Chemical Geology 384 (2014) 168–180

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Evolution of quartz cementation and burial history of the Eau Claire Formation based on *in situ* oxygen isotope analysis of quartz overgrowths

Ayumi Hyodo *, Reinhard Kozdon, Anthony D. Pollington [1], John W. Valley

WiscSIMS, Department of Geoscience, University of Wisconsin-Madison, 1215 West Dayton Street, Madison, WI 53706, USA

ARTICLE INFO

Article history:
Received 14 November 2013
Received in revised form 10 May 2014
Accepted 24 June 2014
Available online 2 July 2014

Editor: D.B. Dingwell

Keywords:
Quartz overgrowth
Oxygen isotopes
Eau Claire Formation
Illinois Basin
SIMS

ABSTRACT

Individual quartz overgrowths in siltstone of the late Cambrian Eau Claire Formation (Fm.) are systematically zoned in oxygen isotope ratio ($\delta^{18}O$). *In situ* analysis of $\delta^{18}O$ was performed with 3 and 15 μm beam spots by secondary ion mass spectrometer (SIMS) on detrital quartz grains and quartz overgrowths. These results from thin lenses within impermeable mudstones reflect samples that were sealed from basin-wide fluid flow and compliment previous studies of more permeable sandstones. Individual grains of detrital quartz (DQ) are homogeneous in $\delta^{18}O$. The average $\delta^{18}O$ values in fine-grained detrital quartz in mudstones and siltstones and in coarser-grained quartz in the Eau Claire Fm., Mt. Simon and St. Peter Sandstones (Ss.) are essentially identical at $\delta^{18}O = 10‰$ VSMOW, suggesting that detrital quartz is dominantly igneous in origin. The $\delta^{18}O$ values of overgrowth quartz (OQ) of buried samples from the Illinois Basin are higher and quartz overgrowths are systematically zoned outward from the detrital cores. These gradients are similar to those from the underlying Mt. Simon Ss., and are best explained by increasing temperatures during burial. Pressure solution is evident in thin section and may have supplied significant silica for overgrowths. In contrast to the deeply buried samples from the Illinois Basin, quartz overgrowths in samples from the Wisconsin Arch are homogeneous and higher in $\delta^{18}O$. Those overgrowths are interpreted as quartz cements formed in a near-surface environment (<40 °C), which is consistent with geological evidence that these rocks were only shallowly buried (<500 m).

Based on these $\delta^{18}O$(OQ) results and the modeled thermal history during burial of the basin, the earliest-formed quartz overgrowths were produced at low temperature from low $\delta^{18}O$(water) around 450 Ma. The $\delta^{18}O$ values in traverses of single overgrowths decrease by up to 9.1‰, showing continued cementation with increased burial, pressure solution, and heating until ~250 Ma. In traverses of the outermost zone of some overgrowths, oxygen isotope values become constant or increase slightly, possibly due to clay mineral dehydration reactions or later fluid infiltration. We present a new cementation and basin evolution model, in which the $\delta^{18}O$ of cement correlates to the age of formation and the late overgrowths formed between 270 and 250 Ma, during and/or after the migration of brines that formed the Pb–Zn deposits of the Upper Mississippi Valley District (270 Ma). Cementation around 270 Ma would have reduced permeability, possibly ending the flow of ore forming brines.

1. Introduction

Understanding pathways, timing, and flux of fluid flow in siliceous sediments is one of the major questions in diagenesis. Fluids in pore spaces commonly deposit or dissolve mineral cements. Oxygen isotope geochemistry of quartz cements, therefore, provides information about paleo-fluids, paleo-temperatures, burial, and diagenetic processes (Milliken et al., 1994; Hervig et al., 1995; Graham et al., 1996; Williams et al., 1997; Schieber et al., 2000; Chen et al., 2001; Hiatt et al., 2007; Kelly et al., 2007; Day-Stirrat et al., 2010; Pollington et al., 2011a; Harwood et al., 2013). Bulk oxygen isotope analysis which mixes detrital and clastic components of clastic sediments could lead to misinterpretations regarding (I) the compositions of detrital grains and thus of their provenance and genesis, (II) the composition of cements and thus of temperatures and timing of diagenesis, and (III) the compositions of fluids involved in diagenesis. New *in situ* results that isolate detrital *vs.* clastic components provide support for improved models for major processes of heating, burial, and mass transport in the crust. Recent improvements in instrumentation, analytical techniques, and sample preparation make it possible to perform multiple *in situ* analyses of $\delta^{18}O$ on a single overgrowth with high precision and accuracy using a secondary ion mass spectrometer (SIMS) and a <10-

* Corresponding author at: Animal Industries Bldg. 225, Department of Ecosystem Science and Management, 2126 TAMU, Texas A&M University, College Station, TX 77843, USA.
E-mail address: ahyodo@tamu.edu (A. Hyodo).
[1] Present address: Nuclear and Radiochemistry, Los Alamos National Laboratory, PO Box 1663 MSJ514, Los Alamos, NM 87545, USA.

http://dx.doi.org/10.1016/j.chemgeo.2014.06.021
0009-2541/

μm beam that consumes a ng-size sample that is about one million times smaller than required by laser fluorination or other techniques (Kelly et al., 2007; Valley and Kita, 2009; Pollington et al., 2011a).

Conditions in thin sand layers surrounded by impermeable shales are of major interest for determining the reservoir sealing properties of shales. In order to reveal differences and similarities of overgrowth formation in sedimentologically and hydrologically different aquifer and aquitard units, Cambrian and Ordovician sand-dominated units in the Illinois Basin were chosen for study. The Basin contains the late Cambrian Eau Claire Formation (Fm.), which is generally impermeable and overlies the Cambrian Mount Simon Sandstone (Ss.), and underlies the Ordovician St. Peter Ss., both of which contain high permeability zones. The Eau Claire Fm. is composed of shale, siltstone, mudstone, and fine-grained sandstone (Ostrom, 1978; Aswasereelert et al., 2008; Bowen et al., 2012; Neufelder et al., 2012). In this study, quartz overgrowths in mudstone, siltstone, and fine-grained sandstone layers within the Eau Claire Fm. and detrital quartz grains were analyzed *in situ* for oxygen isotope ratio.

Burial and fluid history of the Mt. Simon Ss. has been studied using oxygen isotope ratios of cements (Chen et al., 2001; Pollington et al., 2011a). In a pioneering study, Chen et al. (2001) made *in situ* analyses of $\delta^{18}O$ in quartz and feldspar overgrowths (20 μm spots, precision = ±2‰, 2SD). They found increasing values of $\delta^{18}O$ for these cements along a ~700 km traverse, south to north, of the Illinois Basin and Wisconsin Arch and concluded that this trend reflects changes in $\delta^{18}O$ of paleofluids at a constant temperature of 115 °C at ca. 400 Ma. Temperatures were constrained by a limited number of homogenization measurements in fluid inclusions of unknown age (Pitman et al., 1997). More recently, Pollington et al. (2011a) used a newer SIMS instrument that attains smaller analysis pits (5–15 μm) and better precision (0.26–0.66‰). They discovered that single overgrowths on quartz grains are systematically zoned with gradients in $\delta^{18}O$ that are not consistent with the constant temperature hypothesis. Pollington et al. (2011a) proposed that the Mt. Simon Ss. experienced heating, pressure solution, and quartz cementation during burial with little change in the $\delta^{18}O$ values of fluids. The south to north increase in average $\delta^{18}O$ of quartz overgrowth ($\delta^{18}O$(OQ)) is attributed to shallower depths of burial and lower temperatures to the north. Pollington et al. (2011a) show that the measured $\delta^{18}O$(OQ) data from the Mt. Simon Ss. are explained well by a model using the following parameters for quartz growth: equilibrium fractionation of $\delta^{18}O$ between water and quartz (Clayton et al., 1972a; Friedman and O'Neil, 1977); $\delta^{18}O$(water) = −3‰ (*e.g.*, Cambrian seawater, Lohmann and Walker, 1989; Came et al., 2007; Jaffrés et al., 2007); a paleogeothermal gradient of 30 °C/km; 1 km of erosion and uplift after diagenesis; and a surface temperature of 20 °C. Pollington et al. (2011a) proposed that the systematic zoning in quartz overgrowths records concentric growth during the prolonged period of burial and heating. Higher $\delta^{18}O$(early OQ) values reflect formation at shallow depths and lower temperatures. Increasingly lower $\delta^{18}O$(late OQ) values formed at higher temperatures with silica likely supplied by pressure solution in sandstones.

Quartz overgrowths from the Eau Claire Fm. were analyzed to constrain the history of quartz cementation in the Illinois Basin. If paleofluids flowing from south to north in the Illinois Basin caused decreasing $\delta^{18}O$ values for quartz overgrowths of the permeable Mt. Simon Ss., the same trend should not be seen for quartz overgrowths of the Eau Claire Fm., because the fine-grained mudstones permitted little or no fluid flow unlike aquifers such as Mt. Simon and St. Peter Ss. Alternatively, if similar $\delta^{18}O$ gradients are found in fine-grained quartz sealed within the Eau Claire Fm., it supports Pollington's pressure solution hypothesis (Pollington et al., 2011a) with increasing temperatures that does not require significant fluid flow.

The three principal goals of this study are: (1) to identify the source of detrital grains in the Eau Claire Fm., (2) to obtain the $\delta^{18}O$ values of quartz overgrowths in the Eau Claire Fm. aquitard, and to compare those in underlying Mt. Simon Ss. and overlying St. Peter Ss. aquifers, and (3) to test models of the temperature, depth, and timing of quartz cementation in the Illinois Basin and Wisconsin Arch. Ultimately these results will help to improve our understanding of large-scale processes of fluid flow, heating, burial, and mass transport in the crust.

2. Materials and methods

2.1. Samples

Samples of the Eau Claire Fm. are from drill core in one hole in southern Wisconsin, and three holes from Illinois (Fig. 1; Table 1). The Eau Claire Fm. intervals that are the focus of this study consist of interbedded 1–5 cm thick sandstone or siltstone beds and 0.2–1 cm thick mudstone beds. Eleven mudstone, siltstone, and fine-grained sandstone samples were selected from the Eau Claire Fm. in these cores with current burial depths ranging from 85 to 1669 m (Table 1). A sample of the Mt. Simon Ss. was also studied (Fig. 1; Table 1). Sample IDs are based on the sampling State (WI: Wisconsin, IL: Illinois), depth (m) from present surface, and formation (EC: Eau Claire, MS: Mt. Simon).

2.2. Sample preparation

For quartz analysis, rock samples (~1 cm^3) cut from drill core were cast in 2.5 cm-diameter round epoxy mounts with several grains of quartz standard UWQ-1 ($\delta^{18}O$ = 12.33‰ VSMOW; Kelly et al., 2007) placed near the center. They were polished by diamond to a low-relief flat surface (Kita et al., 2009), carefully cleaned, dried in a vacuum oven at ~40 °C for 1 h, and carbon coated. Secondary electron (SE; Fig. 2A), back-scattered electron (BSE; Fig. 2B), and cathodoluminescence (CL; Fig. 2C) images of these samples were acquired using a Hitachi S-3400N Scanning Electron Microscope (SEM) at UW-Madison with an accelerating voltage of 15 kV. The CL system is equipped with a parabolic mirror and photomultiplier that detects luminescence from UV to near-IR (185–850 nm). Overgrowths are darker in CL, whereas detrital quartz is generally brighter. In BSE images, quartz is darker than K-feldspar and dolomite that are also found in the Eau Claire Fm. samples.

2.3. Oxygen isotope analysis

Oxygen isotope ratios of detrital quartz grains and authigenic quartz overgrowths were measured using a CAMECA IMS-1280 secondary ion mass spectrometer at the WiscSIMS Laboratory, Department of Geoscience, UW-Madison. SIMS analysis was performed using 2.3 nA and 30 pA $^{133}Cs^+$ primary ion beams (20 kV total impact voltage) focused to 15 and 3 μm-diameter spot sizes, respectively (Kita et al., 2009; Valley and Kita, 2009; Pollington et al., 2011a). An electron flood gun in combination with the carbon coating of the sample surface was used for charge compensation. Secondary O^- ions were accelerated by 10 kV and detected simultaneously using two Faraday cup detectors for measurements with 15-μm beam spot size, and with one Faraday cup detector and one electron multiplier for 3-μm. The sample measurements were bracketed using a total of eight standard analyses of UWQ-1 quartz, four before and four after every 10 to 16 sample analyses (Supplemental Table 1). The average of these bracketing standard values was used to determine the instrumental bias based on the calibrated UWQ-1 value (Kelly et al., 2007). The values of instrumental bias averaged −4.9‰ (n = 170) for 15 μm and −11.2‰ (n = 72) for 3-μm-diameter pits in UWQ-1. The spot-to-spot reproducibility of each set of bracketing standards was assigned as the measurement uncertainty on individual analyses and averaged ±0.22‰ (2 standard deviations, 2SD) for 15-μm pits and 0.87‰ (2SD) for 3-μm-diameter pits. After measurement by SIMS, all individual analysis pits were imaged by SEM to inspect pit location and structure (Fig. 2D). Data from pits identified as 'irregular' on the basis that they encountered cracks, cavities or inclusions, or overlapped the grain edge or boundary of overgrowths and detrital grains, were considered irregular (Cavosie et al.,

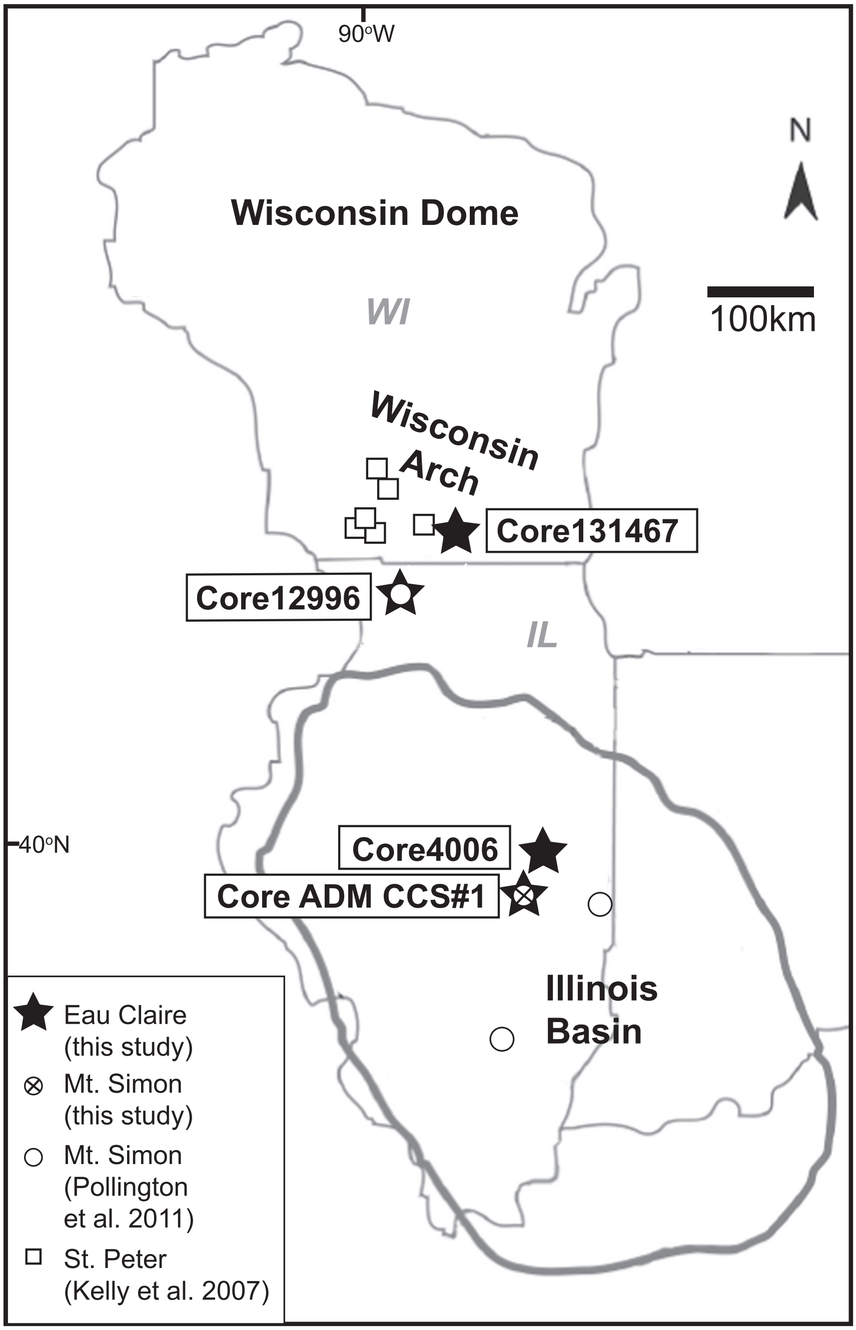

Fig. 1. Map of the Illinois Basin and Wisconsin Arch showing sample locations from this study, Pollington et al. (2011a), and Kelly et al. (2007). Modified after Chen et al., 2001.

2005) and are not included in the discussion. All data are included in the Supplemental Table 1.

3. Results

3.1. Petrographic description

The amounts of quartz cement vary for medium and fine sandstone and thin sand/silt layers embedded in mudstone. For example, in Eau Claire Sample IL390EC (390 m current depth), thick quartz overgrowths (typically 20–50 μm thickness) were observed on 100–300 μm diameter quartz grains (Fig. 3A). In Eau Claire Sample IL353EC (353 m current depth), a few, thin quartz overgrowths (2–4 μm thickness) occur on 10–30 μm diameter quartz grains in thin dolomitic siltstone layers (~1–2 mm thickness) interbedded in fine-grained sandstones examined in this study (Fig. 3B). In mudstone samples (Sample IL1143EC; 1143 m current depth), which contain ~30–40% silt-size quartz and K-feldspar grains and ~60–70% clay-size grains, no quartz overgrowths are evident on quartz grains of a similar size range (~10–30 μm diameter) (Fig. 3C, D).

3.2. The $\delta^{18}O$ of detrital quartz grains

Most detrital quartz grains from the Eau Claire Fm. have oxygen isotope ratios ($\delta^{18}O(DQ)$) from 8 to 11‰ (Fig. 4). The average $\delta^{18}O(DQ)$ is 10.2 ± 2.8‰ (2SD; $n = 159$ except three grains with lower (0.7, 0.9‰) or higher (14.0‰) values) (Supplemental Table 2). The $\delta^{18}O(DQ)$ values from Mt. Simon Ss. range from 6.6 to 12.1‰ (Fig. 4; Supplemental Table 2). The $\delta^{18}O(DQ)$ values (Figs. 4 and 5A) can be compared with St. Peter and Mt. Simon data from previous studies (Kelly et al., 2007;

Table 1
Summary of samples used in this study; EC: Eau Claire Fm.; MS: Mt. Simon Sandstone; WI: Wisconsin Arch; IL: Illinois Basin.

Sample ID	Fm.	Core	Sample locations			Current burial depth (m)	Modeled maximum burial depth (m)	Grain size
				Latitude	Longtitude			
WI84.7EC	EC	131467	WI	43° 01′ 58.61″ N	89° 21′ 40.67″ W	84.7	~500	Coarse silt to very fine sand + fine sand[a]
WI85.2EC	EC	131467	WI	43° 01′ 58.61″ N	89° 21′ 40.67″ W	85.2	~500	Coarse silt to very fine sand + fine sand[a]
IL328EC	EC	12996	IL	42° 26′ 14.31″ N	89° 51′ 28.28″ W	328	1328	Coarse silt to very fine sand
IL338EC	EC	12996	IL	42° 26′ 14.31″ N	89° 51′ 28.28″ W	338	1338	Very fine to fine Sand
IL353EC	EC	12996	IL	42° 26′ 14.31″ N	89° 51′ 28.28″ W	353	1353	Clay to medium silt + fine sand[a]
IL371EC	EC	12996	IL	42° 26′ 14.31″ N	89° 51′ 28.28″ W	371	1371	Medium sand
IL390EC	EC	12996	IL	42° 26′ 14.31″ N	89° 51′ 28.28″ W	390	1390	Medium to coarse sand
IL1143EC	EC	4006	IL	40° 16′ 54.51″ N	88° 25′ 38.68″ W	1143	2143	Fine silt to clay
IL1173EC	EC	4006	IL	40° 16′ 54.51″ N	88° 25′ 38.68″ W	1173	2173	Coarse silt
IL1176EC	EC	4006	IL	40° 16′ 54.51″ N	88° 25′ 38.68″ W	1176	2176	Medium sand
IL1669EC	EC	ADM CCS#1	IL	39° 52′ 35.40″ N	88° 53′ 37.32″ W	1669	2669	Coarse silt to very fine sand
IL1960MS	MS	ADM CCS#1	IL	39° 52′ 35.40″ N	88° 53′ 37.32″ W	1960	2960	Medium to coarse sand

[a] Banded samples.

Pollington et al., 2011a). The δ^{18}O(DQ) results show no correlation with stratigraphic interval, the sample location or burial depth for any of these rock units (Figs. 4, 5A), or with the grain size (Supplemental Table 2).

3.3. The δ^{18}O of quartz overgrowths

The δ^{18}O values of quartz overgrowths, δ^{18}O(OQ), from the Eau Claire Fm. range from 18.8 to 31.9‰ ($n = 155$), and are higher than those of detrital quartz grains (Fig. 4; Supplemental Table 2). The δ^{18}O(OQ) from the Mt. Simon Ss. of the Illinois Basin ranges from 20.9 to 28.7‰ ($n = 26$) (Fig. 4; Supplemental Table 2). The δ^{18}O(OQ) results can be compared with current burial depth (Fig. 5B) and St. Peter Ss. and Mt. Simon Ss. data from previous studies (Kelly et al., 2007; Pollington et al., 2011a).

In samples from the Eau Claire Fm., multiple analyses for δ^{18}O (2–3 analyses using 15 μm spots or 2–9 analyses using 3 μm spots) were obtained within single quartz overgrowths whose thicknesses are typically 8–50 μm. In single quartz overgrowths, the δ^{18}O values of quartz cement closest to the boundary with the detrital quartz grain (*i.e.*, the earliest cement, δ^{18}O(early OQ)) is consistently higher than those of spots closer to the overgrowth rim that formed at a later stage (δ^{18}O(late OQ)). For instance, δ^{18}O(OQ) values from Sample IL1176EC (1176 m current depth) vary smoothly from 27.9‰ in the earliest cement (2 μm from detrital grains) to 20.8‰ in the latest cement (Fig. 6). Similar trends, but of varying magnitudes, are evident in all samples from the Illinois Basin. Importantly, these trends in δ^{18}O(OQ) are seen in samples from permeable sandstones, and sands encased in low permeability mudstones in the Eau Claire. The difference in δ^{18}O between early and late cements in traverses of single quartz overgrowths, Δ^{18}O(early-late), varies from 0.4 to 9.1‰ with one outlier at −0.8‰,

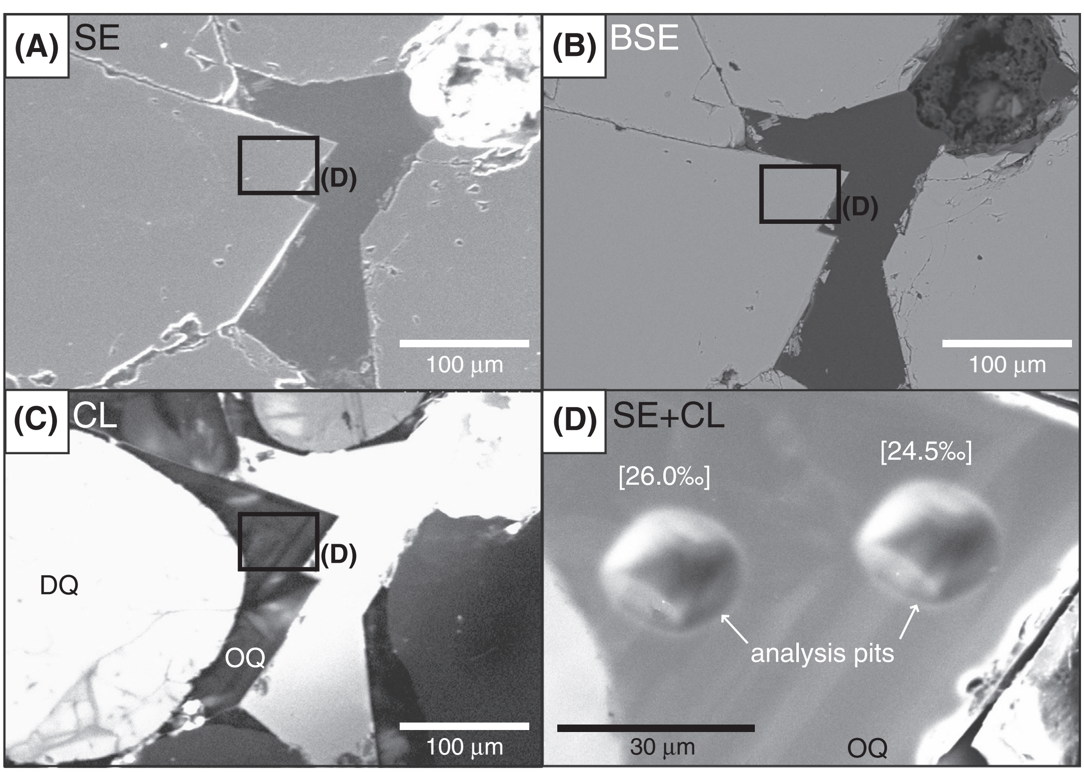

Fig. 2. Scanning Electron Microscope images of detrital quartz grains (DQ) and quartz overgrowths (OQ) (Eau Claire Fm. Sample ID IL390EC): (A) secondary electrons (SE), (B) back-scattered electrons (BSE), (C) cathodoluminescence (CL), and (D) combined SE + CL image enlarged from box in panels A–C showing two large diameter SIMS pits in the quartz overgrowth. Numbers in brackets are measured δ^{18}O values. Scale bars are 100 μm for (A)–(C), and 30 μm for (D).

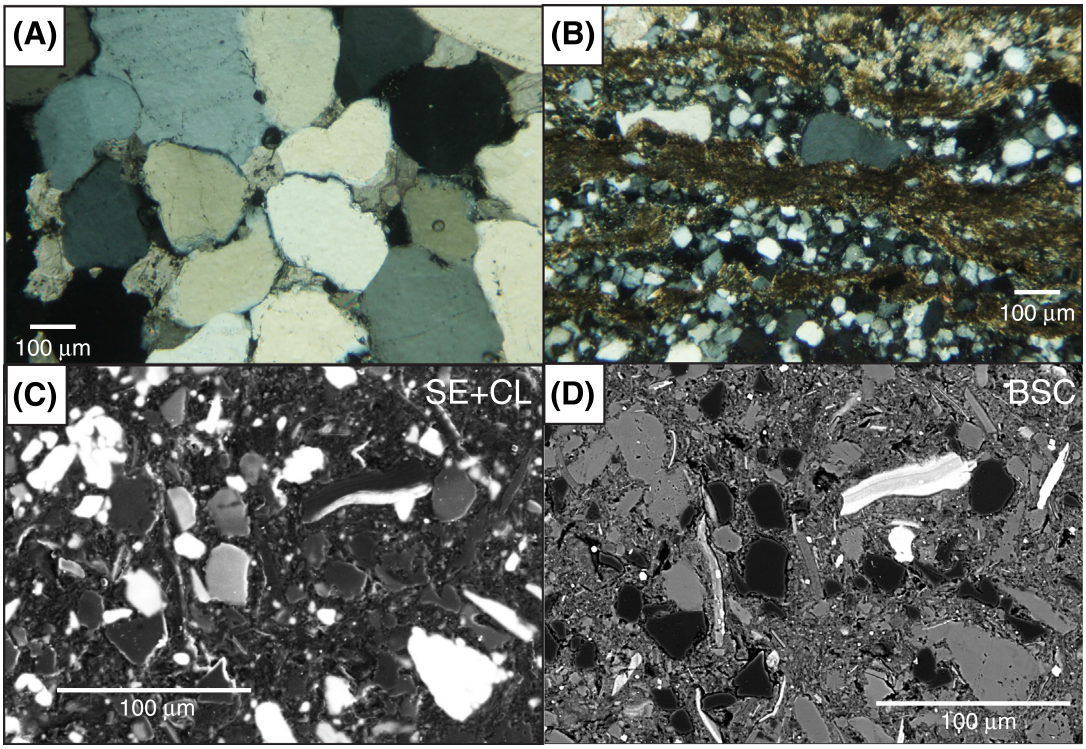

Fig. 3. Petrographic images of IL390EC (A), IL353EC (B) and IL1143EC (C, D). (A) and (B) are cross polarized microscopic images, (C) is a secondary electrons (SE) + cathodoluminescence (CL) combined image, and (D) is a back-scattered electrons image. Scale bars are 100 μm.

and the values of $\Delta^{18}O$(early-late) are greater in deeper samples (Fig. 5C). For most overgrowths, $\delta^{18}O$ decreases monotonically. However, in traverses of some overgrowths, the $\delta^{18}O$ values decrease and then flatten or increase slightly for the youngest quartz (Fig. 6). The $\delta^{18}O$(early OQ) values in single overgrowths (oldest quartz) of all Eau Claire samples in the Illinois Basin are almost identical, tightly clustered, ranging from 27 to 28‰, in samples from 328 to 1669 m of current burial depths (Figs. 4, 5B).

Quartz overgrowths in Wisconsin samples of the Eau Claire Fm. contain higher $\delta^{18}O$ values, ranging from 26.2 to 30.9‰ (average 29.5‰), that are not observed in samples from the Illinois Basin (Figs. 4, 5B). These high-$\delta^{18}O$ cements from the Wisconsin Arch are not zoned, showing no difference in $\delta^{18}O$ between early and late cements (Fig. 5C). These results are similar to those reported by Kelly et al. (2007) and Pollington et al. (2011b) for optically continuous quartz overgrowths St. Peter and Mt. Simon Ss. (respectively) in southern and central Wisconsin.

4. Discussion

4.1. Source of detrital quartz

The sources of detrital quartz in siltstone and mudstone are, in general, not well known. Clayton et al. (1972b) and Blatt (1987) reported a negative relationship between quartz grain size (1 to 25 μm) from North Pacific clays and the corresponding $\delta^{18}O$ values (15 to 19‰). Kennedy and Arikan (1990) used petrographic, SEM, Fourier shape analysis, and oxygen isotope data of the Early Silurian Medina and Early Devonian Oriskany Formations, and proposed that the source of silt size grains (<62 μm) is quartz overgrowths broken off from medium quartz sand and that silt size grains have high $\delta^{18}O$ values (14.3 to 14.9‰). In our study, the oxygen isotope ratios of detrital quartz grains with various grain sizes (10 to 500 μm) were analyzed to test the correlation between grain size and $\delta^{18}O$ value, and to clarify origins of quartz in siltstone/mudstone and in sandstone from the Eau Claire Fm.

The average $\delta^{18}O$(DQ) of 10.2‰ for the St. Peter, Eau Claire, and Mt. Simon samples is consistent with a dominantly igneous origin (*e.g.*, Savin and Epstein, 1970; Hoefs, 2009). A few grains with lower or higher values may have been derived from low-$\delta^{18}O$ magma, or high-$\delta^{18}O$ chert and hydrothermally altered volcanic or metamorphic rocks, respectively (Hoefs, 2009). The $\delta^{18}O$(DQ) results do not correlate to diameters of the detrital grains in cross-section (8 to 800 μm) observed in polished mounts (Supplemental Table 2), in contrast to earlier reports from North Pacific clays (Clayton et al., 1972b; Blatt, 1987) or the Medina and Oriskany formations (Kennedy and Arikan, 1990). One possible explanation for this difference is that the earlier studies employed bulk analysis of grains sorted by sieving, which in other studies has been shown to concentrate fragments of high $\delta^{18}O$ overgrowths in the fine-size fraction (Graham et al. 1996).

4.2. Quartz cementation in the Illinois Basin

The zoning of the $\delta^{18}O$(OQ) and $\delta^{18}O$(OQ) trends against the burial depths observed in the Eau Claire samples are generally similar to those in the underlying Mt. Simon Ss. This comparison is significant because the Eau Claire samples of this study are from thin lenses surrounded by impermeable mudstones which form an aquitard sealing these layers in contrast to the underlying more permeable sandstones. The Mt. Simon sandstone is variably regarded as an aquifer for fluid flow (Bethke, 1986; Arnold et al. 1996). The similarity of $\delta^{18}O$(OQ) trends between the thin sand lenses in the Eau Claire aquitard and the much thicker Mt. Simon aquifer shows that fluid flow was not required to form the quartz overgrowths. This conclusion supports the Pollington cementation model, in which the isotopically-zoned quartz overgrowths in the Mt. Simon Ss. were formed from increasing temperature with depth (~45 to 120 °C), little or no significant fluid flow, and a nearly constant value of $\delta^{18}O$(water) = −3‰ (Pollington et al., 2011a).

In order to evaluate the Pollington model in the Eau Claire Fm., alternative conditions for quartz cementation have been considered including: 1) constant high temperature ~110 °C; 2) constant low

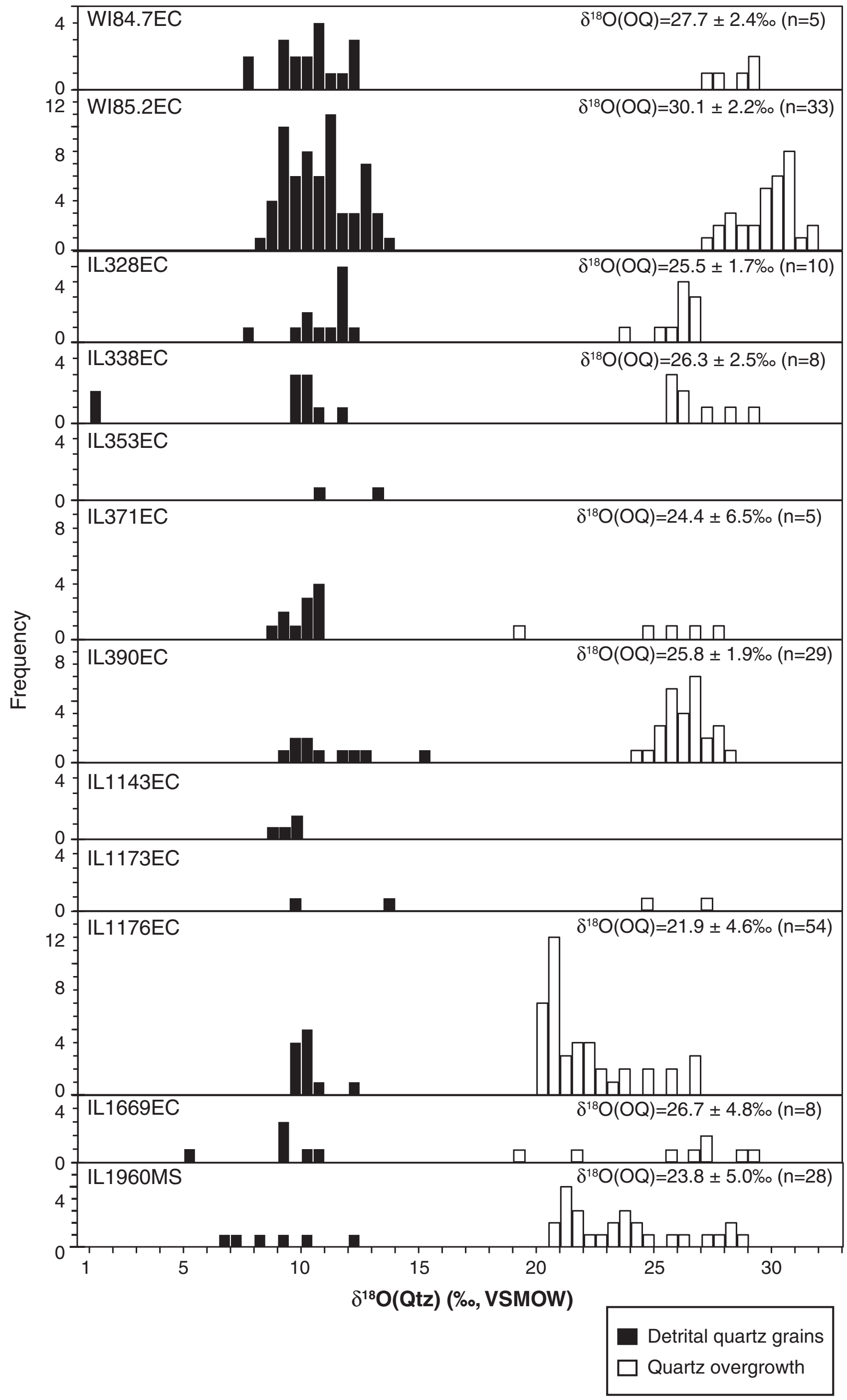

Fig. 4. Histograms of oxygen isotope ratios of quartz from the Eau Claire Fm. and Mt. Simon Ss. measured *in situ*: detrital quartz grains (black) and overgrowths (white). The average $\delta^{18}O \pm 2SD$ of overgrowths, $\delta^{18}O(OQ)$, is shown for each sample. EC: Eau Claire Fm.; MS: Mt. Simon Ss.; WI: Wisconsin Arch; IL: Illinois Basin.

temperature ~45 °C; 3) constant high $\delta^{18}O(water) = +8$‰; and 4) constant low $\delta^{18}O(water) = -3$‰ (Fig. 7). These scenarios are chosen as end-members; it will also be considered if both temperature and $\delta^{18}O$ varied. Any scenario for the formation of these overgrowths must explain the concentric growth zoning with consistently lower $\delta^{18}O$ values of younger quartz. Thus all of the scenarios in Fig. 7 trend from the highest toward the lowest measured value of $\delta^{18}O(OQ)$. The high $\delta^{18}O$ values of the earliest quartz overgrowths (~28‰) in the Eau Claire, Illinois Basin samples might be proposed to form at low temperatures from Cambrian seawater (45 °C, $\delta^{18}O(water) = -3$‰) or at higher temperatures from higher $\delta^{18}O$ fluids. Likewise, the zoning with positive values of $\Delta^{18}O$(early–late OQ) indicates either an increase in temperature or a decrease in the $\delta^{18}O(water)$ synchronous with growth. The scenario of a constant high temperature (#1 in Fig. 7; >100 °C) would suggest that fluids were from deeper in the basin, probably brine, and that quartz overgrowths were precipitated after burial. Such a hydrothermal system would be fluid-dominated and $\delta^{18}O$ values of water would not change in response to precipitating the small amounts of overgrowths observed in this study. This scenario (#1) would require an external process to monotonically decrease the $\delta^{18}O$ value of fluids by nearly ~10‰ in all of the areas sampled in order to explain the observed consistently decreasing $\delta^{18}O$ gradients of single overgrowths. This is viewed as overly fortuitous since we can't envision a source of progressively lower $\delta^{18}O$ water because of

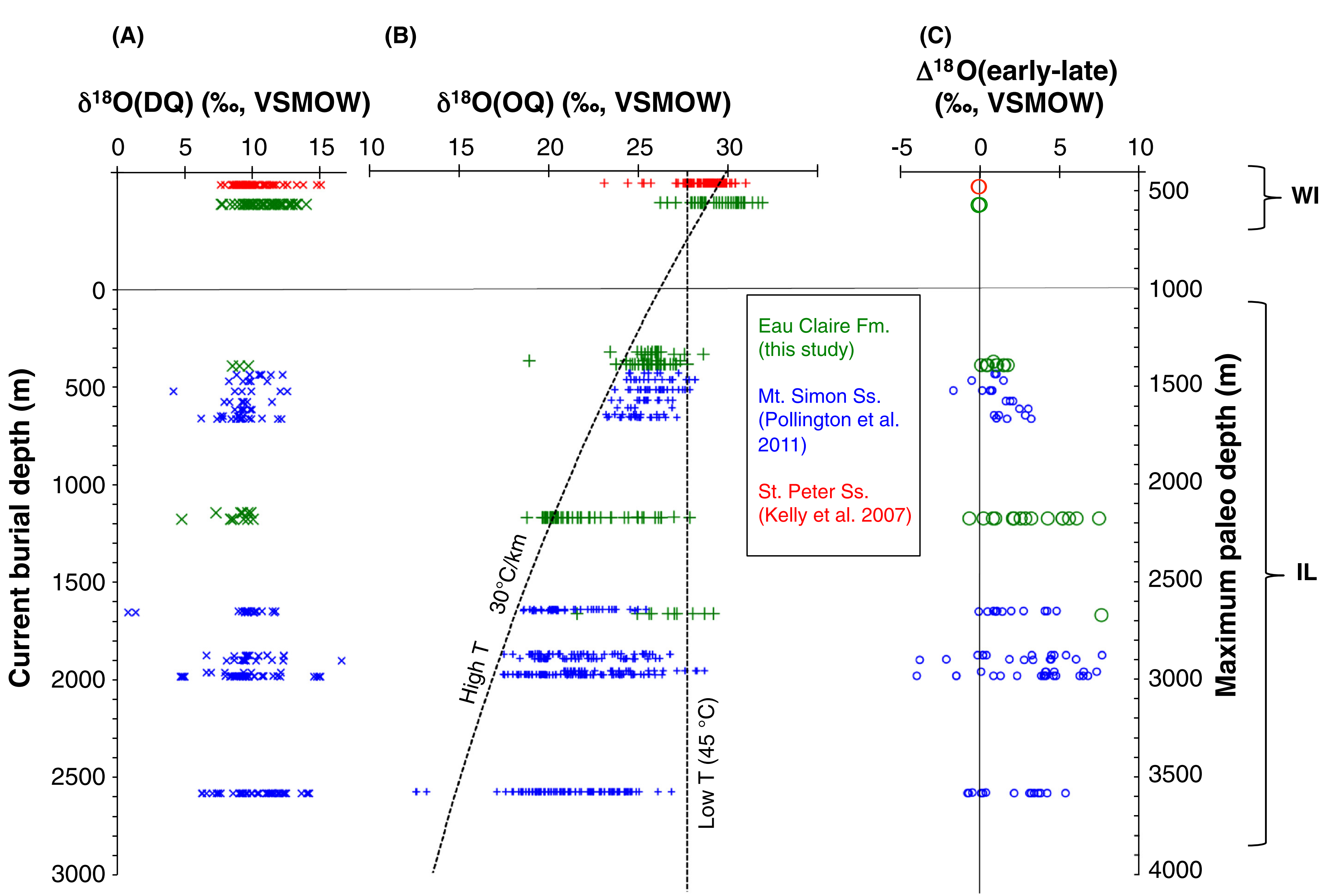

Fig. 5. Oxygen isotope ratios of (A) detrital quartz grains (DQ), (B) quartz overgrowths (OQ), and (C) values of $\Delta^{18}O$(early-late OQ) *versus* burial depth from 11 rock samples of the Eau Claire Formation (green; this study). Samples from the Illinois Basin are plotted *vs.* current depth and maximum paleo-depth, whereas Wisconsin Arch samples are above 0 m to show their different burial and uplift history. The oxygen isotope ratios of quartz from the Mt. Simon Ss. (Pollington et al. 2011a; this study) and the St. Peter Ss. (Kelly et al. 2007) are shown in blue and red, respectively. The dashed "High T" line represents $\delta^{18}O$(OQ) calculated for quartz in equilibrium with water of constant $\delta^{18}O$ (−3‰) and a geothermal gradient of 30 °C/km, see text. The "Low T" line represents quartz formed at 45 °C from the same water. These results are consistent with the model that quartz overgrowths began at similar temperatures throughout the Illinois Basin, but the process was different on the Wisconsin Arch where $\delta^{18}O$(OQ) is higher and not zoned. WI: samples from Wisconsin Arch. IL: samples from Illinois Basin.

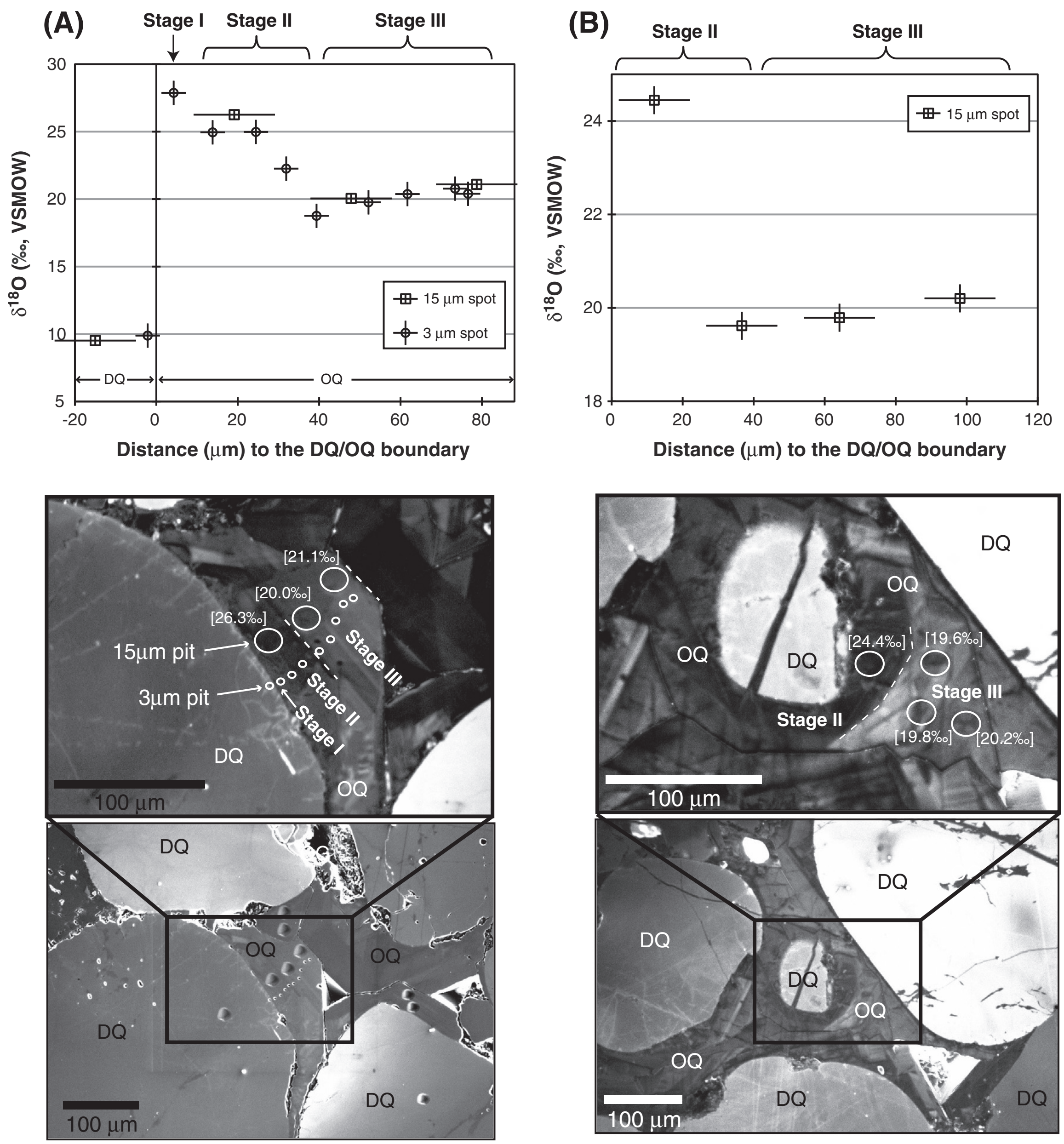

Fig. 6. Two traverses of $\delta^{18}O$ across individual quartz overgrowths in sample IL1176EC (current depth = 1176 m) from the Eau Claire Fm. (A) Overgrowth formation started with the highest $\delta^{18}O$(OQ) value (Stage I). Values of $\delta^{18}O$ decreased (Stage II) and then slightly increased (Stage III). Vertical error bars connote ±2SD. Horizontal error bars correspond to the diameter of the SIMS pit. The SEM (SE + CL) images show pit locations. Numbers in brackets are measured $\delta^{18}O$ values. (B) Values of $\delta^{18}O$ in the traverse of a second grain. Overgrowths with high, decreasing $\delta^{18}O$ values (Stage II) show a dark CL image, whereas those with low $\delta^{18}O$ values but a small increasing trend (Stage III) show a bright CL image.

the low latitude of this area and the absence of gravity-driven fluid flow before the MVT event at 270 Ma.

If temperatures are assumed constant and low (scenario #2 in Fig. 7), then the $\delta^{18}O$ of water that precipitated early overgrowths would be negative, closer to meteoric water or sea water (Cambrian seawater $\delta^{18}O = -3‰$; Lohmann and Walker, 1989; Came et al., 2007; Jaffrés et al., 2007) than brines. To generate the measured low $\delta^{18}O$ values of late-formed overgrowths, the $\delta^{18}O$(water) must have evolved to lower values of ~−13‰. Although $\delta^{18}O$(water) could shift from −3‰ toward lower values by exchange with detrital quartz at low temperature and low water–rock ratio, measured values for brines in Illinois and other basins typically shift in the opposite direction toward higher values, presumably by exchange with high $\delta^{18}O$ carbonates (Hoefs, 2009). In the absence of a process that could cause a systematic fluid-dominated shift of $\delta^{18}O$(water) in both permeable sandstones and impermeable mudstones, the consistent zoning that is measured in quartz overgrowths of both the Eau Claire Fm. and Mt. Simon Ss. suggests that a steady decline in $\delta^{18}O$(water) would be fortuitous and thus that neither scenarios #1 nor #2 are satisfactory explanations of the zoning seen in quartz overgrowths.

Scenario #3 assumes that $\delta^{18}O$(water) was constant and high (#3 in Fig. 7). If so, then temperatures of the fluids that precipitated early overgrowths would have to be above 100 °C and increase further through time to above 250 °C to create the observed decreasing $\delta^{18}O$ trends in single overgrowths. However, the results neither of thermometry nor of numerical thermal modeling support temperatures above 120 °C at any time for the burial depths of the samples used in this study (Bethke, 1986; Arnold et al., 1996; Fishman, 1997; Makowitz et al., 2006) and scenario #3 cannot be correct.

Thus, as concluded by Pollington et al. (2011a) for the Mt. Simon Ss., scenario #4 (Fig. 7) is most likely for the Eau Claire quartz overgrowths: low $\delta^{18}O$(water), little or no change in $\delta^{18}O$(water) through time, and

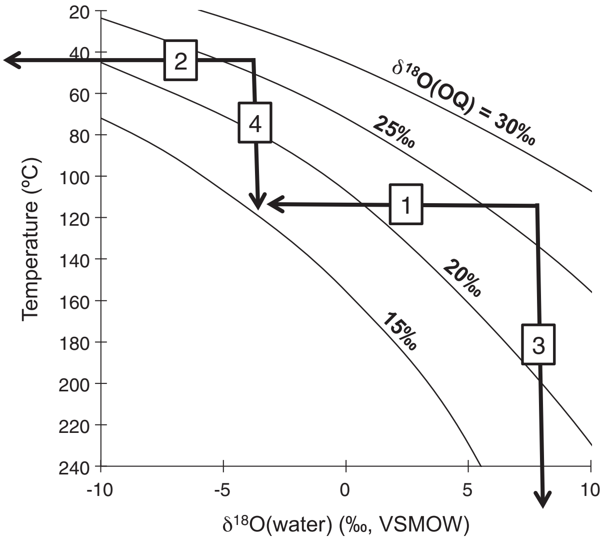

Fig. 7. Values of $\delta^{18}O$(water), $\delta^{18}O$ of quartz and equilibrium temperature (Clayton et al. 1972a). The contours indicate $\delta^{18}O(OQ) = 15, 20, 25$, and 30‰, which span the range of values in zoned quartz overgrowths from the Illinois Basin. Arrows with numbers show four end-member scenarios for the evolution of $\delta^{18}O$(water) and temperature: [1] constant, high temperature; variable $\delta^{18}O$(water); [2] constant, low temperature; variable $\delta^{18}O$(water); [3] constant, high $\delta^{18}O$(water); variable temperature; and [4] constant, low $\delta^{18}O$(water); variable temperature. Scenario #4 is favored in this study; see text.

increasing temperatures due to burial. This scenario is consistent with the interpretation that quartz cements of the Eau Claire Fm. were formed from formation waters that were seawater trapped at the time of deposition. It is not necessary that fluids flow through the rocks under these conditions and silica was sourced locally from pressure solution. This scenario also fits well with a reasonable paleogeotherm during burial (30 °C/km) as described below.

It is likely that in detail events were more complex. Changes in $\delta^{18}O$(water) might be caused by infiltration of meteoric water or other fluid flow possibly accompanied by advection of heat (Bethke, 1986; Stueber and Walter, 1991; Winter et al., 1995). It is also likely that some more permeable units were infiltrated by a large flux of brines at the time of formation of MVT Pb–Zn deposits in the Upper Mississippi Valley district of southwestern Wisconsin and eastern Iowa (270 Ma, Brannon et al., 1992). However, the consistent trends that are observed in $\delta^{18}O$ of quartz overgrowths of both the impermeable Eau Claire Fm. and the permeable Mt. Simon Ss. suggest that the impact of any such events was minor during periods of quartz cementation. While it is also likely that the precipitation of cements was not perfectly continuous during the entire burial period of the Illinois Basin, with the exception of the outer domains of some late quartz (Fig. 6), there is no evidence of discrete quartz cementation events in the Illinois Basin samples.

4.3. Sources of silica

Major sources of silica for quartz cementation in sandstones and mudstones are (1) biogenic silica, (2) mineral reactions such as feldspar dissolution and clay mineral diagenesis, and (3) pressure solution of detrital quartz grains (Bjørlykke and Egeberg, 1993; Worden and Morad, 2000). First, biogenic silica is not observed in the Eau Claire where it outcrops or is shallowly buried (this study; Nelson, 1998). Secondly, transformation from smectite to illite in mudstone could release silica for quartz overgrowth formation (Hower et al., 1976; van de Kamp, 2008; Peltonen et al., 2009). If illitization in mudstones was a major silica source for the overgrowths in the Eau Claire Fm., authigenic quartz should have formed in most mudstones as reported by Peltonen et al. (2009) for the Vøring and Møre Basins (Norwegian Sea), especially in mudstones from deeper burial depths. Although authigenic quartz was not observed in a mudstone sample used in this study, Illitization is a possible silica source for the Eau Claire overgrowths. Pressure solution appears to have been the most important source of silica for the overgrowths in the Eau Claire Fm. as also concluded for the Mt. Simon Ss. (Pollington et al., 2011a). Embayed quartz grain boundaries indicating pressure solution are frequently observed in the Eau Claire samples

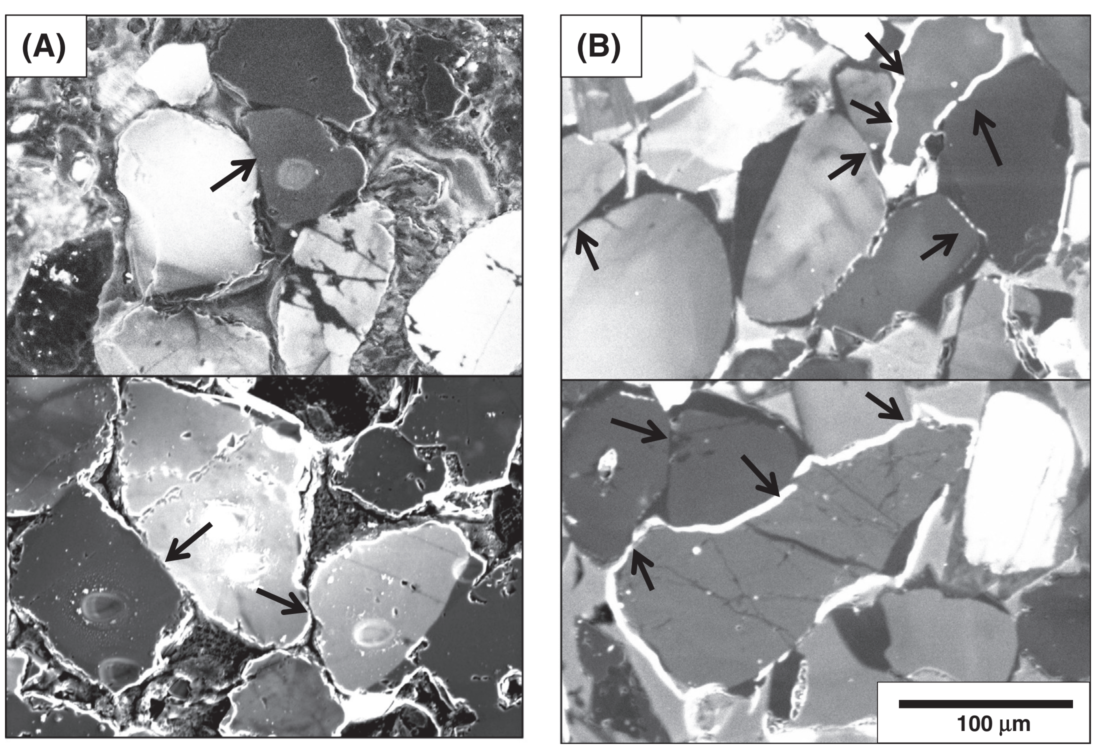

Fig. 8. Cathodoluminescence (CL) images of quartz grain boundaries indicating areas of pressure solution (arrows). Low (A: Sample WI85.2EC, current depth = 85 m) and high (B: sample IL338EC, current depth = 338 m) degrees of pressure solution. These samples are from the Wisconsin Arch and were never buried more than ~500 m.

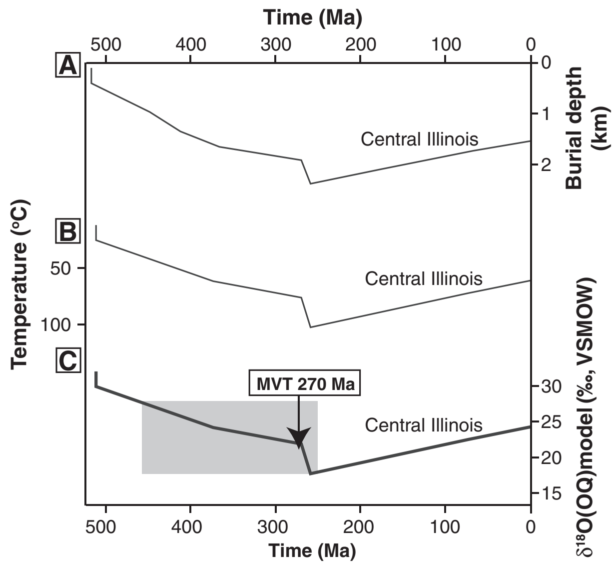

Fig. 9. Burial model for the evolution of the central Illinois Basin: age *versus* (A) burial depth; (B) temperature; (C) $\delta^{18}O$ of quartz overgrowths calculated based on temperature and the quartz cementation model described in text. The gray box indicates the range of the $\delta^{18}O(OQ)$ observed in the Eau Claire and Mt. Simon samples in the Illinois Basin (Pollington et al. 2011a; this study) and the inferred formation age. (A) and (B) are modified after Makowitz et al. (2006).

and pressure solution appears to have increased with depth for the samples of this study (Figs. 3A, 8). Silica was released from pressure solution, requiring quartz-to-quartz grain boundaries, and precipitated as cements in fine-grained sandstones and also in mudstone/siltstone layers interbedded in fine-grained sandstones in the Eau Claire Fm. Silica is less likely to migrate through mudstones that have low permeability. It is likely that rates of sedimentation and burial were a major control on the rate of pressure solution and hence on the growth of quartz overgrowths.

4.4. Quartz cementation and basin evolution

The $\delta^{18}O$ values of overgrowths formed at the greatest paleo-burial depths are calculated assuming scenario #4: a paleogeotherm of 30 °C/km, equilibrium fractionation of $\delta^{18}O$ between water and quartz (Clayton et al., 1972a), a surface temperature of 20 °C, 1 km erosion and uplift, and $\delta^{18}O(\text{water}) = -3‰$ (Cambrian seawater, Lohmann and Walker, 1989; Came et al., 2007; Jaffrés et al., 2007). These values are plotted as the “High T line” in Fig. 5B and compared with the measured $\delta^{18}O(OQ)$ values of the Eau Claire samples. The lowest values of the Eau Claire samples are on or above the “High T line” for each sample, showing that cementation ceased either at this maximum temperature or when overgrowths impinged on adjacent grains. The highest values of $\delta^{18}O(OQ)$ plot on or below the “Low T line” which shows the oxygen isotope value of quartz in equilibrium with water ($\delta^{18}O = -3‰$) at 45 °C. Nearly all values measured in quartz overgrowths of the Illinois basin are between these two lines (Fig. 5B) showing that the assumptions of this model are an excellent fit to the data.

This model can be combined with known burial rates in the Illinois Basin (Fig. 9A) to make predictions including a direct correlation between $\delta^{18}O(OQ)$ of each domain precipitated within a single quartz overgrowth with burial temperature, depth, and date. Rowan et al. (2002) and Makowitz et al. (2006) have established a thermal history of the central Illinois Basin using 1-D Genesis basin models (Fig. 9B). Note that temperatures proposed by Pollington and this study to have formed quartz overgrowths at (~45 to 120 °C) are in the range of the temperature of Rowan and Makowitz's thermal history. Using

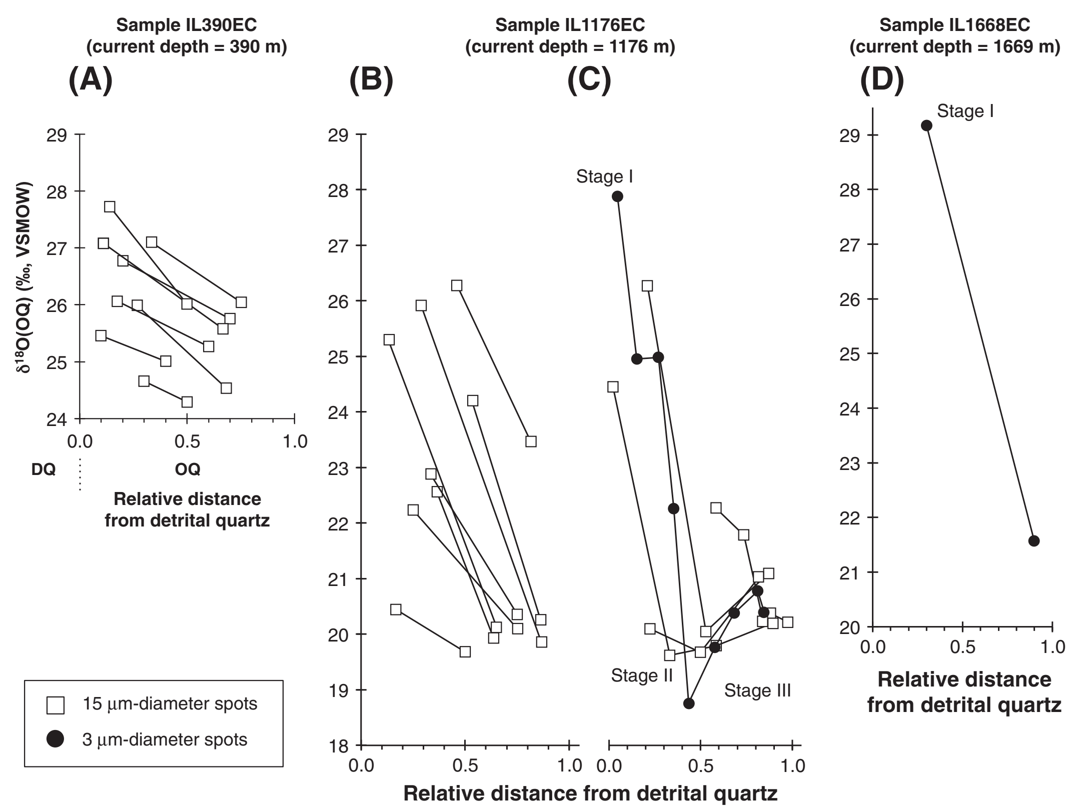

Fig. 10. Values of $\delta^{18}O$ for early- and late-formed domains within single overgrowths measured *in situ versus* the proportional distance from the boundary of the detrital grain to the edge of the overgrowth of Eau Claire samples: (A) Sample IL390EC (current depth = 390 m), (B, C) Sample IL1176EC (current depth = 1176 m), and (D) Sample IL1669EC (current depth = 1669 m). Each line represents a single overgrowth profile. Overgrowths are typically 10–80 μm in thickness. Results from Sample IL1176EC are shown in two plots: single overgrowths analyzed with two beam spots (B), and those with >3 spots (C).

temperatures of this model, $\delta^{18}O(OQ)_{model}$ values predicted at each burial depth are calculated through the burial history (Fig. 9C). Comparison of this theoretical $\delta^{18}O(OQ)_{model}$ and the measured $\delta^{18}O(OQ)$ values from the Eau Claire and Mt. Simon samples (gray box in Fig. 9C) suggests that quartz overgrowth formation in the central Illinois Basin started at ~450 Ma, and terminated at ~250 Ma. It is significant that if this model is correct, the date of formation for each domain of quartz cement can be determined from its measured value of $\delta^{18}O(OQ)$.

Overgrowth formation in the Eau Claire Fm. can be divided into three stages illustrated in different samples (Figs. 6, 10): Stage I is the start of overgrowth formation at ~45 °C, Stage II shows decreasing $\delta^{18}O(OQ)$ with burial and heating, and Stage III shows a flattening or slight increase in $\delta^{18}O(OQ)$. The growth model (Fig. 9) proposes that overgrowth formation started around 450 Ma (Stage I), overgrowths in Stage II formed between ~450 and ~250 Ma, and Stage III, which is observed in only a few samples, is probably cementation that continued for a short time around 250 Ma. The small increase in $\delta^{18}O(OQ)$ during Stage III does not fit the above model and suggests that this sample experienced an additional late fluid event, discussed below.

The uniformly high $\delta^{18}O$(early OQ) values in the overgrowths (~26–28‰ for Stage I) of the Eau Claire Fm. from the Illinois Basin are similar to values of the Mt. Simon Ss. (Fig. 5B). These $\delta^{18}O$(early OQ) values suggest that quartz overgrowths began to form at temperatures of 45 °C. Whereas many silica cements formed at low temperature are fibrous, quartz cements are reported at < 60 °C (*e.g.*, Haszeldine et al., 1984; Williams and Crerar, 1985; Burley et al., 1989; Bjørlykke and Egeberg, 1993; Kelly et al., 2007; Pollington et al., 2011a; Harwood et al., 2013). Some early fibrous cements formed at low temperatures recrystallize to clear quartz (Alexandre et al., 2004), but recrystallization would homogenize the $\delta^{18}O$ zoning, which is opposite of what we have observed in samples. Alternatively, pressure solution can occur at 45 °C (Bjørkum, 1996) and quartz overgrowths can form in quartz arenites with low degrees of silica supersaturation. Amounts of cement formed at low temperature are small because reaction rates are slower (Bjørlykke and Egeberg, 1993; Walderhaug, 1996) and thus early low-temperature quartz overgrowths are expected to be thin, requiring small spot sizes for analysis (Fig. 6) (Pollington et al., 2011a; Harwood et al., 2013).

Nearly all overgrowths continuously decrease in $\delta^{18}O$ from the detrital grain boundary toward the overgrowth rim (Fig. 6A, B, Stage II; Fig. 5C), consistent with increasing temperature during burial in the Illinois Basin. During the period of overgrowth formation, the $\delta^{18}O(OQ)$ values of Sample IL1176EC (1176 m current depth) decrease from ~28 to ~20‰ (Fig. 10B), whereas those of samples from shallower depths in the Illinois Basin (*e.g.*, Sample IL390EC: 390 m, current depth) start at similar values but decrease to only 24–25‰ (Fig. 10A). This difference is likely caused by their maximum paleo-depths. Overgrowth formation in Sample IL390EC terminated when the burial reached the maximum paleo-depth (1390 m) (paleo-temperature of ~60 °C), but overgrowths in Sample IL1176EC continued to form with increasing temperatures until burial reached a depth of ~2200 m (at ~85 °C). These conclusions are consistent with the High T line (Fig. 5B). Likewise, Pollington et al. (2011a) reported that the lowest measured $\delta^{18}O(OQ)$ values are from the greatest paleo-depths (3580 m). It is noted that cementation does not necessarily continue until the deepest burial. Many overgrowths in both the Eau Claire Fm. and Mt. Simon Ss. are seen to impinge on adjacent quartz (examples shown in SEM images of Fig. 6) and appear to have stopped growing earlier without enough space for new overgrowth.

4.5. Late higher $\delta^{18}O$ overgrowths — Stage III

Sample IL1176EC illustrates all three stages in quartz cementation (Fig. 6A). Stage I overgrowth formation started at ~42 °C around 450 Ma ($\delta^{18}O = 27.9‰$; Fig. 6A) and at ~1000 m paleo-depth (Fig. 9A). Stage II continued during burial as temperature increased (Fig. 9B), producing 40 μm of overgrowth with gradually decreasing $\delta^{18}O$ (Fig. 6A). Stage III continued after burial reached the maximum paleo-depth (~2200 m; Fig. 9A), producing the final ~45 μm of overgrowth with a slight increase in $\delta^{18}O(OQ)$ (from 18.8 to 20.8‰; Figs 6A, 10B). A second quartz overgrowth was studied from the same sample and also shows this history, decreasing $\delta^{18}O(OQ)$ values early (Stage II), with a slight increase toward the rim from 19.6 to 20.2‰ late (Stage III in Fig. 6B).

The late Stage III cements in sample IL1176EC (Figs. 6, 10C) formed at different conditions than those from Stage II. The $\delta^{18}O$ values obtained from traverses slightly increase from the middle domain to the rim of the overgrowth by up to 2‰. This increase in the $\delta^{18}O(OQ)$ might have resulted from one of these three processes: (1) temperatures decreased (by ~10 °C), possibly due to uplift of the Eau Claire Fm. (by ~300 m) after maximum burial; (2) new higher $\delta^{18}O$ fluids infiltrated locally during Stage III; or (3) $\delta^{18}O$ values of pore fluids increased slightly, perhaps by dehydration of clay minerals or exchange with carbonates in the Eau Claire Fm. during burial. Temperature changes due to uplift (#1) should have affected Mt. Simon $\delta^{18}O(OQ)$ as well, but a slight increase in $\delta^{18}O(OQ)$ is not observed in Mt. Simon samples (Pollington et al., 2011a), therefore, a temperature decrease is not likely to have caused the late increases in $\delta^{18}O(OQ)$. Flowing fluids (#2) in the thin discontinuous sandstone layers within the Eau Claire Fm., which is dominantly composed of tight interbedded siltstones and mudstones, is also unlikely. If significant amounts of high $\delta^{18}O$ fluids moved through these rocks and caused the increase of $\delta^{18}O(OQ)$, the effects should be more important in the aquifer (Mt. Simon) than in the aquitard (Eau Claire), but this has not been seen.

The third possibility, increasing $\delta^{18}O$ of pore water (#3) due to dehydration of clay minerals or carbonate at the highest temperatures (Longstaffe and Ayalon, 1987) is most likely the cause of late rims on quartz overgrowths. Phyllosilicates are plentiful in the Eau Claire samples and would react at higher temperatures (Suchecki and Land, 1983). The overgrowths formed during Stage III (with low, but slightly increasing $\delta^{18}O(OQ)$ values) show slightly brighter CL images, whereas overgrowths formed earlier (during the Stages I and II) have darker CL or a mixture of dark and bright CL images (Fig. 6). Zoning in CL intensity is typically caused by trace element concentration in quartz (Götte et al., 2011; Lehmann et al., 2011; Rusk et al., 2011). The difference in CL contrast of the overgrowths containing different $\delta^{18}O$ values might thus be associated with different chemical compositions due to the reaction of local clay minerals. At maximum burial of the Eau Claire Fm., temperature peaked and further precipitation of overgrowths probably occurred in fluids being expressed from clay-rich intervals, explaining why the subtle increases in $\delta^{18}O$ are only seen in some overgrowths from deeper burial depths.

4.6. Mississippi Valley-type fluid flow

The lowest $\delta^{18}O$ values of latest quartz overgrowth (from late Stage II to Stage III) are 17 to 20‰ (Fig. 5), and if the Basin Evolution Model is correct, this corresponds to precipitation of cement between 270 and 250 Ma (Fig. 9C). It is commonly accepted that at 270 Ma, deep basin brines migrated through permeable sandstones out of the Illinois Basin to form Mississippi Valley-type (MVT) Pb–Zn deposits in southwestern Wisconsin (Upper Mississippi Valley district) (Sverjensky, 1981; Duffin et al., 1989; Bethke and Marshak, 1990; Brannon et al., 1992). Migration of the brines is commonly interpreted to be caused by uplift south of the Illinois Basin associated with the Ouachita Orogeny (Garven et al., 1993; Rowan and Goldhaber, 1996; Pitman et al., 1997), and duration of the hydrothermal fluid flow may have been brief (~200,000 years, Rowan and Goldhaber, 1995). The formation of the latest cements of the Eau Claire and Mt. Simon samples is thus proposed to be during or after the passage of the MVT fluids. It is possible that late cementation occluded permeability, reduced the flow of brines and terminated MVT ore deposition. Note that if quartz cement caused permeability to be reduced to the point that flow shut down, it doesn't necessarily stop quartz cement from continuing to grow in closed pores as there was a continuous silica supply by pressure solution. As discussed in this paper, the cement of the Eau Claire Fm. and Mt. Simon Ss. in the Illinois Basin could be formed in the absence of fluid flow.

4.7. Quartz overgrowths on the Wisconsin Arch

The $\delta^{18}O$ values of quartz overgrowths observed in the Wisconsin samples are on average ~4‰ higher than the $\delta^{18}O$(early OQ) values of more deeply buried Illinois basin samples (Figs. 4, 5B). Similar high $\delta^{18}O$(OQ) values are reported from the outcrops of Ordovician St. Peter Ss. in southern Wisconsin (Kelly et al., 2007; Fig. 5B) and in the Mt. Simon Ss. from central Wisconsin (Pollington et al., 2011b), suggesting that these overgrowths formed at lower temperatures than shown here for the Illinois Basin. Overgrowths in the Wisconsin samples of the Eau Claire Fm. with $\delta^{18}O$ values of ~30‰ would have precipitated at <40 °C if fluids had $\delta^{18}O = -3$‰. Such low temperatures would require that precipitation started at paleo-depths shallower than those in the Illinois samples, possibly in near-surface, water-table, or silcrete environments (Kelly et al., 2007).

In contrast to the zoned overgrowths of deeply buried samples from the Illinois Basin, overgrowths from the Wisconsin Arch are homogeneous in $\delta^{18}O$. Differences between the $\delta^{18}O$(early OQ) and $\delta^{18}O$(late OQ) values were less than SIMS analytical precision (<0.3‰ for 15 μm pits, and <0.8‰ for 3 μm pits) in traverses of single overgrowths in the Eau Claire samples from Wisconsin, whereas most overgrowths from the Illinois Basin have positive $\Delta^{18}O$(early–late) values (+0.2 to +7.6‰) (Fig. 5C). Kelly et al. (2007) also observed that overgrowths in the St. Peter Ss. from Wisconsin are homogeneous in $\delta^{18}O$. Thus, during cementation in the Wisconsin samples, there was little change in the temperature or $\delta^{18}O$ of fluids, probably due to the shallow burial on the Wisconsin Arch and Dome that never exceeded ~500 m.

5. Conclusions

1. *In situ* oxygen isotope analysis using SIMS provides uniquely high spatial resolution, analytical precision, and accuracy for diagenetic cements for mudstones as for sandstones. These data can be correlated with imaging and other forms of analysis to provide new knowledge of the reservoir sealing properties and diagenetic history.
2. The average $\delta^{18}O$ values of detrital quartz grains (10 to 800 μm diameter) in the Eau Claire Fm. are 10.2 ± 2.8‰, and most values are in the range 8 to 11‰, suggesting a dominantly igneous origin. There is no correlation of $\delta^{18}O$(DQ) and grain diameter observed in cross-section. The $\delta^{18}O$ of detrital quartz is independent of rock unit, sample location, or sample depth. The similarity of detrital quartz in the mudstones, siltstones, and sandstones of the Eau Claire Fm. suggests that sources of detrital quartz are the same as in the Mt. Simon and St. Peter Ss.
3. The $\delta^{18}O$ values along traverses of single quartz overgrowths in siltstones and sandstones from the Illinois Basin show large systematic gradients of up to 9.1‰ over thicknesses less than 100 μm. The highest $\delta^{18}O$(OQ) values within each overgrowth ($\delta^{18}O$(early OQ)) are measured close to the detrital grain and relatively uniform at all current depths. The $\delta^{18}O$(OQ) values gradually decrease with increasing distance from the detrital grain. The differences in $\delta^{18}O$(early OQ) and $\delta^{18}O$(late OQ) values are larger for deeper samples.
4. Temperature, depth, and timing of quartz cements in the Illinois Basin are inferred based on application of a new burial and cementation model to measured $\delta^{18}O$ values of quartz overgrowths in the impermeable Eau Claire Fm. and underlying permeable Mt. Simon Ss. The main controls and timing of quartz diagenesis in the Eau Claire Fm. in the Illinois Basin are the same as in the underlying Mt. Simon Ss. These results support the model that porosity-occluding quartz cements formed with increasing temperatures and pressure solution during burial over a period of ~200 million years in the Illinois Basin. Overgrowth formation started at shallow depths around 450 Ma and continued with increasing temperatures during burial until ~250 Ma. Individual overgrowths stopped growing when the rock reached maximum depth or pore-spaces were filled. Some overgrowths from deeper samples show slightly increasing $\delta^{18}O$(OQ) at the latest formation stage, possibly from clay mineral dehydration reactions or exchange with carbonates.
5. The latest quartz overgrowths have $\delta^{18}O$ below 20‰, which indicate the formation at ca. 250 Ma according to the basin model. If correct, cementation continued during and after the passage of brines that formed the Upper Mississippi Valley Pb–Zn District in southwestern Wisconsin at 270 Ma. Thus, the late cementation after 270 Ma could have reduced permeability and terminated the flow of ore-forming brines.
6. The $\delta^{18}O$ values of quartz overgrowths in the Eau Claire Fm., St. Peter Ss. and Mt. Simon Ss. near the Wisconsin Arch are distinct from those in the Illinois basin that were buried more deeply and heated. Quartz overgrowths on the Wisconsin Arch are homogeneous in $\delta^{18}O$, show little difference in the $\delta^{18}O$(early OQ) and $\delta^{18}O$(late OQ) values, and have much higher $\delta^{18}O$(OQ) values than those from the Illinois Basin. The formation of the Wisconsin Arch overgrowths occurred at lower near-surface temperatures, probably below 40 °C.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2014.06.021.

Acknowledgments

We thank Dave Morse, Sallie Greenberg, and Robert Mumm of the Illinois Geological Survey for providing Illinois samples, and Dave Hart of the Wisconsin Geological and Natural History Survey and Wasinee Aswasereelert (UW-Madison) for providing Wisconsin samples. Brian Hess (UW-Madison) prepared sample mounts. Noriko Kita and Jim Kern assisted with SIMS maintenance and analysis. Maciej Sliwinski and Mike Spicuzza prepared Fig. 3. John Fournelle helped in SEM imaging. Dr. Bruce Selleck reviewed and helped to improve this paper substantially. Two samples (from ADM CCS#1 core) for this project were supplied by the Midwest Geological Sequestration Consortium, funded by DOE (DF-FC26-05-NT42588). This project was funded by DOE (93ER14389). The WiscSIMS Ion Microprobe laboratory is partially funded by NSF (EAR-0319230, 1053466).

References

Alexandre, A., Meunier, J.D., Llorens, E., Hill, S.M., Savin, S.M., 2004. Methodological improvements for investigating silcrete formation: petrography, FT-IR and oxygen isotope ratio of silcrete quartz cement, Lake Eyre Basin (Australia). Chem. Geol. 211, 261–274.

Arnold, B.W., Bahr, J.M., Fantucci, R., 1996. Paleohydrogeology of the Upper Mississippi Valley zinc-lead district. Soc. Econ. Geol. Spec. Publ. 7, 378–389.

Aswasereelert, W., Simo, J.A., LePain, D.L., 2008. Deposition of the Cambrian Eau Claire Formation, Wisconsin: hydrostratigraphic implications of fine-grained cratonic sandstones. Geosc. Wis. 19, 1–21.

Bethke, C.M., 1986. Hydrologic constraints on the genesis of the Upper Mississippi Valley Mineral District from Illinois Basin brines. Econ. Geol. 81, 233–249.

Bethke, C., Marshak, S., 1990. Brine migrations across North America — the plate tectonics of groundwater. Annu. Rev. Earth Planet. Sci. 18, 287–315.

Bjørkum, P.A., 1996. How important is pressure in causing dissolution of quartz in sandstones? J. Sediment. Res. 66, 147–154.

Bjørlykke, K., Egeberg, P.K., 1993. Quartz cementation in sedimentary basins. Am. Assoc. Pet. Geol. Bull. 77, 1538–1548.

Blatt, H., 1987. Oxygen isotopes and the origin of quartz. J. Sediment. Petrol. 57, 373–377.

Bowen, B.B., Ochoa, R.I., Wilkens, N.D., Brophy, J., Lovell, T.R., Fischietto, N., Medina, C.R., Rupp, J.A., 2012. Depositional and diagenetic variability within the Cambrian Mount Simon Sandstone. Environ. Geosci. 28, 69–89.

Brannon, J.C., Podosek, F.A., Mclimans, R.K., 1992. Alleghenian age of the Upper Mississippi Valley zinc lead deposit determined by Rb-Sr Dating of sphalerite. Nature 356, 509–511.

Burley, S.D., Mullis, J., Matter, A., 1989. Timing diagenesis in the Tartan Reservoir (UK North Sea): constraints from combined cathodoluminescence microscopy and fluid inclusion studies. Mar. Petrol. Geol. 6, 98–120.

Came, R.E., Eiler, J.M., Veizer, J., Azmy, K., Brand, U., Weidman, C.R., 2007. Coupling of surface temperatures and atmospheric CO_2 concentrations during the Palaeozoic era. Nature 449, 198–201.

Cavosie, A.J., Valley, J.W., Wilde, S.A., E.I.M.F., 2005. Magmatic $\delta^{18}O$ in 4400–3900 Ma detrital zircons: a record of the alteration and recycling of crust in the Early Archean. Earth Planet. Sci. Lett. 235, 663–681.

Chen, Z.S., Riciputi, L.R., Mora, C.I., Fishman, N.S., 2001. Regional fluid migration in the Illinois basin: evidence from in situ oxygen isotope analysis of authigenic K-feldspar and quartz from the Mount Simon Sandstone. Geology 29, 1067–1070.

Clayton, R.N., Mayeda, T.K., O'Neil, J.R., 1972a. Oxygen isotope exchange between quartz and water. J. Geophys. Res. 77, 3057–3067.

Clayton, R.N., Rex, R.W., Syers, J.K., Jackson, M.L., 1972b. Oxygen isotope abundance in quartz from Pacific pelagic sediments. J. Geophys. Res. 77, 3907–3915.

Day-Stirrat, R.J., Milliken, K.L., Dutton, S.P., Loucks, R.G., Hillier, S., Aplin, A.C., Schleicher, A.M., 2010. Open-system chemical behavior in deep Wilcox Group mudstones, Texas Gulf Coast, USA. Mar. Petrol. Geol. 27, 1804–1818.

Duffin, M.E., Lee, M.C., Klein, G.D., Hay, R.L., 1989. Potassic diagenesis of cambrian sandstones and precambrian granitic basement in UPH-3 Deep Hole, Upper Mississippi Valley, USA. J. Sediment. Petrol. 59, 848–861.

Fishman, N.S., 1997. Basin-wide fluid movement in a Cambrian paleoaquifer — evidence from the Mount Simon Sandstone, Illinois and Indiana. In: Montañez, I.P., Gregg, J. M., Shelton, K.L. (Eds.), Basin-wide Diagenetic Patterns; Integrated Petrologic, Geochemical, and Hydrologic Consideration. Soc. Sediment. Geol. Spec. Publ, 57, pp. 221–234.

Friedman, I., O'Neil, J.R., 1977. Compilation of stable isotope fractionation factors of geochemical interes. In: Fleischer, M. (Ed.), Data of Geochemistry. Geological Survey Professional Paper 440-KK. USGS, Reston.

Garven, G., Ge, S., Person, M.A., Sverjensky, D.A., 1993. Genesis of stratabound ore deposits in the Midcontinent basins of North America: 1, the role of regional groundwater flow. Am. J. Sci. 293, 497–568.

Götte, T., Pettke, T., Ramseyer, K., Koch-Muller, M., Mullis, J., 2011. Cathodoluminescence properties and trace element signature of hydrothermal quartz: a fingerprint of growth dynamics. Am. Mineral. 96, 802–813.

Graham, C.M., Valley, J.W., Winter, B.L., 1996. Ion microprobe analysis of $^{18}O/^{16}O$ in authigenic and detrital quartz in the St. Peter Sandstone, Michigan Basin and Wisconsin Arch, USA: contrasting diagenetic histories. Geochim. Cosmochim. Acta 60, 5101–5116.

Harwood, J., Aplin, A.C., Fialips, C.I., Iliffe, J.E., Kozdon, R., Ushikubo, T., Valley, J.W., 2013. Quartz cementation history of sandstones revealed by high resolution SIMS oxygen isotope analysis. J. Sediment. Res. 83, 522–530.

Haszeldine, R.S., Samson, I.M., Cornford, C., 1984. Dating diagenesis in a petroleum basin, a new fluid inclusion method. Nature 307, 354–357.

Hervig, R.L., Williams, L.B., Kirkland, I.K., Longstaffe, F.J., 1995. Oxygen-isotope microanalyses of diagenetic quartz - possible low-temperature occlusion of pores. Geochim. Cosmochim. Acta 59, 2537–2543.

Hiatt, E.E., Kyser, T.K., Fayek, M., Polito, P., Holk, G.J., Riciputi, L.R., 2007. Early quartz cements and evolution of paleohydraulic properties of basal sandstones in three Paleoproterozoic continental basins: Evidence from *in situ* $\delta^{18}O$ analysis of quartz cements. Chem. Geol. 238, 19–37.

Hoefs, J., 2009. Stable Isotope Geochemistry. Springer Publishers, Berlin.

Hower, J., Eslinger, E., Hower, M.E., Perry, E.A., 1976. Mechanism of burial metamorphism of argillaceous sediment: 1. Mineralogical and chemical evidence. Geol. Soc. Am. Bull. 87, 725–737.

Jaffrés, J.B.D., Shields, G.A., Wallmann, K., 2007. The oxygen isotope evolution of seawater: A critical review of a long-standing controversy and an improved geological water cycle model for the past 3.4 billion years. Earth Sci. Rev. 83, 83–122.

Kelly, J.L., Fu, B., Kita, N.T., Valley, J.W., 2007. Optically continuous silcrete quartz cements of the St. Peter Sandstone: High precision oxygen isotope analysis by ion microprobe. Geochim. Cosmochim. Acta 71, 3812–3832.

Kennedy, A.K., Arikan, F., 1990. Spalled quartz overgrowths and a potential source of silt. J. Sediment. Petrol. 60, 438–444.

Kita, N.T., Ushikubo, T., Fu, B., Valley, J.W., 2009. High precision SIMS oxygen isotope analysis and the effect of sample topography. Chem. Geol. 264, 43–57.

Lehmann, K., Pettke, T., Ramseyer, K., 2011. Significance of trace elements in syntaxial quartz cement, Haushi Group sandstones, Sultanate of Oman. Chem. Geol. 280, 47–57.

Lohmann, K.C., Walker, J.C.G., 1989. The $\delta^{18}O$ record of Phanerozoic abiotic marine calcite cements. Geophys. Res. Lett. 16, 319–322.

Longstaffe, F.J., Ayalon, A., 1987. Oxygen-isotope studies of clastic diagenesis in the Lower Cretaceous Viking Formation, Alberta: implications for the role of meteoric water. In: Marshall, J.D. (Ed.), The Diagenesis of Sedimentary Sequences. Geological Society Special Publication No. 36. Blackwell Scientific Publications, Oxford, pp. 277–296.

Makowitz, A., Lander, R.H., Milliken, K.L., 2006. Diagenetic modeling to assess the relative timing of quartz cementation and brittle grain processes during compaction. Am. Assoc. Pet. Geol. Bull. 90, 873–885.

Milliken, K.L., Mack, L.E., Land, L.S., 1994. Elemental mobility in sandstones during burial — whole-rock chemical and isotopic data, Frio Formation, South Texas. J. Sediment. Res. 64, 788–796.

Nelson, J., 1998. Bedrock geology of the Paducah 1 degree × 2 degrees CUSMAP quadrangle, Illinois, Indiana, Kentucky, and Missouri. USGS Bull. 2150-B.

Neufelder, R.J., Bowen, B.B., Lahann, R.W., Rupp, J.A., 2012. Lithologic, mineralogical and petrophysical characteristics of the Eau Claire Formation: complexities of a carbon storage system seal. Environ. Geosci. 19, 81–104.

Ostrom, M.E., 1978. Stratigraphic relationships of lower Paleozoic rocks of Wisconsin. In: Odom, I.E. (Ed.), Lithostratigraphy, petrology, and sedimentology of Late Cambrian–Early Ordovician Rocks near Madison, Wisconsin. Wisconsin Geological and Natural History Survey Field Trip Guide Book, 3. University of Wisconsin-Extension Geological and Natural History Survey, Madison, pp. 3–22.

Peltonen, C., Marcussen, Ø., Bjørlykke, K., Jahren, J., 2009. Clay mineral diagenesis and quartz cementation in mudstones: the effects of smectite to illite reaction on rock properties. Mar. Petrol. Geol. 26, 887–898.

Pitman, J.K., Goldhaber, M.B., Spoetl, C., 1997. Regional diagenetic patterns in the St. Peter Sandstone: implications for brine migration in the Illinois Basin. U.S. Geol. Surv. Bull. 2094-A, A1–A17.

Pollington, A.D., Kozdon, R., Valley, J.W., 2011a. Evolution of quartz cementation in the Illinois Basin during burial of the Mt. Simon Sandstone: *in situ* microanalysis of $\delta^{18}O$. Geology 39, 1119–1122.

Pollington, A.D., Kozdon, R., Kitajima, K., Strickland, A., Valley, J.W., 2011b. *In situ* O & Si Isotopic Microanalysis of Diagenetic Cements: Basin Brines vs. Weathering, Low vs. High T: Mineralogical Magazine Goldschmidt Conference, Prague, 75, p. 1656.

Rowan, E.L., Goldhaber, M.B., 1995. Duration of mineralization and fluid-flow history of the Upper Mississippi Valley zinc-lead district. Geology 23, 609–612.

Rowan, E.L., Goldhaber, M.B., 1996. Fluid inclusions and biomarkers in the Upper Mississippi Valley zinc-lead district: implications for the fluid-flow and thermal history of the Illinois Basin. USGS Bull. 2094-F, F1–F34.

Rowan, E.L., Goldhaber, M.B., Hatch, J.R., 2002. Regional fluid flow as a factor in the thermal history of the Illinois basin: constraints from fluid inclusions and the maturity of Pennsylvanian coals. Am. Assoc. Pet. Geol. Bull. 86, 257–277.

Rusk, B., Koenig, A., Lowers, H., 2011. Visualizing trace element distribution in quartz using cathodoluminescence, electron microprobe, and laser ablation-inductively coupled plasma-mass spectrometry. Am. Mineral. 96, 703–708.

Savin, S.M., Epstein, S., 1970. Oxygen isotopic compositions of coarse grained sedimentary rocks and minerals. Geochim. Cosmochim. Acta 34, 323–329.

Schieber, J., Krinsley, D., Riciputi, L., 2000. Diagenetic origin of quartz silt in mudstones and implications for silica cycling. Nature 406, 981–985.

Stueber, A.M., Walter, L.M., 1991. Origin and chemical evolution of formation waters from Silurian–Devonian strata in the Illinois basin, USA. Geochim. Cosmochim. Acta 55, 309–325.

Suchecki, R.K., Land, L.S., 1983. Isotopic geochemistry of burial-metamorphosed volcanogenic sediments, Great Valley sequence, northern California. Geochim. Cosmochim. Acta 47, 1487–1499.

Sverjensky, D.A., 1981. Isotopic alteration of carbonate host rocks as a function of water to rock ratio; an example from the Upper Mississippi Valley zinc–lead district. Econ. Geol. Bull. Soc. 76, 154–157.

Valley, J.W., Kita, N.T., 2009. *In situ* oxygen isotope geochemistry by ion microprobe. In: Fayek, M. (Ed.), Secondary Ion Mass Spectrometry in the Earth Sciences. Mineral. Assoc. Canada Short Course, 41, pp. 19–63.

van de Kamp, P., 2008. Smectite-illite-muscovite transformations, quartz dissolution, and silica release in shales. Clay Clay Miner. 56, 66–81.

Walderhaug, O., 1996. Kinetic modeling of quartz cementation and porosity loss in deeply buried sandstone reservoirs. Am. Assoc. Pet. Geol. Bull. 80, 731–745.

Williams, L.A., Crerar, D.A., 1985. Silica diagenesis. II. General mechanisms. J. Sediment. Petrol. 55, 312–321.

Williams, L.B., Hervig, R.L., Bjorlykke, K., 1997. New evidence for the origin of quartz cements in hydrocarbon reservoirs revealed by oxygen isotope microanalyses. Geochim. Cosmochim. Acta 61, 2529–2538.

Winter, B.L., Johnson, C.N., Simo, J.A., Valley, J.W., 1995. Paleozoic fluid history of the michigan basin: evidence from dolomite geochemistry in the Middle Ordovician St. Peter Sandstone. J. Sediment. Res. A65, 306–320.

Worden, R.H., Morad, S., 2000. Quartz cementation in oil field sandstones: a review of the key controversies. In: Worden, R.H., Morad, S. (Eds.), Quartz Cementation in Sandstones. Wiley-Blackwell, Oxford, pp. 1–20.