Evolution of quartz cementation during burial of the Cambrian Mount Simon Sandstone, Illinois Basin: In situ microanalysis of $\delta^{18}O$

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ABSTRACT

The thermal, mechanical, and chemical evolution of a sedimentary basin exerts important controls on porosity and permeability of reservoir rocks. Oxygen isotope ratios of individual diagenetic cements record evidence of this history, but cannot be analyzed accurately by conventional techniques. Recent improvements for in situ analysis by ion microprobe provide high precision and accuracy at a scale of 5–10 m. In combination with cathodoluminescence imaging, in situ analysis of $\delta^{18}O$ (quartz) from the Cambrian Mount Simon Sandstone in the Illinois Basin (USA) reveals gradients within single overgrowths of as much as 7.7‰/50 m. While the inner portions of overgrowths remain approximately constant in $\delta^{18}O$ across the basin, the $\delta^{18}O$ of the rim becomes lower with depth. These data suggest that overgrowths formed during burial and heating, possibly with minimal changes in $\delta^{18}O$ of pore fluids. If $\delta^{18}O(H_2O)$ = –3‰, the highest temperature calculated for the rim of an overgrowth is 107 C at a paleodepth of 3.5 km. The variability both in average $\delta^{18}O$ of overgrowths and patterns from individual overgrowths corresponds with a geotherm of 30 C/km, and there is no evidence of quartz precipitation from higher temperature hydrothermal fluids.

INTRODUCTION

Diagenetic cements and compaction are the most important factors controlling porosity and permeability of a sedimentary rock. Thus, the compositions of diagenetic cements provide the opportunity to understand the thermal and fluid evolution of a basin. Stable isotope ratios preserve evidence of fluid-rock interactions, which can have a pronounced effect on the cementation of a rock. The oxygen isotope fractionation between quartz and water is large (~30‰ at 50 °C) and has been used to calculate temperatures of diagenesis and fluid compositions (e.g., Longstaffe and Ayalon, 1987; Hervig et al., 1995; Graham et al., 1996; Williams et al., 1997; Lyon et al., 2000; Macaulay et al., 2000; Marchand et al., 2002; Kelly et al., 2007; Harwood et al., 2009). If analyzed at an appropriate scale, the spatial and temporal distribution of isotopically distinct cements can be used to investigate whether the history of a basin was dominated by varying fluid composition or by burial heating, but most data have been measured at scales of millimeters to centimeters. Only one in situ study (Chen et al., 2001) of oxygen isotope ratios of diagenetic quartz and/or K-feldspar has investigated the fluid history of the Cambrian Mount Simon Sandstone (Illinois Basin, United States). Chen et al. (2001) made analyses of $\delta^{18}O$ in overgrowths from 11 samples of the Mount Simon Sandstone in and around the Illinois Basin using a 20 m spot size and precision of ±2‰ (2 standard deviations, SD); they detected a gradient in $\delta^{18}O$ from south to north over 700 km and concluded that individual overgrowths are homogeneous in $\delta^{18}O$ and that changing pore-fluid composition at constant temperature was responsible for the variability of overgrowth $\delta^{18}O$ from sample to sample. In this study we employ new instrumentation and procedures that yield significant improvements in accuracy, precision, and spot size (Kelly et al., 2007; Kita et al., 2009; Valley and Kita, 2009) and report gradients of $\delta^{18}O$ within single quartz overgrowths that could not be measured previously. We evaluate the conclusions of Chen et al. (2001) and the competing hypothesis that the observed trends in $\delta^{18}O$ were caused by variable temperatures during burial.

GEOLOGICAL BACKGROUND

The Mount Simon Sandstone is the basal Cambrian sandstone in much of Illinois and Wisconsin (United States) and unconformably overlies the Precambrian basement except in paleotopographic highs (Templeton, 1951). The Mount Simon Sandstone is buried to a maximum depth of ~4250 m in southern Illinois (Fig. 1), ranges in thickness in the Illinois Basin from <91 m to 792 m (Hoholick et al., 1984), and crops out in central and western Wisconsin. Estimates based on vitrinite reflectance, fluid inclusion data, and clay compaction suggest that the Illinois Basin was buried at most 1.2 km deeper than current depths (Altschaeffl and Harrison, 1959; Hoholick et al., 1984; Rowan et al., 2002).

The 19 samples in this study come from 3 cores in Illinois (Fig. 1) and were selected based on variation in depth (394–2581 m) and geographic distribution (430 km north-south). Most of the rocks are quartz arenites; some deep samples are subarkoses as K-feldspar content generally increases with depth. The dominant cements are quartz and K-feldspar overgrowths, with minor later cements (Hoholick et al., 1984). Evidence of detrital quartz pressure solution is observed in all rocks of this study regardless of depth.

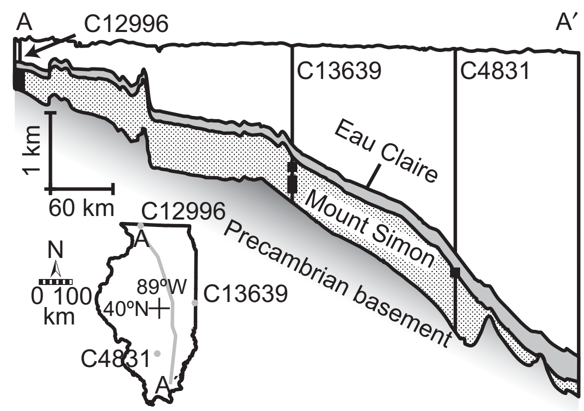

Figure 1. Cross section of Illinois Basin (United States). Vertical lines represent core locations, squares represent depths of samples analyzed. Shaded unit is Eau Claire Formation, which confines Mount Simon aquifer. Vertical exaggeration is 73×. Inset shows locations of core and cross section line (gray) in Illinois. Modified from Kolata (2005).

METHODS

Sample Preparation and Characterization

Samples were cast in 25-mm-diameter epoxy rounds with the quartz standard UWQ-1 (Kelly et al., 2007), and imaged and analyzed at the University of Wisconsin–Madison (UW-Madison) using a scanning electron microscope (SEM) with secondary electron (SE), backscattered electron (BSE), cathodoluminescence (CL), and energy dispersive spectrometry detectors, as well as optical microscopes. Overgrowth quartz cements (OQ) are commonly indistinguishable from the detrital quartz grains (DQ) by optical or SE microscopy, but are distinctly different by CL (Fig. 2).

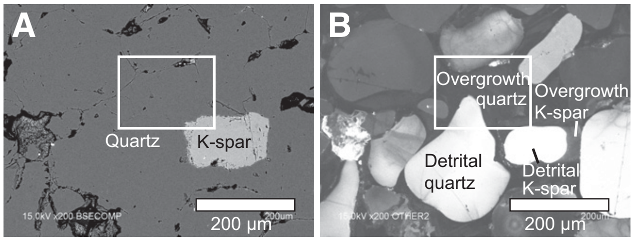

Figure 2. Scanning electron microscope images of Mount Simon Sandstone (09IL-41, 1982 m). A: Backscattered electron microscope image. Quartz and K-feldspar are clearly distinguishable. White rectangle represents area shown in Figure 4. B: Cathodoluminescence (CL) image of same area. Detrital and diagenetic minerals can be distinguished by CL response. This image also shows diagenetic and detrital K-feldspar.

Areas for isotope analysis were selected based on size and abundance of overgrowths (see the GSA Data Repository[1]).

Isotope Analysis

In situ oxygen isotope analyses were performed using a CAMECA IMS-1280 ion microprobe at WiscSIMS (Wisconsin Secondary Ion Mass Spectrometer Laboratory), UW-Madison (Kita et al., 2009; Valley and Kita, 2009). Data were collected from spots ~15 μm and ~5 μm in diameter. During each session, 4 analyses of the UWQ-1 standard were made before and after each set of 10–15 sample measurements. Bracketing standards are used to calculate the instrumental bias in order to correct measured $\delta^{18}O$ values to the Vienna standard mean ocean water scale (Kita et al., 2009), as well as to evaluate the external reproducibility of the measurements. The spot-to-spot reproducibility or external precision of each set of bracketing standards averaged 0.26‰ (2 SD) for 15 μm spots and 0.66‰ (2 SD) for 5 μm spots. Detailed descriptions of the analytical conditions and the instrument setup have been published previously (Kelly et al., 2007; Page et al., 2007; Kita et al., 2009; Valley and Kita, 2009; see the Data Repository).

Ion microprobe spots were targeted based on CL, SE, and BSE images (Fig. 2) taken before isotope analyses. After analysis, each spot was evaluated by SEM to determine (1) if it was located in the overgrowth, detrital grain, or mixed and (2) if any inclusions or irregularities were present in the ion microprobe pit. Spots that overlap the detrital-overgrowth boundary have a mixed $\delta^{18}O$ value and are not considered in discussion of DQ and OQ. Data from spots that comprise two phases (e.g., quartz and epoxy) or feature irregularities (e.g., holes in pit surface) are inaccurate and were discarded. All data are reported in Tables DR1 and DR2 in the Data Repository.

RESULTS

Detrital quartz grains from the Mount Simon Sandstone have an average $\delta^{18}O$ (DQ) value of 9.8‰ ± 3.5‰ (2 SD, n = 134 grains from 19 rocks, Fig. 3A; range = 4.2‰–14.9‰ with outliers at 1.1‰ and 16.6‰). Values of $\delta^{18}O$ (OQ) are more variable than $\delta^{18}O$ (DQ) both for total range (12.6‰–28.2‰ for all samples, n = 593) as well as within individual overgrowths. Two rocks had one overgrowth each that was anomalous in $\delta^{18}O$, out of a total of 10 analyzed. These cements are interpreted as a later generation and are not considered further (Tables DR1 and DR2).

[1]GSA Data Repository item 2011334, sampling and analytical methods, Figure DR1 (sample mount), Figure DR2 (traverse results), and Tables DR1–DR2 (oxygen isotope compositions), is available online at www.geosociety.org/pubs/ft2011.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

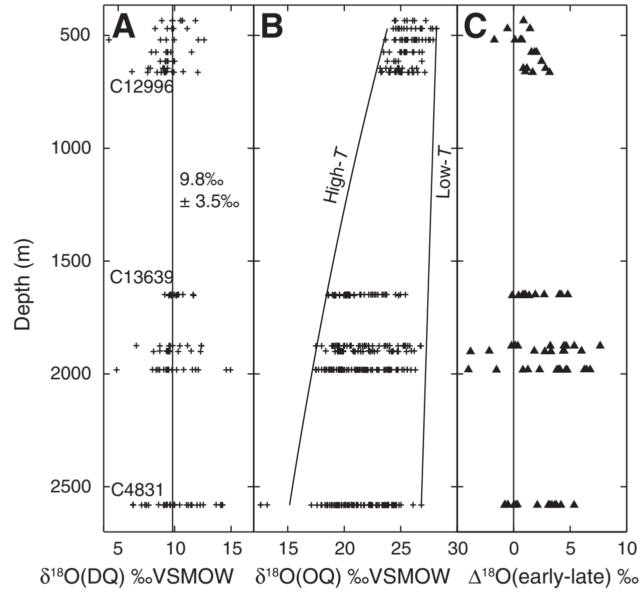

Figure 3. Depth versus $\delta^{18}O$ (quartz) from 19 samples of Mount Simon Sandstone in drill core from Illinois Basin, measured in this study. VSMOW—Vienna standard mean ocean water. A: Vertical line is average value of all analyzed detrital grains from Mount Simon Sandstone. Each cross represents single detrital grain of quartz (DQ). B: Values of $\delta^{18}O$, overgrowth quartz (OQ), show trend to lower values and greater range in progressively deeper samples. High-temperature (*T*) line shows $\delta^{18}O$ (OQ) calculated for quartz in equilibrium with fluid of constant $\delta^{18}O$ (H_2O) = –3‰, assuming paleogeothermal gradient of 30 C/km, 1 km of uplift, and 20 C at surface. Low-*T* line fits highest values of $\delta^{18}O$ (OQ) and does not vary with depth. C: Values of $\Delta^{18}O$ (early-late) indicate that individual OQs are consistently zoned in $\delta^{18}O$; early-formed OQ (adjacent to DQ) versus late-formed OQ (nearest grain boundary). Positive $\Delta^{18}O$ indicates individual overgrowths that have highest $\delta^{18}O$ (OQ) near DQ. Increase in magnitude of $\Delta^{18}O$ (early-late) indicates that there is greater gradient in $\delta^{18}O$ (OQ) values in samples deeper than 1.5 km. Each triangle represents single overgrowth with at least two ion microprobe analyses.

Multiple analyses were made with a 15 μm spot in 78 individual overgrowths from 15 samples to investigate zoning of $\delta^{18}O$ (OQ) (Fig. 3B). Since spots were aimed as close as possible to the edges of the overgrowth, many spots were shown by post-analysis CL imaging to be mixed analyses of DQ and OQ. A total of 73 overgrowths have at least 2 good (not mixed) spots per overgrowth; many of these have multiple analyses. In general, early-grown cements have higher $\delta^{18}O$ (OQ) and vary toward lower values for later cements at the overgrowth rim. The difference between $\delta^{18}O$ (OQ) of the earliest cement and the latest $\delta^{18}O$ (OQ) value is calculated as $\Delta^{18}O$ (early-late) = $\delta^{18}O$ (early OQ) – $\delta^{18}O$ (late OQ). The majority (85%) of $\Delta^{18}O$ (early-late) values within the Illinois Basin are positive (Fig. 3C). The $\delta^{18}O$ (early OQ) values tend to remain relatively constant with present depth (from 0.5 to 2.5 km) while the $\delta^{18}O$ (late OQ) values for individual overgrowths are lower in deeper samples, which leads to the observed pattern of $\Delta^{18}O$ (early-late) magnitudes increasing with depth (Fig. 3C). Detailed traverses were measured on 11 overgrowths using a 5 m spot to investigate $\delta^{18}O$ patterns within the overgrowth. Nine of these overgrowths have $\delta^{18}O$ values that decrease from the earliest (high $\delta^{18}O$) to the latest (low $\delta^{18}O$) spots (Fig. 4; seethe Data Repository); the other two have no clear trend.

DISCUSSION

Values of $\delta^{18}O$ (DQ) from the Mount Simon Sandstone (9.8‰ ± 3.5‰) are indicative of sources dominated by igneous material (e.g., Taylor, 1968).

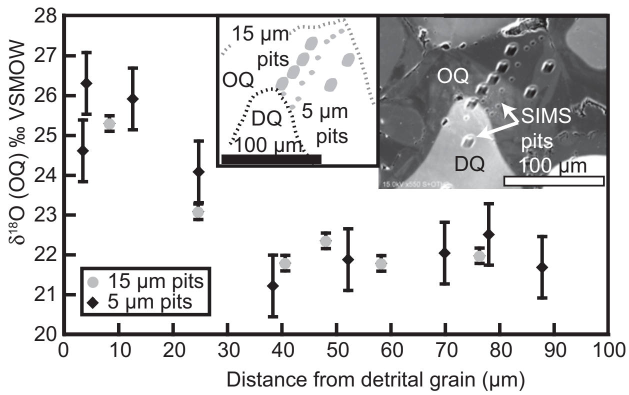

Figure 4. Oxygen isotope ratios measured in this study and projected in traverse of single quartz overgrowth (OQ) shown in Figure 2. Scanning electron microscope image is combined secondary electron and cathodoluminescence. Diagram shows boundaries of detrital grain (DQ) and locations of ion microprobe (SIMS, secondary ion mass spectrometer) pits. Distance is calculated from center of each pit to boundary of detrital grain. Data show overall decrease in $\delta^{18}O$ (OQ) with distance away from detrital boundary and $\Delta^{18}O$ (early-late) = 4.6‰. Detrital grain averages $\delta^{18}O$ (DQ) = 4.9‰. Data from spots that overlap detrital-overgrowth boundary are not plotted. Error bars are 2 standard deviation. VSMOW—Vienna standard mean ocean water.

The distribution of $\delta^{18}O$ (DQ) values does not vary with location or depth. In contrast, rocks deeper in the basin have both a wider range of $\delta^{18}O$ (OQ) values as well as lower minimum $\delta^{18}O$ (OQ) values (Fig. 3). The highest $\delta^{18}O$ (OQ) value in each rock, regardless of depth, is closest to the DQ boundary and relatively constant at ~26‰. The lowest value, however, varies significantly and correlates with the depth of the sample.

Two end-member models can be considered for genesis of the quartz cements that are variable in $\delta^{18}O$: (1) the temperature was constant and pore fluid $\delta^{18}O$ varied, or (2) pore fluid $\delta^{18}O$ was constant and temperature varied. We evaluate the extent to which each model can explain the observed trends in $\delta^{18}O$, both basin wide and at the scale of single overgrowths.

For model 1, if temperature is held constant and fluid composition is varied, the most likely explanation for fluid variation is flow of systematically lower $\delta^{18}O$ fluids through buried sandstones in the Illinois Basin. This is the model proposed by Chen et al. (2001), who concluded that fluids varied from low to high $\delta^{18}O$ values; however, the single overgrowth results of this study require that if fluids vary in $\delta^{18}O$, they vary in the opposite direction. Limited fluid inclusion data within quartz overgrowths in the Mount Simon Sandstone give a homogenization temperature (T_h) range of 100–130 °C (average 115 °C) for OQ (Fishman, 1997); however, without more sampling, the timing of fluid inclusions is uncertain. If temperature was constant at 115 °C, then the initial $\delta^{18}O$ (H_2O) was ~+9‰ to precipitate the earliest overgrowths ($\delta^{18}O$ = +28.5‰; Clayton et al., 1972; Friedman and O'Neil, 1977). Constant, elevated temperatures of 115 °C could have resulted from heated fluids flowing from deeper in the basin (late in the history, after burial), and in a fluid-dominated system, $\delta^{18}O$ (H_2O) would not be altered by precipitation of small amounts of cement. However, the monotonic variation of $\delta^{18}O$ (H_2O) from high early values to progressively lower values that is necessary to generate the observed $\delta^{18}O$ (OQ) trends would be fortuitous and unlikely. This is exactly the reverse of what is observed in basin brines; values shift toward higher $\delta^{18}O$ due to water-rock interactions (Clayton et al., 1966). In addition, the initial $\delta^{18}O$ (H_2O) values (+9‰ for assumed T = 115 °C) for model 1 are 10‰ higher than early Paleozoic seawater (~−5‰ to −1‰; Came et al., 2007; Jaffrés et al., 2007). For modern basins, values of $\delta^{18}O$ (H_2O) as high as +9‰ are only found in the most saline brines that are interpreted to be highly evolved remnants of formation fluids (Clayton et al., 1966).

If, as assumed in model 1, these overgrowths formed at a constant temperature in response to basin-wide fluid movement, then the oxygen isotope results require that the circulating fluids varied systematically across the Illinois Basin, with $\delta^{18}O$ (H_2O) evolving through time from high $\delta^{18}O$ to lower $\delta^{18}O$, and that this fluid evolution was more extreme in the deeper parts of the basin. Furthermore, since the predicted fluid flow in the Illinois Basin is updip toward our sample localities, it would require an unlikely coincidence for larger values of $\Delta^{18}O$ (early-late) to be found only in the deepest parts of the basin, where presumably less fluid alteration would have occurred relative to the shallow, northern samples. Thus model 1 cannot satisfactorily explain the observations.

For model 2, $\delta^{18}O$ (H_2O) is constant and temperature increases in order to cause the observed trend to lower $\delta^{18}O$ (OQ). Such growth of overgrowths would be expected during burial and heating. In this situation, fluid flow is possible, but not required. The fluid flux could be nil if cementation is all facilitated by pressure solution. The observed patterns in $\delta^{18}O$ (OQ) values then provide constraints on changes in temperature. Using a constant $\delta^{18}O$ (H_2O) of −3‰ (approximately early Paleozoic seawater), a temperature of 40 °C would correspond to precipitation of the highest $\delta^{18}O$ (early OQ) value of +28.5‰ and 107 °C would correspond to the lowest $\delta^{18}O$ (late OQ) value of +17.5‰. If a constant $\delta^{18}O$ (H_2O) of −1‰ is used instead, the calculated precipitation temperatures range from 50 to 124 °C. The variability in temperature is ~70 °C regardless of fluid composition, consistent with growth during burial and increasing temperature. This range of temperatures corresponds to a geotherm of 30 °C/km (high-T line in Fig. 3). While precipitation is slow below 80 °C, thin syntaxial quartz overgrowths can precipitate at temperatures below 40 °C, especially in slowly cementing clean quartz arenites (Kelly et al., 2007). The quartz overgrowths show a consistent, basin-wide pattern where the earliest generation of quartz (adjacent to DQ) has similar high $\delta^{18}O$ (OQ) values, and overgrowths are zoned outward toward lower values. This pattern suggests that all quartz overgrowths started at the same conditions, that temperature and/or fluid composition varied systematically, and that growth stopped at different times for different samples, either when porosity was occluded or when burial ceased. Pressure solution can begin early in the burial history (Stone and Siever, 1996), and will provide a source of silica for overgrowth formation. This is consistent with the interpretation that overgrowth formation started relatively early in the burial history (ca. 400 Ma; Duffin et al., 1989; Fishman, 1997). The temperatures calculated from overgrowths in this study and the temperature-time curve used by Fishman (1997) suggest that quartz cementation occurred over a period of 100 m.y.

The genesis of base-metal sulfide ores in the Upper Mississippi Valley Pb-Zn district is generally attributed to expulsion of metal-rich brines from sandstone aquifers deep in the Illinois Basin northward onto the Wisconsin dome ca. 270 Ma (Sverjensky, 1981; Duffin et al., 1989; Brannon et al., 1992). The results of this study suggest that quartz cements formed significantly before Mississippi Valley–type ores. The correlation of increasing magnitude of $\Delta^{18}O$ (early-late) with depth fits model 2 well, where temperature increased during quartz growth. This conclusion indicates that overgrowths started to form at shallow depths in all rocks at relatively low temperatures and continued to grow during burial and heating, with little to no variation in $\delta^{18}O$ (H_2O). Both pressure solution and fluid flow are permitted and likely in this model, but temperature exerts the dominant control of $\delta^{18}O$ (OQ). The fact that quartz overgrowths are zoned both in $\delta^{18}O$ and CL response suggests a protracted growth history. The detailed shapes of $\delta^{18}O$ (OQ) versus distance plots are interesting and qualitatively correspond with CL zonation. It is possible that quartz precipitation was not a long continuous process, but rather occurred in a series of punctuated events. However, the details of this zonation are beyond the scope of this study and invite future investigation.

CONCLUSIONS

Oxygen isotope variability in diagenetic quartz provides a useful tool for investigating the thermal and fluid evolution of the Illinois Basin. High-precision ion microprobe analyses with 5 m and 15 m spots reveal consistent trends in diagenetic quartz $\delta^{18}O$ values, both regionally in the Illinois Basin and within single quartz overgrowths. These trends represent continued, though possibly punctuated, quartz growth with increasing temperatures during burial. If quartz precipitated from fluids similar to Paleozoic seawater, then measured values indicate precipitation from fluids that initially were relatively cool but increased by ~70 °C over the duration of burial and quartz growth. The fluids that formed the cements in these rocks are not related to the Mississippi Valley–type deposits in Wisconsin. The growth of quartz cements in the Mount Simon Sandstone track the burial of the Illinois Basin and further study will provide useful constraints for basin evolution models. The new ability to study isotope zoning within single quartz overgrowths should prove useful in many diagenetic settings.

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