotopes of $\delta^{18}\text{O}$ and δD were measured by cavity ring-down spectroscopy on a Picarro water isotope analyzer (model L1102-I). This method is based on the near-infrared adsorption spectrum of the gas species. Brine samples were vacuum-distilled off-line before analysis. Precision for $\delta^{18}\text{O}$ is $\pm 0.3\text{‰}$ and for δD is $\pm 2\text{‰}$, with values reported relative to Vienna Standard Mean Ocean Water (V-SMOW).

3.2.2 Sr isotope analysis

Strontium isotope analyses of the brines and powders were performed at the Department of Geology, University of Illinois at Urbana-Champaign, using a Nu Plasma high-resolution multicollector inductively coupled plasma mass spectrometer. Strontium purification was done with an Eichrom Sr-spec

resin in 0.2-mL Teflon columns with nitric acid media. Samples were compared with the following standards: National Institute of Standards and Technology SRM 987, Eimer & Amend, and an in-house coral standard (Faure, 2001) with an external precision of 0.003%.

3.2.3 Dissolved ion analysis and bulk geochemistry

Dissolved ion analysis was performed at the Public Service Laboratories of the Illinois State Water Survey, Prairie Research Institute, University of Illinois at Urbana-Champaign. Brine concentrations of major anions of Cl^- and Br^- were measured by ion chromatography following USEPA Method 300.0 (Pfaff, 1993). Cation concentrations were determined by inductively coupled argon plasma-atomic emission spectrometry following USEPA Method 200.7. Quality assurance and quality control procedures for field and laboratory methods were consistent with standards ASTM D4448-01 (ASTM International, 2007) and ASTM D3856-11 (ASTM International, 2013). Analytical error for anions was $\pm 5\%$, and for cations was $\pm 3\%$ for the brine samples. Qualitative bulk geochemistry of rock cores drilled from basement rock and at various depths within the Mt. Simon Sandstone was determined at the Illinois State Geological Survey by X-ray diffraction (XRD) crystallography (model Scintag XDS2000).

4. RESULTS

4.1. Isotopes

The water isotopes of brine in the Mt. Simon Sandstone ranged from -34 to -22‰ for δD and from -5.0 to -2.8‰ for $\delta^{18}\text{O}$ (Table 1; Fig. 2). Oxygen isotopes of the Mt. Simon brine showed $\sim 2\text{‰}$ variation with depth, whereas hydrogen isotopes showed a greater trend toward lighter values approaching the cap rock of the Eau Claire Formation. The average depletion in δD was $\sim 7\text{‰}$ from heavier values in the Lower Mt. Simon to lighter values in the Upper Mt. Simon. The overlying Ironton-Galesville brine had an average δD of -54‰ ($\pm 1.9\text{‰}$) and an average $\delta^{18}\text{O}$ of -7.2‰ ($\pm 0.32\text{‰}$; Table 1). Regulatory compliance wells (G-101 to G-104), which tap the deepest potable groundwater source for the

area in Pennsylvanian strata (depth of ~43 m), showed average δD values of -41‰ (± 0.9) and average $\delta^{18}\text{O}$ values of -6.5‰ (± 0.13 ; Fig. 2). Fig. 2 shows the local meteoric water line (dashed line; Panno et al., 2005), the global meteoric water line (GMWL, solid line), and the Standard Mean Ocean Water isotope value (SMOW) as a reference.

The brine $^{87}\text{Sr}/^{86}\text{Sr}$ values became less radiogenic with increasing distance from basement rock. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the brine in the Mt. Simon Sandstone ranged from a maximum value of 0.7116 in zone 3 (2105 m depth) to a value of 0.7110 in zone 9 (1714 m depth). The overlying Ironton-Galesville brine had $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.7109 and 0.7105 (Table 1).

Results of bulk rock, feldspar grain, and clay matrix analyses for $^{87}\text{Sr}/^{86}\text{Sr}$ values are presented in Table 2. In the Upper Mt. Simon, the average $^{87}\text{Sr}/^{86}\text{Sr}$ value of the bulk rock matrix was 0.75415 ($n=2$). In the Lower Mt. Simon, a bulk analysis of several individual feldspar grains showed average $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.77162 ($n=6$), the bulk rock matrix had a $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.72979 ($n=8$), and clay rich samples showed average $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.71763 ($n=9$).

4.2 Ion and bulk geochemistry

The dominant ions in the Mt. Simon Sandstone brine were Cl^- , Na^+ , and Ca^{2+} , with lesser amounts of K^+ and Sr^{2+} . Total dissolved solids concentrations in the Mt. Simon brine ranged from 208,467 to 150,840 mg/L, with the greatest concentration in the Lower Mt. Simon unit. The Ironton-Galesville brine showed significantly lower TDS values, ranging from 68,895 to 63,645 mg/L (Table 1). Concentrations of the measured ions were greater in the Lower Mt. Simon unit compared with the Upper Mt. Simon unit. The average Cl^- concentration in the Lower Mt. Simon brine ($\sim 119,700$ mg/L) was greater than the concentration in the Upper Mt. Simon unit brine ($\sim 92,800$ mg/L). Sodium concentration followed a similar pattern, with $\sim 48,300$ mg/L in the Lower Mt. Simon unit brine decreasing to $\sim 38,500$ mg/L in the Upper Mt. Simon, as did Ca^{2+} with $\sim 21,300$ to $14,500$ mg/L and K^+ with ~ 2120 to 1660 mg/L, respectively, in the Lower to Upper Mt. Simon brines. Strontium decreased by almost half, from concentrations of ~ 800 mg/L in the Lower Mt. Simon to ~ 440 mg/L in the Upper Mt. Simon (Table 1).

Qualitative analysis by XRD revealed dominant quartz and K-feldspar mineralogy for the Mt. Simon sandstone grains (Table 3). Bulk matrix analysis of the transition zone of the pre-Mt. Simon unit, between the Mt. Simon Sandstone and basement rock at a depth of 2124 m, showed predominantly quartz mineralogy and no feldspar grains. In the weathered zone of the basement rock (2140 m), the feldspar content was almost entirely K-feldspar. In less weathered basement rock (2141 m), the feldspar content was largely split between low-temperature albite and K-feldspar.

5. DISCUSSION

5. Geochemical variation and evolution of brines

Composition of the Mt. Simon brine is distinct from the estimated composition of Early Cambrian seawater or modern seawater. Table 4 shows concentrations in millimoles per kilogram (mmol/kg) of H₂O for the major ions in seawater from Early Cambrian and modern oceans (Mason, 1966; Fontes and Matray, 1993; Holland et al., 1996; Lowenstein and Risacher, 2000; Brennan et al., 2004; Babel and Schreiber, 2014) compared with the average brine composition of the Mt. Simon. The Mt. Simon brine contains several times the concentrations of the major ions Na⁺, K⁺, Ca²⁺, and Cl⁻ compared with those in modern or Early Cambrian seawater. This chemistry reflects the complexity of evolution of the Mt. Simon brine since the Cambrian Period involving water/rock interaction, mixing of waters, and salt effects on isotope activity.

5.1. Na–Ca–Cl brines: Na deficit and Ca excess

Although several methods have been used to characterize deep basin fluids, Davisson and Criss (1996) proposed that the majority of basin fluids are closely related to a Basinal Fluid Line (BFL). The BFL is a regression model composed of more than 800 samples worldwide from various lithologic basins. The model is based on the hypothesis that the hydrosphere is dominated by seawater and the upper crust is dominated by feldspar minerals. Under such circumstances, a 2 Na for 1 Ca exchange is expected in evolving basin fluids as plagioclase undergoes albitization. This process results in the Ca excess and Na deficiency trend observed within deep basin brines worldwide. The general regression model developed

by Davisson and Criss (1996) uses concentrations of Na^+ , Ca^{2+} , and Cl^- in fluids to calculate milliequivalents per liter (meq/L) for a Ca excess and Na deficiency. The Ca excess and Na deficiency model represents the extent of reaction between deep saline brines and bedrock aquifers. With this model, seawater plots at the origin on an excess–deficit graph. The BFL has a y-intercept of 140 (Fig. 3).

Brines within the Illinois Basin are dominated by Na^+ , Ca^{2+} , and Cl^- . Total dissolved solids concentrations for the Ironton-Galesville brine are ~66% less than those observed for the Mt. Simon brine. Both the Mt. Simon and Ironton-Galesville brines are >90% Na–Ca–Cl by concentration. Brines of Ordovician strata are composed of ~88% Na–Ca–Cl by concentration, whereas younger Mississippian and Pennsylvanian brines appear almost entirely composed of Na–Ca–Cl (~97 to 99%; Stueber et al., 1993; Stueber and Walter, 1994; Table 5). This characteristic of Na–Ca–Cl-dominated brine is common in older brines that have sufficiently reacted with igneous bedrock (Davisson and Criss, 1996; Hanor and McIntosh, 2006). The original Ca-plagioclase becomes albitized from Na-rich seawater, which releases Ca^{2+} into solution, thereby increasing the Ca concentration and reducing the Na concentration. The presence of the low-temperature albite, from results of the XRD analysis (Table 3), suggests the possibility that some basement feldspars were albitized by reacting with deep saline groundwater. The immediately underlying Precambrian basement unit is composed of a highly weathered porphyritic rhyolite. The occurrence of feldspar phenocrysts increases with depth. At a depth of around 2189 m, the basement rock becomes predominantly granodiorite that is largely composed of plagioclase and pyroxene (Freiburg et al., 2014). The potential for deep circulating saline groundwater to albitize some of the basement feldspars is present although not directly evident.

Although Illinois Basin brines are dominated by Na^+ , Ca^{2+} , and Cl^- , the Cambrian brines are different from younger brines in the Illinois Basin. This may be because the age and isolation of these brines allows more reaction time between the basement rock and brine. Fig. 3a shows the Cambrian-age brines in relation to the BFL and Fig. 3b shows the extrabasinal brines of various ages from the eastern Ohio and southwest Arkansas basins, the Michigan and Alberta Basins, and the Canadian Shield. The Mt.

Simon brine has a regression line with a negative and smaller y-intercept (considering the origin at 0, 0) than the BFL. The y-intercept of about -21 for the Mt. Simon brine suggests a strong signature of seawater in the brine. The Lower Mt. Simon brine overlays the BFL, whereas the Upper Mt. Simon and Ironton-Galesville brines show less effects of albitization.

5.2. $\delta^{18}\text{O}$ and δD variation in Cambrian brines

Isotope variability of $\delta^{18}\text{O}$ and δD offers insight into the origin and history of the brines. Here, we used a dual approach to investigating the isotope character of these brines. First, $\delta^{18}\text{O}$ and δD composition is used to characterize the Mt. Simon brine as a sedimentary brine and to examine potential mixing of the brine with other basinal brines. Isotope activities are then used to address isotope effects sensitive to saline environments. For example, an isotope salt effect is observed in brines because of the interactions of dissolved electrolytes and water molecules forming hydration spheres that can affect the activity of isotopes in water molecules. Important processes influenced by this isotope salt effect are evaporation, mineral precipitation, and mineral-rock interaction (Horita et al., 1993). We calculated the isotope activities of the Mt. Simon and Ironton-Galesville brines as well as those of younger Illinois Basin brines and external basin brines. We then compared these activities with known geochemical processes affecting brine chemistry.

The Mt. Simon brine is dominated by Na-Ca-Cl ions as the dissolved salts (Table 1). Therefore, a marine origin for the brine can be assumed. Sources for isotope variability in oxygen and hydrogen values of the brine include (1) excessive evaporation, (2) isotope exchange reactions between brines and silicate or carbonate minerals, (3) precipitation of minerals from solution, and (4) mixing of waters of other origins (Faure and Mensing, 2005). In the case of brine mixing with waters of different origins, past research supports three potential sources: (1) meteoric waters, recent or ancient, (2) connate seawater diagenetically modified, and (c) metamorphic fluids (Horita, 2005).

The water isotope compositions observed in the Mt. Simon brine suggests that isotope exchange with the crystalline basement mineralogy has not had a significant influence on the $\delta^{18}\text{O}$ and δD character

of the brines. Indeed, whole-rock analysis of basement granite (~1390 Ma) in Illinois showed $\delta^{18}\text{O}$ values of ~7‰ (SMOW; Kombrink and Clayton, 1983), which is significantly more enriched in ^{18}O than the values observed in the Mt. Simon brine. Previous studies suggest brines within parts of the Illinois Basin may be enriched in ^{18}O through isotopic exchange between brine and carbonate rocks at temperatures more elevated than those experienced in the shallower parts of the basin (Clayton et al., 1966). A notable lack of readily soluble minerals such as carbonates exist in the Mt. Simon Sandstone; therefore, host rock mineralogy of the Mt. Simon is likely not a significant factor contributing to the overall $\delta^{18}\text{O}$ and δD isotope trend observed in this brine.

The Mt. Simon brine is similar to many other brines in sedimentary basins that plot to the right or below the meteoric water line (Fig. 4a). Alternatively, high-salinity brines (>10,000 mg/L of TDS) that are sourced from crystalline rocks show $\delta^{18}\text{O}$ and δD trends that plot above or to the left of the GMWL, such as the Canadian Shield brines (Frape et al., 1984; Kloppmann et al., 2002; Fig. 4b). Brine isotope compositions of the nearby Michigan and Arkansas sedimentary basins plot below the GMWL along with the Cambrian brines of this study. By comparison, the Michigan Basin brines exhibit water isotope compositions more similar to the Cambrian-hosted brines in this study, whereas the southwest Arkansas basin brines are systematically more enriched in ^{18}O and, to a lesser extent, in δD . The Mt. Simon and Ironton-Galesville brines appear more isotopically influenced by meteoric water than do the southwest Arkansas basin brines.

Consistent δD values in the Lower Mt. Simon become notably depleted in the Upper Mt. Simon by ~9‰ (Table 1). The Mt. Simon Sandstone contains basically no carbonates and few other exchangeable minerals under low-temperature conditions. The dominant mineralogy in the Mt. Simon Sandstone is quartz. Feldspar minerals constitute up to 22% of the whole-rock mineralogy in parts of the Lower Mt. Simon and up to 13% in the Upper Mt. Simon, and illite/smectite clays constitute up to ~19% in sections of the Lower Mt. Simon (Freiburg et al., 2014). The Upper Mt. Simon brine δD values could be influenced by diagenetic clays or clays in the overlying shales of the Eau Claire. However, this

influence is likely too small to account for the ~9‰ depletion observed in the Mt. Simon brine. If environmental conditions are such that the temperature and the water/rock ratio is low, then a Rayleigh distillation process can be used for a general characterization of the isotopic evolution of the water during hydrolysis of clays (Kloppmann et al., 2002). Using the fractionation equation for hydrogen between kaolinite and water from Sheppard and Gilg (1996),

$$1000 \ln \alpha_{\text{kaolinite-water}} = [(-2.2 \times 10^6)/T^2] - 7.7, \quad (2)$$

where T is temperature in Kelvin, we can determine a fractionation factor to estimate isotopic changes resulting from a Rayleigh fractionation process. Considering a temperature of ~50 °C for the brine, less than a 2‰ depletion in δD can be attributed to hydrogen exchange during the hydrolysis of clays to kaolinite. Similar effects are expected for illite and smectite. As such, δD values are likely to reflect the mixing of two dissimilar bodies of water, as Stueber and Walter (1991) suggested for other brines in the Illinois Basin.

According to Stueber and Walter (1991), the reservoir of δD in the brines to the reservoir of δD in the hydrous minerals from diagenetic processes is so large that at low temperatures, the formation of these diagenetic minerals will have a negligible effect on the brine δD reservoir. Therefore, δD is considered conservative with respect to exchange with bedrock mineralogy and covariant trends. The amount of available exchangeable oxygen in minerals may be large compared with the amount of oxygen in water and has greater potential to be affected by water–rock interactions. Fig. 5a,b shows the relationship between Cl⁻ (mg/L) concentration in the Mt. Simon brine and δ¹⁸O and δD compositions. Oxygen-18 and δD exhibit a strong covariance with Cl⁻ (mg/L; $r^2 = 0.98$ for δD and δ¹⁸O). This relationship implies that water isotopes and Cl⁻ concentrations are conservative and that brine–rock reactions did not significantly influence the isotope composition of the brine waters (Stueber and Walter, 1991). The extended regression line for the Mt. Simon δD and Cl⁻ (mg/L) passes through the Ironton-Galesville brine (Fig. 5a). This suggests that the Ironton-Galesville brine and Mt. Simon brine originally shared a similar brine source or that some mixing between the two brines has occurred. The extended

regression line for $\delta^{18}\text{O}$ does not intersect these brines. Subsequent water–rock interactions with carbonate minerals (Emrich, 1966) may have altered the Ironton-Galesville brine toward isotopically more enriched $\delta^{18}\text{O}$ values (Fig. 5b).

Recent Pleistocene recharge has been an important influence for some Illinois Basin brines, such as the Silurian-Devonian carbonate aquifers of the Illinois Basin (McIntosh et al., 2002) and some Ordovician groundwater samples (Siegel and Mandle, 1984). Person et al. (2007) estimates that Pleistocene glacial recharge has approximate isotope values ranging from -25 to -9‰ for $\delta^{18}\text{O}$ and from -62 to -190‰ for δD . Water isotope composition in the Mt. Simon brine does not suggest influences from glacial meltwaters and is unique compared with other basinal brines (Fig. 4). If the regression line for the Mt. Simon brine is extended to the GMWL, the regression line for this brine intersects the isotopic value for modern meteoric water in Illinois. This suggests a strong meteorological component to the Mt. Simon brine, likely during a climate regime unaffected by glacial conditions and similar to one today.

Data from Clayton et al. (1966) include Cambrian- through Pennsylvanian-age brines in the Illinois Basin. These data plot along a line extending on both sides of the GMWL (Fig. 5). However, the extension above (i.e., to the left of) the GMWL and the shallow slope are atypical of data reported more recently from the same formations within the Illinois Basin (Siegel and Mandle, 1984; Stueber and Walter, 1991, 1994). The reasons for the differences are beyond the scope of this investigation, and we chose to use more recent stable isotope data for comparison in our investigation.

Dissolved salts in water can alter the $\delta^{18}\text{O}$ and δD partitioning between water and other phases because of the hydration of ions, known as the isotope salt effect. Therefore, water isotope activities are more appropriately used for assessing the effects of geochemical interactions between the brines and other phases involving processes such as evaporation, mineral precipitation, and water–rock interactions (Horita et al., 1993). The activities for $\delta^{18}\text{O}$ and δD of the Mt. Simon and other brines were calculated using the experimental parameters and methodology of Horita et al. (1993, 1994). The effect of salt on

brines is an additive property. Therefore, effects from individual salts can be summed to assess the overall salt effect on the isotopes in the brine. Single salt effects are evaluated using the equation

$$10^3 \ln \Gamma = m(a + b/T), \quad (3)$$

where Γ is the isotope ratio of the salt divided by the isotope ratio of the pure vapor, m is the molality, T is temperature in Kelvin (K), and a (molality⁻¹) and b (K × molality⁻¹) are experimental parameters.

Environmental temperature was evaluated at 52 °C for the Mt. Simon and Ironton-Galesville brines, which is the average downhole temperature measured on-site. Multiple salts are evaluated according to the following equation:

$$10^3 \ln \Gamma_{\text{mixed salt soln}} = \sum 10^3 \ln \Gamma_{\text{mixed salt soln}} = \sum [m_i(a_i + b_i/T)], \quad (4)$$

where i represents the individual salts. Salt concentrations were estimated based on the molar concentration of individual ions in the brine. The dominant salts in the Mt. Simon brine are NaCl and CaCl₂, and minor salts of KCl, MgCl₂, Na₂SO₄, and MgSO₄ were evaluated. The estimated delta value (δ) for the isotope activity is evaluated using the relationship between isotope activity and composition scales:

$$\delta_{\text{activity}} \cong \delta_{\text{composition}} + 10^3 \ln \Gamma. \quad (5)$$

The isotope salt effect or isotope activity was calculated for the $\delta^{18}\text{O}$ and δD values for each zone in the Mt. Simon (zones 2–9) and Ironton-Galesville (zone 10 and 11) brines (Table 1). Within the Mt. Simon, δD values were more affected than $\delta^{18}\text{O}$ values by the salt concentrations. Overall, the $\Delta^{18}\text{O}_{\text{composition-activity}}$ was <1‰, whereas $\Delta\text{D}_{\text{composition-activity}}$ was about –15‰. Salt effects on the Ironton-Galesville brine were considerably less. The direction of change was also different for $\delta^{18}\text{O}$ and δD . The activity ratios for $\delta^{18}\text{O}$ were relatively depleted compared with the measured composition of the brine, whereas δD activity ratios were enriched relative to the measured brine composition.

The regression line for the water isotope activity in the Mt. Simon brine is very similar to the GMWL, with a similar slope but a deuterium excess of ~21‰ instead of 10‰ for the GMWL (Fig. 6a). This relationship also shows the importance of the meteoric water influence on the brine. Horita (2005)

created a general pattern of isotope evolution of water based on the activities of δD and $\delta^{18}O$, which is overlain on Fig. 6a,b in gray. If meteoric water affecting the brine was isotopically similar to that today (-6.3‰ $\delta^{18}O$ and -40‰ δD ; Clayton et al., 1966), or at least not glacially sourced, and brine seawater was originally 0‰ $\delta^{18}O$ and 0‰ δD , then the dominant influences on the Mt. Simon brine would have been dilution with meteoric water and evaporite dissolution. Effects from the evaporation of seawater appear to have had less of an impact on the brine than were originally proposed by Panno et al. (2013) based on Cl^- ion ratios. Rather, high ion concentrations in the Mt. Simon brine possibly originated from dissolution of evaporites, which suggests a mixing of brines within the Mt. Simon because evaporites do not occur in this formation. Based on Cl/Br ratio work from Panno et al. (2013), these evaporites were not likely concentrated in halite but rather possibly anhydrite or gypsum. If these evaporites were nonhydrous, then the water isotope composition would not be affected but the isotope activity ratios would change. Although the effect is relatively small, the dissolution of hydrous evaporites would result in the original isotope composition of the brine becoming enriched in ^{18}O and depleted in deuterium (Chacko et al., 2001). This is the direction change observed in the water isotope values when isotope activity is compared with isotope composition of the Mt. Simon brine. Clay membrane filtration may also have played an important role. Coplen and Hanshaw (1973) showed that ^{16}O and 2H preferentially pass through a shale layer under pressure, leaving the remaining brine enriched in ^{18}O and deuterium and concentrated in dissolved salts, although the isotope effect of this process is a magnitude less than those of other isotope fractionation processes. Low-temperature water–rock interactions also appear to have had a minimal impact on the water isotopes of the Mt. Simon brine.

The water activities were calculated for extrabasinal brines and younger Illinois Basin brines for comparison with Mt. Simon brine (Table 6; Fig. 6b). The Canadian Shield brines are sourced from igneous bedrock and are largely affected by low-temperature water–rock interactions (Frape et al., 1984). Reported influences on the Michigan Basin brines (Silurian and Devonian) include water–rock interactions, especially with carbonates, hydration waters from evaporative minerals, dilution by meteoric

water, and brine concentration via seawater evaporation (Wilson and Long, 1993a,b). The Smackover Formation brine of southwest Arkansas is reported to have been influenced by seawater evaporation, dilution with meteoric water, water–rock interactions with carbonates, and hydration waters from evaporite minerals (Moldovanyi and Walter, 1992; Moldovanyi et al., 1993). Ordovician brine of the Illinois Basin is thought to have been largely influenced by subaerial evaporation of seawater and dilution with meteoric waters, including Pleistocene glacial recharge (Stueber and Walter, 1994). Silurian–Devonian brine of the Illinois Basin is thought to be mostly affected by seawater evaporation; water–rock interactions, especially with carbonates and clays; and dilution with meteoric water. The processes affecting the Mt. Simon brine isotope activities appear different from those of the surrounding brines and brines of the overlying strata. The Mt. Simon brine does not appear to have been significantly influenced by the effects of seawater evaporation to the extent that the southwest Arkansas basin brine was affected, nor has the Mt. Simon brine been significantly influenced by water–rock interactions, as have the Canadian Shield brines. Processes affecting the Michigan Basin brines and the Mt. Simon brine share similar characteristics, with the notable exception of carbonate dissolution in the Michigan Basin brines.

Deuterium and $\delta^{18}\text{O}$ brine evolution for the Mt. Simon brine involved a complicated history. Water isotope compositions show that the Mt. Simon brine is distinct from brines in younger Illinois Basin strata, although comparisons of conservative Cl^- concentrations and δD suggest that the Ironton–Galesville and Mt. Simon brines may have a common source or mixing component of brine. If the δD – $\delta^{18}\text{O}$ composition regression line of the Mt. Simon brine is extended, the line passes near the value for modern meteoric water for the Illinois Basin, suggesting a strong meteoric component to evolution of the brine. Evidence of Pleistocene glacial meltwater is not observed in the isotope values of the Mt. Simon brine. The δD – $\delta^{18}\text{O}$ activity regression line [$\delta\text{D} = (7.5 \times \delta^{18}\text{O}) + 20.9$] is very similar to the GMWL and supports meteoric water as having a significant role in brine isotopic evolution. The dominant geochemical interactions with the Mt. Simon brine appear to have been dilution with meteoric water and evaporite dissolution. The source of the dissolved evaporites was outside the Mt. Simon Sandstone and

likely involved mixing with brines of other origins. With the exception of carbonate interaction, the Michigan Basin brines and the Mt. Simon brine appear to have experienced similar geochemical influences that affected the water isotope activity.

5.3. Brine $^{87}\text{Sr}/^{86}\text{Sr}$ isotopes and Sr concentration

The Sr concentrations in the Mt. Simon (~694 mg/L) and Ironton-Galesville (~136 mg/L) brines are notably greater than those of modern seawater, 7.74 mg/L (Holland, 1984; Table 1), and are more radiogenic than seawater estimates throughout the Phanerozoic (Viezer et al., 1999). Thus, the Mt. Simon brine has either mixed with other more radiogenic brines or undergone water-rock interactions. The average Mt. Simon brine exhibits a $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.71144 (± 0.000224) with a small dilution gradient and slightly lower radiogenic values toward the Upper Mt. Simon. Fig. 7a compares Sr concentrations and isotope ranges of brines from Cambrian through Carboniferous age within the Illinois Basin. Strontium concentrations vary from ~10 to >1000 mg/L, and isotope values range from estimated seawater values to 0.71162. Fig. 7b shows the range of brine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for Cambrian through Pennsylvanian strata. The Mt. Simon brine is more radiogenic than are other Illinois Basin brines. In Upper Ordovician strata, brines are characterized by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.70817 to 0.71043, with an average Sr concentration of ~345 ppm (Stueber and Walter, 1994; Table 5). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the Silurian-Devonian strata brines (0.7092–0.7108) are less radiogenic than those observed in the Mt. Simon brines (0.7110–0.7116). Therefore, although mixing with brines of the Illinois Basin is possible, this is likely not an important source of Sr in the Mt. Simon brine.

Bedrock mineralogy within the Mt. Simon Sandstone and the underlying Argenta Formation and basement igneous rock are expected to contribute to, if not control, the Sr isotope signature of the Mt. Simon brine. Rock-sourced Sr isotope analyses were measured from powdered samples of feldspars, clay matrix, and bulk host rock sampled from the basement igneous rock, the Argenta, and the Lower and Upper Mt. Simon Sandstone (Table 2; Fig. 8). The bulk rock powders and the feldspar grain powders from the Mt. Simon and underlying Argenta Formation and basement rock are notably more radiogenic than are the dissolved Sr within the Mt. Simon brine. This result suggests that the Mt. Simon brine

$^{87}\text{Sr}/^{86}\text{Sr}$ values are not isotopically equilibrated with the whole-rock or feldspar $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Mt. Simon Sandstone, Argenta Formation, or igneous basement. This disequilibrium between brine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and host rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios has been noted in previous studies (McNutt et al., 1984, 1987, 1990; Franklyn et al., 1991), which have suggested that the current host rock does not always control Sr isotope chemistry in the brines. Rather, more soluble mineral phases, such as fracture mineralization, may be controlling the brine $^{87}\text{Sr}/^{86}\text{Sr}$ values. For the Mt. Simon brine, green clay clasts within the Mt. Simon sandstone and highly weathered clay material from the Argenta and saprolitic top of the basement rock appear to be the main sources of *in situ* Sr. These samples are represented by stars in Fig. 8. Stueber et al. (1987) reported that in younger Illinois Basin brines, clay minerals in shales and sandstones were the only significant source of radiogenic Sr in the Illinois Basin. The bedrock mineralogy and brine Sr geochemistry of the Mt. Simon appear to follow a similar trend. This result suggests that deep-seated basement brines may have upwelled and mixed with Mt. Simon brines.

5.4. Possible origins of Mt. Simon brine

The Mt. Simon brine represents a complex evolutionary history only touched upon in this study. Despite the elevated salinity of this brine (~195,000 mg/L), no known bedded evaporites occur in the Mt. Simon Sandstone (Hanor and McIntosh, 2006; Freiburg et al., 2014). Geochemical comparisons from this study and Panno et al. (2013) suggest Ordovician and younger Illinois Basin brines have been largely isolated from the Mt. Simon brine. Panno et al. (2013) presented halide chemistry that suggests the Ironton-Galesville brine mixed with the Mt. Simon brine. The brine $\delta^{18}\text{O}$ and δD isotope composition and comparisons with Cl^- concentrations also suggest mixing with or similar origins as the Ironton-Galesville brine. The water isotope composition and activity suggest a strong meteorological component to the Mt. Simon brine, but the isotope activity ratios do not suggest a significant influence from the evaporation of seawater. Rather, the dissolution of evaporites, with only a small component of halite due to the low Cl/Br ratios, and dilution with meteoric water appear to have had greater influences on brine evolution.

Comparisons of Na deficiency and Ca excess in regional deep saline brines (Fig. 4) show that the Cambrian brines are different from surrounding basinal brines with regard to albitization. The Lower Mt. Simon brine correlates closely with the BFL, whereas the Upper Mt. Simon and Ironton-Galesville brines appear slightly less influenced by albitization of the deep-seated brines. The relatively low y-intercept of approximately -21 suggests the Mt. Simon brine has a strong seawater signature. Future comparisons of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved sulfate in the Mt. Simon brine with sulfate deposits across the region may provide insight into correlations with other brines.

The mechanism for brine migration from external basins is still a topic of debate. Several potential mechanisms have been proposed, including (1) fluid flow driven by sediment compaction caused by either sedimentation rate or tectonic compression, (2) fluid flow driven by density gradients, (3) topography-driven fluid flow, or (4) seismic-induced flow along active faults (i.e., Bethke et al., 1991; Sverjensky and Garven, 1992). Unfortunately, until a more certain fluid source is established, the mechanism for fluid flow will remain highly speculative.

A study by Chen et al. (2001) measured $\delta^{18}\text{O}$ values of authigenic K-feldspars, quartz overgrowths, and cements throughout the Mt. Simon Sandstone. The authors concluded that the trend observed in $\delta^{18}\text{O}$ compositions indicated a basinal fluid migration from south to north. Chen et al. (2001) proposed the thick accumulation of sediments associated with the failed Reelfoot Rift and Rough Creek Graben complex that was active in the Middle Cambrian as a potential source of fluids for the Mt. Simon brine. Alternatively, Panno et al. (2013), who studied the halide chemistry of these Cambrian brines, suggested an external source, possibly from the Black Warrior or Arkoma Basin via the Reelfoot Rift, although the timing of brine intrusion remains more speculative. Geochemical characteristics from the present study suggest that the Michigan Basin brines share a similar brine evolution history, with the exception of carbonate influences on the Michigan Basin brines.

6. CONCLUSIONS

This investigation highlights the unique character of the Cambrian-hosted brines of the Mt. Simon Sandstone and Ironton-Galesville Formation and their geochemical relation to other Illinois Basin and intracontinental brines. Much of the evolutionary history of the Mt. Simon brine at the IBDP site appears to be preserved within the fluid geochemistry. The Mt. Simon brine is likely connate seawater and recirculating deep-seated brines that have been diluted with meteoric water and influenced by the dissolution of evaporites with a minimal halite contribution based on Cl/Br ratios (Panno et al., 2013). The Ironton-Galesville brine is also likely originally connate seawater that mixed with other brines and meteoric waters, including possibly Pleistocene glacial recharge. The Mt. Simon brine predominantly appears geochemically conservative and unique compared with other Illinois Basin brines. The Michigan basin brines share more geochemical similarities to the Mt. Simon brine than the brines of other intracratonic basins evaluated based on water isotope compositions and activities. The Canadian Shield brines are largely influenced by water-rock interaction with igneous bedrock and exhibit distinctly different isotope activity trends from sedimentary-hosted brines. The southwest Arkansas brines appear to have been strongly influenced by evaporation of seawater. The major conclusions of this investigation are as follows:

1. The Ca- excess vs. Na-deficiency comparison with the Basinal Fluid Line suggests the Mt. Simon and Ironton-Galesville brines have been influenced by the effects of albitization and plot very close to the Basinal Fluid Line. These Cambrian-hosted brines appear to have a different albitization history than other regional basin brines and a strong component of seawater;
2. The Mt. Simon brine has a significant meteorological component of a nonglacial character which limits the timing of groundwater interaction;
3. The more radiogenic strontium isotope values of the Mt. Simon brine separate it from other brines in the Illinois Basin. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Mt. Simon brine appear to be in isotopic equilibrium with the more soluble clays in the Mt. Simon Sandstone and underlying Argenta

Formation and weathered basement rock and implies contributions from deep bedrock brines to the overall Mt. Simon brine geochemistry;

4. Unlike the Ironton-Galesville, the Mt. Simon brine appears to be geochemically distinct from other Illinois Basin brines. Water-rock interaction with the predominantly sandstone lithology of the Mt. Simon would not produce the geochemistry observed in the brine; therefore, the geochemical composition of the Mt. Simon brine has been significantly influenced from sources outside the Illinois Basin during the evolution of this Cambrian-hosted brine;
5. The Mt. Simon brine appears to have been influenced by similar geochemical processes as the Michigan Basin brines except for the presence of carbonate dissolution in the Michigan Basin brines;
6. Future research that includes isotope analysis of dissolved SO_4^{2-} in the brines may narrow the possible origins of the Mt. Simon brine.

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782

1 Table 1
2 Physical and chemical characteristics of Mt. Simon and Ironton-Galesville Cambrian brines (concentrations in mg/L)^{a,b,c,d}
3

Zone	Depth (m)	Temp (°C)	Density (g/cm ³)	pH units	$\delta^{18}\text{O}$ (‰) composition	$\delta^{18}\text{O}$ (‰) activity ^d	δD (‰) composition	δD (‰) activity ^d	n	⁸⁷ Sr/ ⁸⁶ Sr	n
Z11	1490	43	1.043	6.9	-7.4 (±0.27)	-7.6	-56 (±0.7)	-50	3	0.7105	1
Z10	1515	44	1.046	6.9	-6.9 (±0.21)	-7.2	-52 (±0.8)	-48	3	0.7109	1
Z9	1714	46	1.101	6.3	-4.9 (±0.40)	-5.5	-32 (±1.5)	-20	3	0.7110	1
Z8	1770	48	1.110	6.4	-5 (±0.36)	-5.6	-34 (±1.6)	-21	3	0.7112	1
Z7	1944	50	1.136	5.8	-3.8 (±0.57)	-4.7	-25 (±1.1)	-10	4	0.7115	1
Z6	2010	51	1.138	6.4	-3.6 (±0.65)	-4.5	-25 (±3.0)	-9	4	0.7115	1
Z5	2036	48	1.137	6.4	-2.9 (±0.36)	-3.7	-23 (±1.7)	-7	5	0.7115	1
Z4	2072	48	1.141	6.3	-2.8 (±0.25)	-3.7	-22 (±1.4)	-6	4	0.7116	1
Z3	2105	50	1.139	6.4	-2.9 (±0.16)	-3.8	-23 (±0.6)	-6	4	0.7116	1
Z2	2116	50	1.138	6.8	-3 (±0.26)	-3.8	-24 (±1.6)	-8	3	0.7116	1

4
5

6 Table 1 (continued).

Ca ²⁺	Mg ²⁺	Sr ⁺⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	TDS	n
5135 (±0)	948 (±20)	134 (±5)	16,465 (±105)	502 (±19)	36,084 (±794)	1234 (±14)	63,645	2
5375 (±87)	942 (±5)	138 (±4)	17,918 (±108)	577 (±18)	39,378 (±778)	1185 (±48)	68,895	2
13,379 (±29)	1943 (±11)	379 (±11)	37,614 (±296)	1687 (±1)	88,776 (±1816)	917 (±14)	150,840	2
15,785 (±85)	2101 (±10)	500 (±13)	39,526 (±214)	1641 (±0)	96,849 (±2239)	643 (±13)	172,870	2
21,186 (±812)	2273 (±80)	772 (±24)	46,990 (±1460)	2227 (±75)	119,527 (±2446)	254 (±78)	203,760	3
21,787 (±682)	2359 (±82)	789 (±30)	48,036 (±1777)	2201 (±88)	120,457 (±2735)	312 (±27)	205,275	3
20,400 (±1295)	286 (±133)	753 (±49)	47,434 (±2908)	2085 (±110)	118,460 (±2103)	323 (±14)	202,980	5
21,583 (±244)	2311 (±71)	786 (±22)	48,500 (±1757)	2110 (±23)	121,025 (±918)	325 (±1)	205,525	4
22,240 (±270)	2370 (±33)	813 (±9)	49,583 (±397)	2083 (±14)	119,975 (±411)	376 (±1)	207,300	4
20,953 (±1586)	2255 (±170)	758 (±54)	48,043 (±3477)	2068 (±9)	119,000 (±265)	366 (±3)	208,467	3

^{a,b,c}General brine properties.

^aZone (Z) 2 to Z7: Lower Mt. Simon Formation; Z8 to Z9: Upper Mt. Simon Sandstone; Z10 to Z11: Ironton-Galesville Formation.

^bAll physical values except temperature were measured at the wellhead after field parameters stabilized and do not represent *in situ* conditions.

Temperature values are from instruments deployed in each of the Verification Well #1 monitoring zones after swab sampling was completed. Field parameters are physical measurements depth, temperature, density, and pH, and chemical analyses were performed in the respective laboratories following sample collection.

^cStandard deviation or standard error for analytical analyses are in parentheses; n = number of analyses for the analytes.

^dIsotope salt effect calculated following Horita et al. (1993, 1994): $10^3 \ln \Gamma^{18}\text{O} = \sum [m_i(a_i + b_i/T)]$ where m = molality, T = temperature (K), *i* is the *i*th salt, and experimental parameters of *a_i* (molality⁻¹) and *b_i* (K × molality⁻¹) were determined for NaCl, KCl, MgCl₂, CaCl₂, Na₂SO₄, and MgSO₄. These values were used to calculate the brine δ¹⁸O and δD activities. Temperature was set at 52 °C for calculations.

Table 2

⁸⁷Sr/⁸⁶Sr values for selected rock matrix samples^a

Zone/unit	Depth (m)	⁸⁷ Sr/ ⁸⁶ Sr	<i>n</i>	Sample description
Upper Mt. Simon	1677	0.76276	1	Pink sand matrix
	1677	0.74554	1	Black shaley sand matrix
Lower Mt. Simon	2043	0.72094	1	Bulk white clay matrix in red sandstone
	2066	0.77397	1	Pink feldspar grains
	2066	0.71095	1	Green clay clasts*
	2072	0.73697	1	Bulk red oxidized crumbly coarse sandstone
	2080	0.71701	1	Mudstone layer
	2087	0.73295	1	Bulk matrix with basement clasts and feldspars
	2089	0.71216	1	Green clay clasts*
	2094	0.74559	1	Bulk matrix sandstone
	2094	0.73630	1	Clay buildup transition zone
	2097	0.75421	1	Basement clasts; transition zone; no clay
	2106	0.83330	1	Pink and white feldspar grains
	2107	0.82963	1	Pink feldspar grains
	2119	0.76308	1	White feldspar grains from red siliciclastic matrix
	2119	0.72741	1	Red siliciclastic matrix
Argenta	2119	0.72365	1	Clay transition zone
	2122	0.71341	1	Clay drape*
	2124	0.71440	1	Red siliciclastic matrix with few feldspar grains*
	2125	0.71189	1	Conglomerate with red clay matrix*
	2129	0.71238	1	Conglomerate with red clay matrix*
Transition zone	2137	0.71044	1	Top of basement; saprolitic porphyritic rhyolite*
Basement	2140	0.71167	1	Weathered feldspar grains (very soft) from rhyolite*
	2140	0.71635	1	Bulk rhyolite sample
	2141	0.72693	1	Pink feldspars from rhyolite

^aExternal precision for analytical standards is 0.003%; an asterisk (*) represents the starred symbols in Fig. 8; *n* = number of analyses for the analyte.

24 Table 3
 25 X-ray diffraction analysis of bulk rock powders from drill cores of the Mt. Simon Formation (1677 to 2106 m), pre-Mt. Simon Formation (2119 to
 26 2124 m), and basement rock (2140 to 2141 m)^a
 27

Depth (m)	% Clay	% Quartz	% K-feldspar	% Plagioclase	% Calcite	% Dolomite	% Siderite	% FeS
1677	3	62	22	2	1	3	6	0
2072	1	78	15	1	1	2	1	1
2106	1	87	10	1	1	1	1	0
2119	2	71	19	2	1	1	2	2
2124	5	86	3	1	0	1	2	2
2140	5	53	28	1	1	2	4	6
2141	6	37	23	28	1	3	2	0

28 ^aPlagioclase mineralogy at 2141 m depth is low-temperature albite. Rows total approximately 100%.
 29

30 Table 4
 31 Comparison of Early Cambrian and modern seawater chemistry with that of the Mt. Simon Formation brines^a
 32

Major ion	Early Cambrian seawater ^b	Mt. Simon brines	Modern seawater ^{b,c}
Na ⁺	450	1,988	485
K ⁺	9	52	11
Ca ²⁺	37	495	11
Mg ²⁺	44	91	55
Cl ⁻	605	3,202	565
SO ₄ ²⁻	8	4	29
Mg ²⁺ /Ca ²⁺	~1	0.18	5.2

33 ^aConcentrations are reported in mmol/kg of H₂O.
 34 ^bMason (1966); Fontes and Matray (1993); Holland et al. (1996); Lowenstein and Risacher (2000); Babel and Schreiber (2014).
 35 ^cBrennan et al. (2004).
 36
 37

38 Table 5
39 Brine $\delta^{18}\text{O}$, δD , and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope values of Illinois Basin brines: Cambrian- to Pennsylvanian-age aquifers^a
40

Source	Stratigraphic age	$\delta^{18}\text{O}$ brine	δD brine	<i>n</i>	$^{87}\text{Sr}/^{86}\text{Sr}$	TDS (mg/L)	% Ca–Na–Cl brines	Reference
Lower Mt. Simon Fm	Cambrian	–3.1 (±0.31)	–23.4 (±1.07)	24	0.7116	Total Mt. Simon Formation 194,627	Total Mt. Simon Formation 92	This study
Upper Mt. Simon Fm	Cambrian	–4.4 (±0.01)	–30.2 (±0.52)	6	0.7111			
Iron-ton-Galesville Fm	Cambrian	–6.9 (±0.26)	–53.2 (±2.33)	6	0.7107	66,270	91	This study
St. Peter-Prairie du Chien-Jordan Fms	Cambrian/Ordovician	–8 (±0.70)	–55 (±6.0)	12	NA	NA	NA	Siegel and Mandle, 1984
Galena Fm	Ordovician	–2 (±2.7)	–29 (±13.0)	18	0.70817—0.71043	99,686	88	Stueber and Walter, 1994
Galena Fm	Ordovician	NA	NA	NA	0.70848—0.71040	NA	NA	Stueber et al., 1987
Multiple Fms	Silurian	–2 (±2.6)	–27 (±12.3)	9	0.70922—0.71084	NA	NA	Stueber and Walter, 1991
Multiple Fms	Silurian	NA	NA	NA	0.70913—0.71084	NA	NA	Stueber et al., 1987
Multiple Fms	Devonian	–2 (±2.0)	–26 (±8.6)	3	0.70931—0.71028	NA	NA	Stueber and Walter, 1991
Multiple Fms	Devonian	NA	NA	NA	0.70955—0.71007	NA	NA	Stueber et al., 1987
Multiple Fms	Mississippian	NA	NA	NA	0.70995—0.71041	50,363	99	Stueber et al., 1987, 1993
Spoon Sandstone	Pennsylvanian	NA	NA	NA	0.71052—0.71051	119,328	97	Stueber et al., 1987, 1993
Decatur, Illinois	Pennsylvanian	–6.5 (±0.13)	–41.2 (±0.93)	151	NA	NA	NA	This study

^a*n* = number of samples; standard deviation of replicates in parentheses; NA = data not available; TDS = total dissolved solids.

43 Table 6
44 Intracontinental water isotope compositions and estimated activities

Formation/ basin brine	Sample ID/reservoir	$\delta^{18}\text{O}$ comp. (‰)	$\delta^{18}\text{O}$ activity (‰)	δD comp. (‰)	δD activity (‰)	No. samples	Reference
Southwest (SW) Arkansas	H ₂ S	6.0	4.7	−13	10	12	Moldovanyi and Walter, 1992; Moldovanyi et al., 1993
	Northwestern	4.8	3.4	−11	12	6	
	Northern	1.8	1.1	−23	−10	4	
	Eastern	4.4	3.3	−18	1	1	
	Southern	6.3	5.2	−16	4	4	
Michigan Basin: Devonian	Barea/Traverse	−1.4	−2.4	−33	−9	9	Wilson and Long, 1993a
	Dundee	−2.5	−3.9	−39	−17	18	
Michigan Basin: Silurian		−0.3	−1.4	−40	−5	5	Wilson and Long, 1993b
Canadian Shield	YK-17	−14.4	−16.1	−71	−43	1	Frape et al., 1984
	YK-15	−19.1	−19.8	−123	−111	1	
	YK-32	−16.9	−18.2	−91	−68	1	
	YK-33	−18.1	−19.3	−105	−85	1	
	T-93	−11.7	−14.2	−53	−17	1	
	T-94	−14.4	−16.4	−79	−56	1	
	T-95	−15.6	−16.4	−79	−56	1	
	T-97	−13.2	−14.3	−77	−62	1	
	S-138	−10.9	−12.7	−44	−14	1	
	S-139	−10.3	−12.1	−42	−12	1	
	S-144	−10.8	−12.6	−45	−15	1	
	S-147	−10.9	−12.7	−39	−9	1	
	S-149	−11.3	−13.1	−33	−3	1	
Illinois Basin							
Ordovician strata	Galena Fm	−2.0	−2.3	−29	−23	18	Stueber and Water, 1994

Silurian strata	−2.0	−2.3	−27	−20	6	Stueber and Walter, 1991
Devonian strata	−2.0	−2.4	−26	−19	3	

Figure 1

Figure 2

Figure 3

Figure 4

(a)

(b)

Figure 5

Figure 7

Figure 8

Figure Captions

Fig. 1. Location of the sampling site, Illinois Basin–Decatur Project Verification Well #1 (VW1), in relation to the Illinois Basin and surrounding basins (from Panno et al., 2013). The basin cross-section A-A' shows the depositional strata of the Illinois Basin.

Fig. 2. Mt. Simon $\delta^{18}\text{O}$ and δD water isotope compositions in relation to Ironton-Galesville brines, local meteoric water isotope signatures for the Illinois Basin–Decatur Project study site (LMWL), and groundwater from Pennsylvanian strata compliance wells. GMWL = global meteoric water line; SMOW = Standard Mean Ocean Water; V-SMOW = Vienna Standard Mean Ocean Water.

Fig. 3. Sodium-deficit and Ca-excess plot for (a) the Cambrian brines of the Illinois Basin brines and (b) extrabasinal brines compared with the Basinal Fluid Line (BFL) outlined in Davisson and Criss (1996). Individual lines: (1) Canadian Shield (Precambrian) from Frape et al. (1984); (2) and (3) Michigan Basin brines (Paleozoic) from Wilson and Long (1993a,b); (4) southwest Arkansas basin (Mesozoic) from Moldovanyi and Walter (1992); (5) the BFL global regression [$\text{Ca excess} = 0.967(\text{Na deficit}) + 140.3$; $R = 0.981$] from Davisson and Criss (1996); (6) eastern Ohio basin (Paleozoic) from Lowry et al. (1988); and (7) Alberta Basin of Canada (Paleozoic and Mesozoic) from Connolly et al. (1990).

Fig. 4. (a) Water isotope composition ($\delta^{18}\text{O}$ and δD values) for Mt. Simon and Ironton-Galesville brines compared with Illinois Basin-wide brines from Cambrian- to Pennsylvanian-age strata. With the exception of one Silurian outlier, Ordovician, Silurian, and Devonian groundwaters plot along a similar trend which is similar to values of the Cambrian Ironton-Galesville brine. Data from Clayton et al. (1966) are labeled separately. Ordovician data are from Stueber and Walter (1994) and Siegel and Mandle (1984); Silurian and Devonian data are from Stueber and Walter (1991). Modern seawater values are from Babel and Schreiber (2014). (b) Extrabasinal brines compared with the Mt. Simon and Ironton-Galesville brines. Data source: Canadian Shield from Frappe et al. (1984); Michigan Basin (Devonian) from Wilson and Long (1993a); Michigan Basin (Silurian) from Wilson and Long (1993b); Arkoma Basin from Moldovanyi et al. (1993). GMWL = global meteoric water line; V-SMOW = Vienna Standard Mean Ocean Water.

Fig. 5. (a) Deuterium (δD) and (b) $\delta^{18}\text{O}$ isotope composition ratios of Cambrian brines compared with Cl^- (mg/L) concentration. Regression line ($r^2 = 0.98$) is for Mt. Simon brines. The extended regression line is represented by the dashed line. Modern seawater values are from Babel and Schreiber (2014). Meteoric water values are from Clayton et al. (1966). V-SMOW = Vienna Standard Mean Ocean Water.

Fig. 6. Oxygen-18 ($\delta^{18}\text{O}$) and δD water isotope activities for the (a) Ironton-Galesville and Mt. Simon brine and (b) compared with other basinal brines. The activities were calculated following methodology in Horita et al. (1993, 1994). Isotopic evolution of water based on activities shown in gray is from Horita (2005). Note that meteoric water values from Illinois (interglacial values)

are about -6‰ for $\delta^{18}\text{O}$ and -40‰ for δD . The isotope activity and composition are the same for meteoric or fresh water.

Fig. 7. (a) Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) compared with Sr concentrations (mg/L) for Illinois Basin brines. Cambrian data from this study; Ordovician data from Stueber and Walter (1994); Silurian and Devonian data from Stueber and Walter (1991, 1994); Mississippian and Pennsylvanian data from Stueber et al. (1993) and Stueber and Walter (1994). (b) Basin-wide stratigraphic column showing the published range of $^{87}\text{Sr}/^{86}\text{Sr}$ values in groundwater and notable aquitards of the Eau Claire Formation, Maquoketa Shale, and New Albany Shale (references same as panel a). Cambrian seawater value from Montañez et al. (1996) and stratigraphic column reconstructed from Kolata and Nimz (2010): P = Pennsylvanian; M = Mississippian; D = Devonian; S = Silurian; O = Ordovician; C = Cambrian; pC = Precambrian.

Fig. 8. Stratigraphic column from igneous basement to the Ironton-Galesville Formation showing the relationship between brine and rock $^{87}\text{Sr}/^{86}\text{Sr}$ values (see Table 2). The $^{87}\text{Sr}/^{86}\text{Sr}$ values from clay clasts in the lower Mt. Simon and secondary clays of the Argenta and igneous basement are similar to those of the Mt. Simon brine. Bulk rock and feldspars show greater radiogenic values.