



A sulfate conundrum: Dissolved sulfates of deep-saline brines and carbonate-associated sulfates

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Abstract

Sulfates in deeply circulating brines and carbonate-associated sulfates (CAS) within sedimentary units of the Cambrian strata in the Illinois Basin record a complex history. Dissolved sulfate within the Mt. Simon Sandstone brines exhibits average $\delta^{34}\text{S}_{\text{SO}_4}$ values of 35.4‰ and $\delta^{18}\text{O}_{\text{SO}_4}$ values of 14.6‰ and appears to be related to Cambrian seawater sulfate, either original seawater or sourced from evaporite deposits such as those in the Michigan Basin. Theoretical and empirical relationships based on stable oxygen isotope fractionation suggest that sulfate within the lower depths of the Mt. Simon brines has experienced a long period of isolation, possibly several tens of millions of years. Comparison with brines from other stratigraphic units shows the Mt. Simon brines are geochemically unique. Dissolved sulfate from brines within the Ironton-Galesville Sandstone averages 22.7‰ for $\delta^{34}\text{S}_{\text{SO}_4}$ values and 13.0‰ for $\delta^{18}\text{O}_{\text{SO}_4}$ values. The Ironton-Galesville brine has mixed with younger groundwater, possibly of Ordovician to Devonian age and younger. The Eau Claire Formation lies between the Mt. Simon and Ironton-Galesville Sandstones. The carbonate units of the Eau Claire and stratigraphically equivalent Bonnetterre Formation contain CAS that appears isotopically related to the Late Pennsylvanian-Early Permian Mississippi Valley-type ore pulses that deposited large sulfide minerals in the Viburnum Trend/Old Lead Belt ore districts. The $\delta^{34}\text{S}_{\text{CAS}}$ values range from 21.3‰ to 9.3‰, and $\delta^{18}\text{O}_{\text{CAS}}$ values range from +1.4‰ to -2.6‰ and show a strong covariance ($R^2 = 0.94$). The largely wholesale replacement of Cambrian seawater sulfate signatures in these dolomites does not appear to have affected the sulfate signatures in the Mt. Simon brines even though these sulfide deposits are found in the stratigraphically equivalent Lamotte Sandstone to the southwest. On the basis of this and previous studies, greater fluid densities of the Mt. Simon brines may have prevented the less dense Mississippi Valley-type fluids from interacting with these deeply circulating brines. Progressive *in situ* quartz cementation that occurred in the Mt. Simon Sandstone contemporaneous to the ore pulses may also have precluded fluid migration. The Mt. Simon brines appear to be a mixture of evaporated connate Cambrian seawater, recirculating deep-seated crystalline basement brines, and meteoric water.

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1. INTRODUCTION

The evolution of the Cambrian seas witnessed a distinctive time in Earth history. Seawater sulfate concentrations

were low, ~3.5 times less concentrated than modern seawater (Brennan et al., 2004). Nevertheless, the estimated $\delta^{34}\text{S}$ values of Cambrian seawater sulfate are some of the most enriched in Phanerozoic history, having general values of +30‰ and extreme values reported as +50‰ (e.g., Claypool et al., 1980; Kampschulte and Strauss, 2004; Schröder et al., 2004; Hough et al., 2006; Gill et al., 2007). Episodes of increased pyrite burial, widespread ocean anoxia, and influences of bacterial sulfate reduction

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are thought to have played the main roles in seawater sulfur evolution through the Cambrian (e.g., Hough et al., 2006; Algeo et al., 2015). Phanerozoic seawater sulfate isotope values, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$, have been estimated from evaporite deposits and carbonate-associated sulfates (CAS) with significant success (e.g., Claypool et al., 1980; Kampschulte and Strauss, 2004). In this study, we sought to determine whether the complicated history of Cambrian seawater sulfate is preserved within and could be unraveled from deep-seated Cambrian brines.

The Mt. Simon Sandstone is a unique Cambrian environment that hosts deep-saline brines that are geochemically distinct from surrounding intrabasinal brines and extrabasinal brines. Suspected sources for these Cambrian-hosted brines are original Cambrian seawater, meteoric water, and deep-seated circulating groundwater (Panno et al., 2013; Labotka et al., 2015). Understanding the geochemical evolution of brines provides essential insights into numerous geological processes, such as water–rock interaction and groundwater chemistry and movement. More recently, deep-saline brines have been investigated for their suitability as storage reservoirs for carbon sequestration (e.g., Locke et al., 2013). Isotopes of dissolved sulfate offer direct, critical information about the formational and evolutionary history of fossil brines, including their origin, seawater components, mixing or dilution potential, sulfide oxidation and sulfate reduction, and microbial influence (e.g., Kampschulte and Strauss, 2004; Gill et al., 2011; Rennie and Turchyn, 2014).

This investigation utilizes the isotopes of sulfur and oxygen in dissolved sulfate from deep-seated brines of the Cambrian-aged Mt. Simon and Ironton-Galesville Sandstones in addition to CAS from the Cambrian-aged Eau Claire Formation and stratigraphically equivalent Bonneterre Formation from the midcontinent of North America. No sulfate deposits are documented in the Mt. Simon Sandstone. The Eau Claire Formation separates the younger Ironton-Galesville Sandstone from the underlying Mt. Simon Sandstone. The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of CAS from the carbonate units and evaporite deposits of the Eau Claire and Bonneterre Formations may represent a sulfate source for the Mt. Simon and Ironton-Galesville brines. During the Late Pennsylvanian and Early Permian, pulses of Mississippi Valley-type (MVT) ore fluids were emplaced throughout Middle Cambrian and Lower Ordovician carbonate rocks in North America (Gregg and Shelton, 2012). Evidence of these MVT ore fluids have been observed in the Lamotte Sandstone of Missouri, which is stratigraphically equivalent to the Mt. Simon Sandstone. These ore sulfide deposits exhibit a range of $\delta^{34}\text{S}$ values distinct from Cambrian seawater sulfate values. Analysis of the sulfate isotopes from the Mt. Simon and Ironton-Galesville brines and the CAS of the Cambrian carbonate units of the Eau Claire and Bonneterre Formations will help determine the potential sources of sulfate in these Cambrian sandstone-hosted brines. This investigation explores the possible origins and preservation potential of dissolved sulfate, CAS, and evaporites in the Cambrian environment and the implications for environmental reconstruction during the Cambrian.

2. GEOLOGICAL ENVIRONMENT

2.1. General overview

Initial groundwater sampling for the deep-seated brines began with the Illinois Basin–Decatur Project (IBDP). The IBDP is part of a large carbon sequestration research effort conducted by the Illinois State Geological Survey as the lead agency with the Midwest Geological Sequestration Consortium. Efforts are funded through the U.S. Department of Energy Carbon Storage Program. A deep borehole (VW1) was drilled in 2009 in Decatur, Illinois (39°50.1' N; 89°51.5' W; Fig. 1), to a depth of 2155 m, penetrating the Mt. Simon Sandstone in the Illinois Basin, which is ~457 m thick at this location. The thickest section of the Mt. Simon in the Illinois Basin lies northwest of the IBDP site and is ~792 m in thickness.

The Mt. Simon Sandstone, Eau Claire Formation, Bonneterre Formation, and Ironton-Galesville Sandstone are all Cambrian strata that are part of the Sauk Sequence. This sedimentary sequence in Laurentia covers Precambrian to Lower Ordovician strata deposited ~543 to 490 million years ago (Kolata, 2010; Figs. 1 and 2). Sauk II,

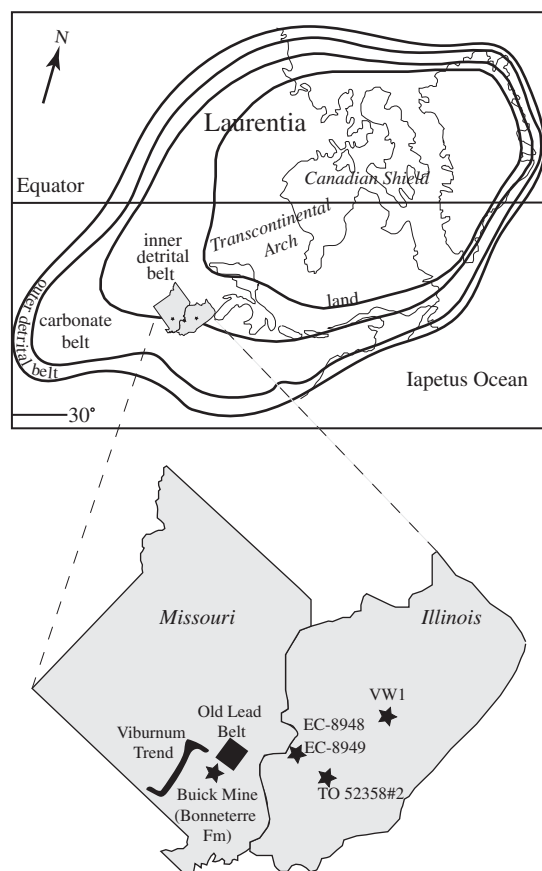


Fig. 1. Location of VW1 and Eau Claire and Bonneterre Formation dolomite samples (stars) and the Old Lead Belt and Viburnum Trend ore deposits in relation to the depositional environment of the Illinois Basin in Laurentia during the Late Cambrian.

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