Geochemical Preservation of the Steptoean Positive Carbon Isotope Excursion (SPICE) Event in Dolomites of the Furongian Franconia Formation in the Illinois Basin

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Illinois State Geological Survey PRAIRIE RESEARCH INSTITUTE **Front cover:** Thin-section photomicrograph of a fossiliferous and oolitic dolomite from the Franconia Formation at 1,429.5 m depth.

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ABSTRACT

The Cambrian Steptoean Positive Carbon Isotope Excursion (SPICE) is a well-documented global event that marked geochemical excursions in the world's oceans and terrestrial environments. A core from the Franconia Formation, which lies on the southwestern edge of the Illinois Basin, appears to have captured the carbon-isotope excursion associated with the SPICE. In this section of the Illinois Basin, the SPICE is contained within the Sauk III sequence. Marine carbonates typified the initial deposition of the Franconia Formation, which later transitioned into a shallow clastic-dominated environment as sea level lowered in the Furongian Epoch. Although extensive dolomitization has occurred, the δ^{13} C values of the carbonate were able to track the SPICE closely, revealing a peak enrichment value of 4.9‰. Carbonate-associated sulfate $\delta^{34}S$ values showed characteristic enrichment in ³⁴S during the Furongian, but these values did not exhibit a notable trend. This study emphasizes the potential for isotope geochemical preservation in carbonates despite extensive dolomitization and identifies the timing and local environmental conditions capturing the SPICE.

INTRODUCTION

The geochemical evolution of the Earth's seas progressed gradually over the Phanerozoic Eon but was punctuated by episodes of relatively abrupt and dramatic changes. Understanding these relatively rapid and significant geochemical perturbations in the marine record is essential for deciphering the Earth's evolution. In the Cambrian, four major positive carbon isotope excursions are recognized in the carbonate record (Babcock et al. 2015). These isotope excursions are related to global changes in the ocean carbon cycle, anoxic or euxinic conditions, and eustatic sea level changes. These excursions may also have reflected a more local response to greater environmental changes (Schiffbauer et al. 2017). During the Paiban Stage of the Furongian Epoch, the Steptoean Positive Carbon Isotope Excursion (SPICE) was a global marine event preserved in sedimentary rocks that documented changes in the physicochemical properties of the world's oceans (e.g., Montañez et al. 2000; Saltzman et al.

2000, 2004, 2011; Cowan et al. 2005; Gill et al. 2007. 2011: Dahl et al. 2014: Wotte and Strauss 2015). The SPICE documents a global event of evolving carbon and sulfur isotope properties in the ocean reservoir characterized by relatively enriched $\delta^{13}C$ values of dissolved inorganic carbon and δ^{34} S values of marine sulfate compared with most of the Phanerozoic ocean history (Claypool et al. 1980; Kampschulte and Strauss 2004; Gill et al. 2007). Other geochemical reservoirs have preserved the SPICE, namely, organic carbon reservoirs (Ahlberg et al. 2008; Saltzman et al. 2011; Woods et al. 2011; Hammer and Svensen 2017), phosphatic carbon reservoirs (Cowan et al. 2005), δ^{238} U sediment values (Dahl et al. 2014), and molybdenum concentrations in marine sediments (Gill et al. 2011). The link between positive excursions in marine $\delta^{13}C$ and δ^{34} S values is believed to be tied to the rapid burial of organic carbon, leading to elevated microbial sulfate reduction in marine sediments and resulting in pyrite precipitation (Saltzman et al. 2000, 2004; Gill et al. 2007). With a rise in sea level during the beginning of the SPICE, deep ocean anoxic zone waters are suspected to have progressed onto the shelf, creating reduced O₂ levels in shallower seas (Elrick et al. 2011; Gill et al. 2011; Lee and Riding 2018). Lowered O₂ levels in the oceans would have enhanced the preservation potential and burial of reduced organic carbon and pyrite. Anoxic or euxinic conditions, or both, are often inferred based on the idea that isotope excursions of carbonate carbon ($\delta^{13}C_{CO3}$) and carbonate-associated sulfate $({}^{34}S_{CAS})$ are tracking burial rates of organic matter and pyrite formation within the Cambrian seas. Uranium isotopes (Dahl et al. 2014) and molybdenum concentrations (Gill et al. 2011) within Cambrian carbonates have also been used to document the extent of ocean anoxia for the SPICE.

During the Furongian Epoch, Laurentia straddled the equator, and the Illinois Basin lay just south of the equator (Kolata 2010; Figure 1). The Illinois Basin existed as the transition zone between the inner detrital belt and the carbonate belt of shallow epeiric seas. The study area appears to have been part of a high-energy intertidal environment that transitioned into a clastic-dominated environment straddling the inner detrital belt landward and the Great American Carbonate Bank seaward (Saltzman et al. 2004; Runkel et al. 2012). As the sea level regressed, this area became a moat-like or deltaic environment that was characterized by a low-energy wave base and low sedimentation rate. Runkel et al. (1998) described this area of the Great American Carbonate Bank as a slowly subsiding shelf in the cratonic interior.

With an estimated duration of 2-4 million years (Myr), marine carbonates deposited during the SPICE showed a positive 3‰ to 5‰ shift in δ^{13} C values (Saltzman et al. 1998). In a recent study, Schiffbauer et al. (2017) documented this event in the carbon isotopes of the Bonneterre and Davis Formations in central Missouri. These locations were lagoonal regions in the Furongian seas. The Bonneterre and Davis Formations in Missouri are time equivalent to the Eau Claire and Franconia Formations examined in this study. Here, we report our investigation of the carbon and oxygen isotope compositions of carbonate and the sulfur isotope composition of carbonate-associated sulfate (CAS) from a core in the Illinois Basin in an effort to infer the geochemical conditions during early dolomitization and thus evaluate the preservation potential and environmental history of the Furongian carbonates of Laurentia within the Illinois Basin.

METHODOLOGY

Sample Location, Collection, and Petrography

In 1959, the Mississippi River Company drilled a borehole and collected core C-8948, a 2.5-inch-diameter core (38°39.81N, 89°46.30W) that penetrated the entire Franconia Formation in Madison County, Illinois. The core was archived at the Illinois State Geological Survey (ISGS; Shaw and Sargent 1989). The Franconia Formation in core C-8948 was logged at depths of 1,403.1 to 1,432.0 m below surface, with a thickness of 29 m.

The study site within the Illinois Basin represents the inner detrital to carbonate shelf environment of these epeiric seas. The Franconia Formation is part of the global Furongian Series and the North American Croixan Series (Palmer 1981; Kolata 2010; Babcock et al. 2015). At the



Figure 1 Modern-day location (top) and paleogeographic location (bottom) of the study area on Laurentia during the Upper Cambrian. Bottom figure modified from Kolata (2010).

study site in Madison County, Illinois, the Franconia Formation is a predominantly carbonate unit that lies unconformably over the Eau Claire Formation (Figure 2). The Eau Claire Formation in Ohio ends near the beginning of the Steptoean Stage (Babcock et al. 2015). Eastward in the Illinois Basin toward the paleoshoreline, the Ironton Sandstone and Galesville Sandstone separate the Eau Claire from the Franconia Formation (Freiburg et al. 2014). These clean quartz sandstone units are absent from the sampled core in this study, which lies on the western edge of the Illinois Basin (Figure 2). In southern

Illinois, the Eau Claire grades into the carbonate-dominated time-equivalent Bonneterre Formation. Thin sections were prepared according to standard petrographic methods. Analyses were made by using plane-polarized light microscopy and cathodoluminescence microscopy. Cathodoluminescence was observed with a Reliotron advanced cathodoluminescence instrument (Relion Industries, Bedford, Massachusetts) mounted on a Nikon Eclipse E400 polarizing microscope (Nikon Instruments Inc., Melville, New York), which was also used for the plane-polarized light microscopy (Figure 3a-f).

Bulk Isotope Analysis

$\delta^{{\scriptscriptstyle 13}}C$ and $\delta^{{\scriptscriptstyle 18}}O$ of Carbonates

Samples for carbonate isotope analysis were taken every 1.5 m except where some footage was missing because of loss during extraction of the core owing to the friable nature of that segment. Samples for sulfate isotope analysis were taken at every 3 m depth in the core (Table 1). Samples FC 1 to FC 5 are carbonate cements in siliciclastic-dominated mineralogy of the upper Franconia. Samples FC 6 to FC 19 are carbonate mineralogies, predominantly dolomite with occasional calcite cements in the lower portion of the core. Care was taken to avoid the calcite cements and sample only the dolomite facies in all samples. The carbon and oxygen isotope compositions of carbonate ($\delta^{13}C_{cO3}$ and $\delta^{18}O_{cO3}$) and the sulfur isotope composition of sulfate ($\delta^{34}S_{SO4}$) of CAS of the Franconia Formation were analyzed. Isotopes are reported in delta notation (δ) in per mille (∞):

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

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.

Approximately 1 to 3 mg of carbonate powder was collected with a 0.5-inch carbide-tipped drill bit and drill. Secondary veins and calcite spar were carefully avoided. The carbonate powder samples were roasted at 380 °C for 1 hour in a muffle furnace to remove any traces of organic carbon. Isotope analyses of carbon and oxygen were performed at the ISGS Geochemistry Laboratory. The carbonate samples were reacted with 100% phosphoric acid (H_aPO₄) at 75 °C by using a Kiel Carbonate single-sample acid bath device (Thermo Fisher Scientific, Waltham, Massachusetts) connected to a Finnigan-MAT 252 isotope ratio mass spectrometer (Thermo Electron Corporation, Waltham, Massachusetts). The National Bureau of Standards (NBS) carbonate standards NBS-18 (carbonatite; $\delta^{13}C = -5.014\%$ Vienna Pee Dee Belemnite [V-PDB]; $\delta^{18}O = -23.2\%$ V-PDB) and NBS-19 (limestone; $\delta^{13}C = 1.95\%$ V-PDB;



Figure 2 Generalized stratigraphic column for core C-8948. The Franconia Formation unconformably overlies the Eau Claire Formation in southwest Illinois. The Franconia Formation in which the SPICE is contained at the site is designated as part of the Sauk III sequence in the Upper Cambrian. The Franconia Formation transitioned from a shallow marine carbonate into a clastic-dominated nearshore environment as sea level lowered (Kolata 2010).

 $\delta^{18}O = -2.20\%$ V-PDB) were used for isotope correction (Friedman et al. 1982). Isotope values of $\delta^{18}O$ and $\delta^{13}C$ of the carbonate were expressed relative to V-PDB with a 2σ internal precision of $\pm 0.04\%$ for carbon and $\pm 0.14\%$ for oxygen. The oxygen isotopes were expressed relative to Vienna Standard Mean Ocean Water (V-SMOW) for the interpretation of source water temperatures via Equation 2:

 $δ^{18}O(V-PDB) = 0.97002$ × $δ^{18}O(V-SMOW) - 29.98,$ (2)

(Coplen et al. 1983; Brand et al. 2014).

Extraction and Isotope Analysis of Carbonate-Associated Sulfate $\delta^{34}S_{so4}$

Approximately 6–7 g of carbonate powder was collected with a 0.5-inch carbidetipped drill bit and drill. Secondary veins, calcite spar, and pyrite deposits were carefully avoided. Carbonate-associated sulfate samples were prepared for isotope analysis of $\delta^{34}S_{S04}$ values at the ISGS. The extraction of CAS from carbonate samples followed the method of Gill et al. (2011). Each powdered sample was placed into a 250-mL beaker with 100 mL of 10% sodium chloride (NaCl) solution made with 18 megaohm centimeters $(M\Omega \cdot cm)$ of water. Samples were covered and allowed to react for 24 hours with occasional stirring. The 10% NaCl rinse removed soluble sulfates, especially those sulfates derived from the oxidation of metal sulfides. The 10% NaCl rinse was carefully decanted, and the powders were rinsed twice with 18 M Ω ·cm of water, carefully decanting each time. The samples were then treated with a 4% sodium hypochlorite (NaOCl) solution, mixed well, and allowed to react for 48 hours with occasional stirring. This treatment removed organically bound sulfur and metastable sulfides from the sample. The quantity of sulfides, specifically pyrite, was not assessed before extraction; therefore, the presence of sulfides must be considered. Any sulfides present could have been oxidized in the following steps. Samples were thoroughly rinsed twice with 18 MQ·cm of water and carefully decanted. Next, a 4 N hydrochloric acid (HCl) solution was slowly added to each

sample, allowing for rapid effervescence. Samples were allowed to digest in acid solution for 1 hour with occasional gentle stirring. The remaining solution was centrifuged and vacuum filtered (using 0.45-µm Millipore filters) to remove any insoluble residue. A 1.2 M barium chloride (BaCl₂) solution was added to each filtered and acidified sample. Samples were allowed to react at room temperature for 3 days to allow for complete barium sulfate (BaSO₄) precipitation from the acidified solution. The BaSO precipitate was separated from the solution via vacuum filtration with 0.45-µm Millipore filters, collected, and allowed to dry. The dried sample was powdered with a mortar and pestle.

The BaSO₄ precipitates were analyzed for $\delta^{34}S_{CAS}$ values. No fractionation was assumed to have occurred between the precipitation or dissolution of BaSO₄ and dissolved sulfate at low temperatures (110-350 °C; Kusakabe and Robinson 1977), and any ions remaining in the aqueous solution were not measured. Isotope analysis was conducted at the Stable Isotope Laboratory at the University of Tennessee, Knoxville. The BaSO (s) power was packed in tin capsules with a divanadium pentaoxide-silicon dioxide $(V_2O_2-SiO_2)$ additive for conversion of the sulfate to sulfur dioxide (SO, g) following the methods of Yanagisawa and Sakai (1983) and Ueda and Krouse (1986). The tin capsules were combusted at high temperature in a helium atmosphere in the presence of excess oxygen by using a Costech ECS 4010 Elemental Analyzer gas chromatograph (Costech Analytical Technologies, Inc., Valencia, California). The gas chromatograph directed the resultant $SO_{a}(g)$ into the continuous-flow Thermo Finnigan Delta Plus isotope ratio mass spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts), where the isotopes were separated and measured. The δ34S values are reported relative to Vienna Canyon Diablo Troilite (V-CDT). Samples were compared with internal and international standards for precision and accuracy. The standard deviation for $\delta^{34}S$ values measured of the isotope standard NBS-127 (BaSO₄; δ^{34} S = 20.3‰ V-CDT; Halas and Szaran 2001) was 0.37% (n = 3) and that for International Atomic Energy Agency standard IAEA-SO-6 (BaSO₄; δ³⁴S = -34.1‰ V-CDT; Halas and Szaran 2001)



Figure 3 Photomicrographs of thin sections from the Franconia Formation at various depths over the 29-m interval showing the stratigraphic progression of dolomite- to siliciclastic-dominated mineralogy: (a) 1,429.5 m, plane-polarized light (PPL); (b) 1,418.2 m, PPL; (c) 1,411.2 m, PPL; (d) 1,411.2 m, cathodoluminescence (CL); (e) 1,409.7 m, PPL; (f) 1,403.1 m, PPL. Photomicrographs (a), (b), (c), and (d) are carbonate-dominated lithologies with increasing siliciclastic content. Increasing quartz grains are especially evident in (d) under CL. Photomicrographs (e) and (f) show the siliciclastic-dominated mineralogy of the Upper Franconia with noted carbonate cements. Scale bar is 200 µm.

					Difference, %	
Sample	Depth, m	$\delta^{13}C_{CO3}$, ‰ (V-PDB)	$\delta^{18}\text{O}_{\text{CO3}}$, ‰ (V-SMOW)	n	δ ³⁴ S _{CAS} , ‰ (V-CDT)	n
FC 1	1,403.1	-2.2 (0.02)	23.0 (0.01)	2	39.7 (10.22)	2
FC 2	1,404.4	-2.4 (0.04)	23.4 (0.06)	2		
FC3	1,406.7	-0.8 (0.06)	24.4 (0.09)	2	40.0 (3.02)	2
FC4	1,408.2	-1.3 (0.02)	24.0 (0.13)	2		
FC 5	1,409.7	-0.5 (0.05)	24.7 (0.06)	2	48.3	1
FC 6	1,411.2	-0.1 (0.03)	24.5 (0.00)	2		
FC 7	1,412.7	0.5 (0.02)	24.3 (0.15)	2	37.3 (1.76)	2
FC 8	1,414.3	1.1 (0.01)	24.7 (0.10)	2		
FC 9	1,415.8	2.1 (0.01)	24.4 (0.04)	2	43.4 (4.39)	2
FC 10	1,417.3	2.4 (0.01)	24.1 (0.09)	2		
FC 11	1,418.2	4.9 (0.02)	24.4 (0.07)	2	48.6 (3.93)	2
FC 12	1,418.8	3.4 (0.01)	24.4 (0.08)	2		
FC 13	1,420.4	4.1 (0.00)	24.4 (0.07)	2	41.6 (2.21)	2
FC PA	1,421.0	4.7 (0.03)	25.3 (0.29)	3		
FC 14	1,425.9	4.4 (0.05)	24.3 (0.00)	2		
FC 15	1,426.5	3.2 (0.02)	23.9 (0.09)	2	41.0 (1.36)	2
FC 16	1,428.3	2.4 (0.00)	23.7 (0.01)	2		
FC 17	1,429.5	0.9 (0.03)	24.1 (0.10)	2	42.2 (2.06)	2
FC 18	1,431.0	0.6 (0.01)	24.1 (0.02)	2		
FC 19	1,432.0	0.0 (0.01)	24.2 (0.10)	2		

Table 1 Isotope analyses for $\delta^{13}C_{CO3}$ and $\delta^{18}O_{CO3}$ values of carbonate and $\delta^{34}S_{CAS}$ values of carbonate-associated sulfate (CAS) in the Franconia Formation¹

¹Values in parentheses indicate standard error. V-PDB, Vienna Pee Dee Belemnite; V-SMOW, Vienna Standard Mean Ocean Water; V-CDT, Vienna Canyon Diablo Troilite.

was 0.53‰ (n = 3). Individual samples were run in duplicate, and percentage differences were noted for δ^{34} S_{SO4} values (Table 1, Figure 4c).

RESULTS

Mineralogy, Petrography, and Environment

The Franconia Formation transitioned from a shallow marine high-energy environment in the lower sections of the core toward a deltaic-influenced environment during a marine regression sequence (Freiburg et al. 2014). Thin sections of the core shown in Figure 3 illustrate these environmental changes. The lower Franconia Formation was predominantly coarsely crystalline, dolomitized oolitic and fossiliferous carbonate with traces of pyrite (Figure 3a). The ooids and fossil fragments were largely composed of a single generation of dolomite and had pore spaces filled with multiple generations of euhedral dolomite crystals.

Clay-rich stylolites, which appeared to have formed before dolomitization, were prominent. Fossil fragments, possibly brachiopod fragments, were visible in hand specimens. Quartz, feldspar, and glauconite were notably absent from this lower section. The middle Franconia Formation (Figure 3b) was characterized by coarse and fine crystalline dolomite, with notable quartz and feldspar grain contributions. Glauconite pellets were common, with evidence of bioturbation in the finer grained dolomite matrix. The clastic mineralogical content increased with shallowing core depth. At 1,411.2 m depth (Figure 3c, 3d), the mineralogy was a sandy dolomite with abundant detrital feldspar and quartz throughout. Cathodoluminescence highlighted the abundant detrital quartz and feldspar in a dolomitic matrix (Figure 3d). Glauconite pellets were sparse. Coarse and often euhedral dolomite exhibited at least two prominent growth generations, with the earlier generation dominating. The first generation had a bright pink to

purple color, whereas the second and less abundant generation showed a darker quenched luminescence. Dolomite cement constituted most of the matrix, and minor clay minerals exhibited a dull green luminescence. At 1,409.7 m depth (Figure 3e), the increasing siliciclastic content resulted in a siltstone to mudstone lithology with abundant muscovite, quartz, and feldspar grains. Glauconite pellets were common. Dolomite cements were present throughout. Near the top of the Franconia Formation, at 1,403.1 m depth (Figure 3f), the lithology was dominated by fine-grained sandstone composed of quartz and feldspar grains with minor carbonate cements. Interbedded finer grained silty layers contained muscovite. Both dolomite and calcite cements were present throughout the sandstone matrix. Calcite cements appeared to be more commonly associated with pyrite cements that were concentrated along burrows. Glauconite pellets were common throughout.



Figure 4 Chemostratigraphic profiles of (a) $\delta^{13}C_{CO3}$, (b) $\delta^{18}O_{CO3}$, and (c) $\delta^{34}S_{CAS}$ of the carbonates in the Franconia Formation. The SPICE event is evident in the $\delta^{13}C$ trend enriching from 0‰ at the base of the Franconia to 4.9‰ at the peak of the SPICE and returning to <0‰ in the siliciclastic-dominated mineralogy of the Upper Franconia. The SPICE is supported by $\delta^{34}S_{CAS}$ values showing a significant $\delta^{34}S$ enrichment during the Upper Cambrian, likely associated with intense bacterial sulfate reduction activity. No significant correlation exists between $\delta^{13}C$ and $\delta^{18}O$ of the carbonate, providing partial evidence that dolomitization did not replace the isotopic signatures of the Cambrian paleoenvironment. V-PDB, Vienna Pee Dee Belemnite; V-SMOW, Vienna Standard Mean Ocean Water; V-CDT, Vienna Canyon Diablo Troilite.

Isotope Geochemistry

The $\delta^{13}C_{CO3}$ isotope system exhibited an enrichment trend toward heavier values near the midsection of the Franconia Formation (Table 1, Figure 4a). At the base of the Franconia Formation (1,432.0 m), the $\delta^{13}C_{CO3}$ values were near 0‰. The carbon isotope values increased sequentially to a maximum of 4.9‰ at 1,418.2 m depth, after which the $\delta^{\scriptscriptstyle 13}C_{_{CO3}}$ values decreased sequentially to $\leq -2\%$ at the top of the formation at 1,403.1 m depth. The isotopic range of $\delta^{13}C_{CO3}$ values over the thickness of the Franconia Formation was 7.7‰. The $\delta^{34}S_{_{CAS}}$ values showed the greatest enrichment, >48‰, at depths of 1,418.2 and 1,409.7 m (Figure 4c). The most isotopically depleted value, 37‰, occurred at 1,412.7 m. The isotopic range of $\delta^{34}S_{_{CAS}}$ values was approximately 11‰.

The $\delta^{18}C_{\rm CO3}$ (V-SMOW) values at the base of the formation were 24.2‰, with a maximum value of 25.3‰ at 1,421.0 m depth. The $\delta^{18}C_{\rm CO3}$ values showed a minimum of 23.0‰ at the top of the formation at 1,403.1 m depth. The isotopic range of $\delta^{18}C_{\rm CO3}$ values over the length of the Franconia Formation was 2.3‰ (Table 1, Figure 4b).

DISCUSSION

The study area lay on the edge of the Illinois Basin and was part of a shallow epeiric sea in the Furongian Epoch near the paleoshoreline of Laurentia. The lower part of the Franconia Formation is a fairly pristine oolitic limestone. Over time, as the global sea level dropped, silica content increased. Deposition at the top of the Franconia Formation was dominated by carbonate-cemented quartz sandstone. The presence of glauconite suggested a shallow marine environment (Hegab et al. 2016, and references therein). The presence of abundant glauconite may also indicate a low rate of sedimentation in a weakly reducing environment common during a transgression of sea level (McRae 1972; Huggett and Gale 1997). The entire Franconia Formation at this location is 29 m thick. Although the scattered pyrite suggested periods of anoxic conditions, the presence of fossil fragments and bioturbation suggested this environment was generally well oxygenated, and pyrite may be mostly associated with confined pore waters in sediments or brief episodes of anoxia. Saltzman et al. (2004) also reported abundant glauconite in carbonate sediments that recorded the Sauk II-Sauk III transition and the SPICE in Iowa, which was described as a moat environment (Runkel et al. 2012). This description was similar to the texture and mineralogy observed in the Franconia Formation core C-8948.

During diagenesis, the original limestone was dolomitized. Despite dolomitization, the $\delta^{\scriptscriptstyle 13}C_{_{CO3}}$ values of the original carbonate appear to have been well preserved. Indeed, the δ^{13} C values of nearby dolomites of the Bonneterre and Davis Formations were also preserved and exhibited the positive isotope excursion that documented the SPICE (Schiffbauer et al. 2017). The present study may be the first record of the SPICE in the Illinois Basin, and it possibly corroborates many other isotope excursions associated with the SPICE, such as in Missouri (Gill et al. 2011; Schiffbauer et al. 2017), Iowa, Utah, Nevada (Saltzman et al. 1998, 2004), Tennessee, Virginia (Gerhardt and Gill 2016), and Newfoundland (Hurtgen et al. 2009) in Laurentia as well as global localities (e.g., Saltzman et al. 2000; Lindsay et al. 2005; Wotte and Strauss 2015; Hammer and Svensen 2017; Liu et al. 2017).

The timing, environment, and synchronicity of the SPICE varied somewhat across different depositional basins (e.g., Cowan et al. 2005: Gill et al. 2007. 2011: Elrick et al. 2011; Schiffbauer et al. 2017). The δ^{13} C depth profile exhibited in the present study is contained within the carbonate facies of the Franconia. The Franconia Formation consists of the sediments associated with the inner detrital belt of the Iapetus Ocean surrounding Laurentia. This area appears to have experienced the effects of the SPICE after Schiffbauer et al. (2017) documented this event in nearby southeast Missouri in the Bonneterre and Davis Formations and Saltzman et al. (1998, 2004) and Gerhardt and Gill (2016) documented localities in Laurentia. The Eau Claire Formation in this study area is time equivalent to the Bonneterre Formation, and the Davis Formation is time equivalent to the Franconia Formation (Willman et al. 1975; Figure 2). The present study is coincident with the conclusions of Schiffbauer et al. (2017), who suggested that the surrounding equatorial carbonate environments were affected by an encroachment of offshore-sourced, 13C-enriched waters that were likely anoxic or euxinic. Lee and Riding (2018) examined marine oxygenation during the early Paleozoic and believed anoxic water encroached onto carbonate platforms during the SPICE, straining shallow-water communities. Several others (e.g., Palmer 1984; Saltzman et al. 2000, 2015; Gill et al. 2011) also reached this conclusion. These low-oxygen conditions in shelf waters during the SPICE were supported by evidence of (1) coeval positive δ^{34} S excursions in marine sulfate (Gill et al. 2007, 2011; Hurtgen et al. 2009), (2) decreased molybdenum enrichment (Gill et al. 2011), and (3) negative δ^{238} U excursions (Dahl et al. 2014).

As Schiffbauer et al. (2017) suggested, the preservation of the SPICE was likely a function of facies and carbonate-platform geometry exhibiting local controls on carbon productivity in response to changes in global ocean chemistry. In the aforementioned study, the shallow-water cores showed the onset of the SPICE occurring several meters below the Bonneterre (Sauk II)-Davis (Sauk III) boundary and peaking several meters above this stratigraphic boundary. In the present study, the SPICE appeared to be contained within the Franconia Formation after the Sauk III boundary. The base of the Franconia Formation exhibited δ^{13} C values around 0‰, and then sequentially enriched to values of 4.9‰ at midsection before decreasing to $\leq -2\% \delta^{13}$ C values at the top of the Franconia Formation. The ¹³C-depleted values at the top of the Franconia Formation may partly reflect greater deltaic and terrestrial influences or possibly organic carbon reoxidation because of restricted circulation within the area. The abundance of glauconite suggests a shallow marine environment with slow rates of deposition.

Dolomitization and Diagenesis

Diagenesis can alter the isotope composition of carbonates. Several studies have attempted to suggest limited alteration of an isotope system by diagenesis based on evidence from sources such as petrography; cathodoluminescence; and Mn/Sr, Mg/Ca, $\delta^{18}O_{CO3}$, and $^{87}Rb/^{86}Sr$ values (e.g., Kaufman et al. 1993; Kaufman and Knoll 1995; Wotte and Strauss 2015). Although these criteria are site specific, we investigated the possibility of minimal alteration to the carbon and oxygen isotopes of these dolomites. The effects of diagenesis on carbonates of the Franconia Formation appeared to have occurred under low-temperature conditions. If the $\delta^{\rm 18}O_{\rm CO3}$ values were greater than -10% (V-PDB), some studies have considered this one indication of a potentially less altered oxygen isotope signal within the carbonate matrix (Kaufman et al. 1993; Wotte and Strauss 2015). The $\delta^{18}O_{CO3}$ values for the Franconia Formation ranged from -7.6‰ to -5.4‰ (V-PDB) or 23.0‰ to 25.3‰ (V-SMOW; Table 1, Figure 4b). Although the original oxygen isotope signal was probably reset during diagenesis, the dolomitizing fluids were likely low-temperature groundwater or seawater that did not significantly alter the carbon isotope values. The relationship between the $\delta^{18}O_{_{CO3}}$ and $\delta^{13}O_{_{CO3}}$ values of the Franconia Formation carbonates showed a weak correlation (r^2 of 0.25), possibly suggesting only a weak effect on the $\delta^{\rm \scriptscriptstyle 13}O_{_{\rm CO3}}$ values by postdepositional alteration.

The dolomite-water isotope equilibrium equation determined by Horita (2014) was utilized to estimate fluid temperatures during dolomitization:

$$\begin{array}{l} 10^{3} \ln \alpha_{\text{(dolomite-water)}} = 3.14 \\ \times (10^{6}/T^{2}) - 3.14, \end{array}$$
(3)

where α is the fractionation factor between dolomite and water for oxygen and T is temperature in Kelvin. If the dominant dolomitizing fluid had an isotopic range of 0% to -3% (V-SMOW) similar to Cambrian seawater (Lohmann and Walker 1989: Came et al. 2007: Jaffrés et al. 2007), then a temperature range of 66 to 48 °C would be calculated for dolomitizing fluids (Table 2). It is important to note that although the formation of dolomite at temperatures <100 °C is theoretically possible through extrapolation based on laboratory experiments, dolomite has not been successfully synthesized at these low temperatures in laboratory experiments (Gregg et al. 2015, and references therein).

Preservation of Carbonate-Associated Sulfate

A previous study by Gill et al. (2008) demonstrated the robustness of sulfate isotope values in CAS for representing original coeval seawater sulfate despite the influence of meteoric water diagenesis. Nevertheless, post-diagenetic whole-isotopic replacement of the CAS within the carbonate lattice does occur. The Franconia and Eau Claire Formations in core C-8948 are separated by an erosional unconformity. Labotka et al. (2016) previously reported sulfate isotope values of CAS within the Eau Claire Formation from core C-8948 and discovered that sulfate isotopes had been replaced with ore signatures from the Late Pennsylvanian-Early Permian ore pulses of Mississippi Valley-type fluids. Sulfate ³⁴S_{SO4} values of Eau Claire CAS were between 9‰ and 21‰. These ore fluid signatures were notably different from typical Cambrian sulfate seawater $\delta^{34}S_{SO4}$ values of >30‰ (Kampschulte and Strauss 2004; Hurtgen et al. 2009; Gill et al. 2011). The results of the present investigation showed CAS values measuring >30‰ δ^{34} S (Figure 4c), which suggested that these ore fluids did not affect the isotope composition of the CAS of the Franconia Formation carbonates. The extent of the influences from the Mississippi Valley-type ore fluids associated with the Ouachita Orogeny appeared to be restricted to the end of the Eau Claire Formation depositional sequence

Temperature, °C	Temperature, K	$10^3 \ln lpha_{(dolomite-water)}$	Estimated sea water $\delta^{\rm 18}{\rm O}$ value, ‰ (V-SMOW)
70	343.15	23.53	0.67
68	341.15	23.84	0.36
66	339.15	24.16	0.04
64	337.15	24.48	-0.28
62	335.15	24.81	-0.61
60	333.15	25.15	-0.95
58	331.15	25.49	-1.29
56	329.15	25.84	-1.64
54	327.15	26.20	-2.00
52	325.15	26.56	-2.36
50	323.15	26.93	-2.73
48	321.15	27.30	-3.10

Table 2 Calculated dolomitization temperatures based on potential $\delta^{\rm 18}O$ values for the Cambrian seas^1

¹These estimates are based on the equation by Horita (2014) for oxygen isotope equilibrium

fractionation between dolomite and water, $10^3 \ln \alpha_{(dolomite-water)} = 3.14 \times (10^6/T^2) - 3.14$ (where *T* is in Kelvin). Average $\delta^{18}O_{V-SMOW}$ value for the Franconia Formation carbonate is 24.2‰ (0.49). Values in parentheses indicate standard error. V-SMOW, Vienna Standard Mean Ocean Water.

for the central Illinois Basin (Labotka et al. 2016).

The Cambrian Steptoean Positive Carbon Isotope Excursion

The timing of the SPICE may have varied across depositional basins. The Franconia Formation within the Sauk III sequence appeared to track the regression of sea level and the occurrence of the SPICE. The base of the Franconia Formation was a coarsely crystalline dolomite with distinct neomorphosed ooids and fossils and no evidence of detrital grains or glauconite. This higher energy marine environment transitioned into a lower energy deltaic-influenced environment with the influx of quartz sand and feldspar grains. This clastic influence marked the onset of the regression at approximately 1,418 m. The quartz sandstone composing the top of the Franconia Formation suggested a significantly lower sea level associated with an advancing shoreline. This carbonate-to-siliciclastic transition marked the Sauk II and Sauk III sequence boundary in cores from an Upper Mississippi Valley site in Iowa, where the shallowing seas led to siliciclastic deposition (Runkel et al. 1998; Saltzman et al. 2004). In nearby Missouri, the SPICE crossed the Bonneterre-Davis boundary, which marked the Sauk II-Sauk III transition at this location (Schiffbauer et al. 2017). In

this study, the Sauk II-Sauk III transition occurred at the erosional unconformity between the Eau Claire Formation and stratigraphically overlying Franconia Formation (Kolata 2010). Here, the SPICE was contained within the Franconia Formation and therefore after the previously defined Sauk III boundary.

The small thickness of less than 30 m of sediment and abundant glauconite above the basal dolomitized oolitic and fossiliferous limestone possibly suggests a slow rate of deposition of the Franconia Formation at C-8948. In central Illinois, the Franconia Formation spanned hundreds of meters in thickness (Kolata 2010). The progression from a back-reef environment toward a moat-like environment is evidenced by the slow rate of deposition (Saltzman et al. 2004: Runkel et al. 2012) and abundant glauconite, pyrite, and mottling likely caused by burrowing activity. In a low-energy marine environment with slow rates of accumulation, an oxygenated environment influenced by pockets of anoxic conditions and possibly euxinic conditions is plausible.

The carbonate isotope values showed a distinct trend toward $\delta^{13}C$ enrichment and subsequent depletion characteristically associated with the SPICE. On the basis of the $\delta^{13}C_{\rm co3}$ values in the Franconia core, the peak of the SPICE appeared

to occur between depths of 1,425.9 and 1,420.4 m (Table 1, Figure 4a). The base of the Franconia Formation exhibited $\delta^{13}C_{co3}$ values of 0‰ and subsequently trended to 4.9‰ before trending back to lower values of -2.2% at the top of the formation. This was the first record of the SPICE event in the Illinois Basin. Despite extensive dolomitization, the carbonate isotope stratigraphy appeared to have survived, with original δ^{13} C values capturing this isotope excursion. The preservation of original $\delta^{\scriptscriptstyle 18}O_{\scriptscriptstyle CO3}$ was considerably less definitive, but the oxygen isotopes did suggest a low temperature for the dolomitizing fluids (Table 1, Figure 4b).

Sulfur isotopes of CAS from the Franconia Formation carbonates were comparable with δ^{34} S values for the Furongian reported in the literature (e.g., Hough et al. 2006; Gill et al. 2007, 2011; Wotte and Strauss 2015). No direct evidence was observed of sulfides oxidizing to sulfates during the extraction process; nevertheless, this possibility cannot be ruled out. The average $\delta^{34}S_{_{CAS}}$ value for the Franconia Formation was 43‰, with $\delta^{34}S_{_{CAS}}$ values up to 48‰ (Table 1, Figure 4c). Pulses of rapid burial of organic matter may have triggered extensive microbial sulfate reduction activity and resulted in the observed enriched sulfate $\delta^{34}S_{_{CAS}}$ values. Because the sulfate concentrations in the Furongian seas

were suspected to be low, excursions of $\delta^{34}S_{\text{CAS}}$ values influenced by microbial sulfate reduction activity may likely have correlated with the amount of organic carbon produced and buried (Hurtgen et al. 2009). Despite this likelihood, distinct correlations between carbon and CAS isotopes were not observed. The absence of a definitive sulfur isotope trend may have indicated some degree of diagenetic alteration to the original seawater sulfate signal.

CONCLUSIONS

The Franconia Formation in the western Illinois Basin appeared to capture the SPICE and is the first documentation of this event in the Illinois Basin. This section preserved a well-defined $\delta^{\scriptscriptstyle 13}C$ stratigraphic record, with $\delta^{\rm 13}C_{_{CO3}}$ values exhibiting an enrichment trend beginning at 0‰, peaking at 4.9‰, and returning to -2.2% at the end of the Franconia Formation. Episodic pulses of anoxic or euxinic deep marine waters, or both, encroaching onto shelf waters, as suggested by several previous studies, was a probable cause for this positive $\delta^{13}C_{co3}$ excursion observed in the Franconia carbonates. The timing of the SPICE in the Franconia Formation appeared to be different from that in other localities, with the carbonate excursion being contained within the Sauk III sequence. The timing of the SPICE may be more a function of local conditions and carbonate platform geometry responding to global signals. As such, the timing and impact of the SPICE in various locations likely varied slightly.

Dolomite-water equilibrium isotope equations estimated fluid temperatures of 66 to 48 °C during dolomitization of these carbonates. Minimal isotope effects attributable to dolomitization of these carbonates emphasized the potential for paleoenvironment preservation in these ancient carbonates. Sulfur isotopes within the carbonate lattice also appeared to have survived dolomitization to a great extent, with values ranging from 37‰ to 48‰. The $\delta^{34}S_{CAS}$ values of carbonates within the Franconia Formation showed no correlation with carbon isotopes but did exhibit the 34S-enriched values observed during the Furongian. Nevertheless, these CAS isotope values did not capture direct evidence of the SPICE.

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