

^{PS} In-Situ, Micron-Scale $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ Analyses (by SIMS) of Chemo-Isotopically Claire Formation, Illinois Basin, USA*

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Abstract

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of zoned carbonate cements of diagenetic origin can be measured in-situ on the sub-10- μm scale using Secondary Ion Mass Spectrometry (SIMS). A critical aspect of analytical methods advancement is the continued development of standards for correcting systematic, compositionally-dependent - but generally highly non-linear - sample matrix effects that bias measured isotope ratios. Precision is a trade-off with beam size and, depending on the isotope system, varies between $\pm 0.3\text{‰}$ (2SD; 10 μm beam, $\delta^{18}\text{O}$) and $\pm 1.0\text{‰}$ (2SD; 3 μm beam for $\delta^{18}\text{O}$, 5-10 μm beam for $\delta^{13}\text{C}$). Analyses on this scale enhance the spatial resolution in applied problems relating to carbonate diagenesis and carbonate cementation of sandstone-shale systems. For example, by preserving petrographic relations between two different authigenic cement phases exhibiting equilibrium growth textures (e.g. dolomite-quartz overgrowths), in-situ $\delta^{18}\text{O}$ measurements provide a temperature constraint for a particular stage of cementation that is independent of assumptions about the $\delta^{18}\text{O}$ of porewaters from which cements precipitated. Transects across early-to-late cement generations provide a clearly-resolved, zone-by-zone account of changes in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ which elucidate the evolution of diagenetic conditions, including (1) temperature during progressive burial and heating, (2) isotopically-distinct fluid/brine migration events, (3) the progression of organic matter (OM) maturation, and (4) the reaction of smectite \Rightarrow illite clay, which affects porewater $\delta^{18}\text{O}$.

A regional case study of dolomite-ankerite cements in the sandy-shaly Late Cambrian Eau Claire Formation of the Illinois Basin reveals systematic depth-related C- and O-isotope zoning (early-to-late $\delta^{18}\text{O}$: $-5\Rightarrow -16\text{‰}$ VPDB, $\delta^{13}\text{C}$ $\sim 0\Rightarrow -10\text{‰}$ VPDB). $\delta^{18}\text{O}$ -based T-modeling - using both internal and external constraints on porewater $\delta^{18}\text{O}$ - indicates heating to $\sim 90^\circ\text{C}$ during basin subsidence, and additional conductive heating to $\sim 130^\circ\text{C}$ during the basin-scale, Late Paleozoic hot brine migrations through the underlying Mt. Simon sandstone aquifer that resulted in regional Mississippi Valley-type ore body formation. The $\delta^{13}\text{C}$ of the latest cement generations indicates only a moderate contribution of OM-derived, isotopically-light C, reflecting the overall organic-leanness of Eau Claire sediments (TOC $< 0.5\%$). These results

compliment SIMS studies of $\delta^{18}\text{O}$ in quartz-overgrowths of the Eau Claire and Mt. Simon formations (Hyodo et al., 2014; Pollington et al., 2011).

Selected References

Hyodo, Ayumi, Reinhard Kozdon, Anthony D. Pollington, and John W. Valley, 2014, Evolution of quartz cementation and burial history of the Eau Claire Formation based on in situ oxygen isotope analysis of quartz overgrowths: *Chemical Geology* 384, p. 168-180.

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

In-situ, Micron-Scale $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ Analyses (by SIMS) of Chemo-isotopically Zoned Carbonate Cements of Diagenetic Origin –

A Case Study on the Implications for the Thermal and Burial History of the Eau Claire Fm., Illinois Basin (U.S.A.)

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Abstract

The $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ of zoned carbonate cements of diagenetic origin can be measured in-situ on the sub-10- μm scale using Secondary Ion Mass Spectrometry (SIMS). A critical aspect of analytical methods advancement is the continued development of standards for correcting systematic, composition-dependent - but generally highly non-linear - sample matrix effects that bias measured isotope ratios [1,2]. Precision is a trade-off with beam size and, depending on the isotope system, varies between $\pm 0.3\text{‰}$ (2SD; 10 μm beam, $\delta^{18}\text{O}$) and $\pm 1.0\text{‰}$ (2SD; 3 μm beam for $\delta^{18}\text{O}$, 5-10 μm beam for $\delta^{13}\text{C}$).

Analyses on this scale provide unprecedented spatial resolution in applied problems relating to carbonate diagenesis and carbonate cementation of sandstone-shale systems. For example, by preserving petrographic relations between two different authigenic cement phases exhibiting equilibrium growth textures (e.g. dolomite-quartz overgrowths), in-situ $\delta^{18}\text{O}$ measurements provide a temperature constraint for a particular stage of cementation that is independent of assumptions about the $\delta^{18}\text{O}$ of porewaters from which cements precipitated. Transects across early-to-late cement generations provide a clearly-resolved, zone-by-zone account of changes in $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ which elucidate the evolution of diagenetic conditions, including 1) temperature during progressive burial and heating, 2) isotopically-distinct fluid/brine migration events, 3) the progression of organic matter (OM) maturation and 4) the reaction of smectite-to-illite, which affects porewater $\delta^{18}\text{O}$.

A regional case study [3] of dolomite-ankerite cements in the sandstone beds of largely silty-shaly Late Cambrian Eau Claire Fm of the Illinois Basin reveals systematic depth-related C- and O-isotope zoning (early-to-late $\delta^{18}\text{O}$: 25 to 14‰ VSMOW, $\delta^{13}\text{C}$ ~0 to -9‰ VPDB). $\delta^{18}\text{O}$ -based temperature-modeling - using both internal and external constraints on porewater $\delta^{18}\text{O}$ - indicates heating to ~85°C during basin subsidence, and additional conductive heating to ~120°C at the basin-scale, late Paleozoic hot brine migrations through the underlying Mt Simon sandstone aquifer that resulted in regional Mississippi Valley-type ore body formation. The $\delta^{13}\text{C}$ of the latest cement generations indicates only a minor contribution of OM-derived, isotopically-light C, reflecting the overall organic-leaness of Eau Claire sediments (TOC <0.5%). These results complement SIMS studies of $\delta^{18}\text{O}$ in quartz-overgrowths of the Eau Claire, Mt Simon and St Peter Fms [4,5,6].

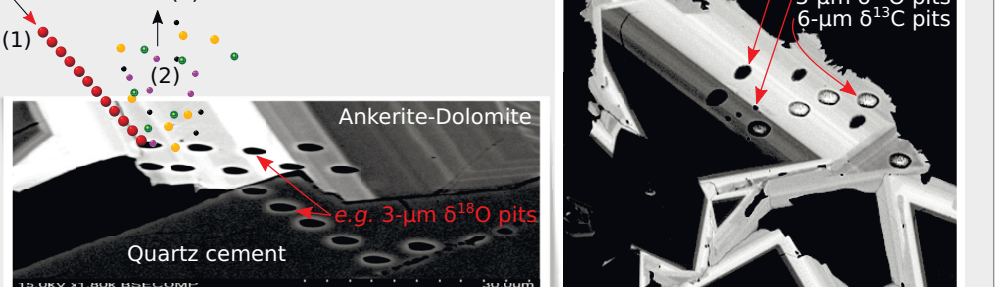
Analytical Method

SIMS (secondary ion mass spectrometry)

Briefly,

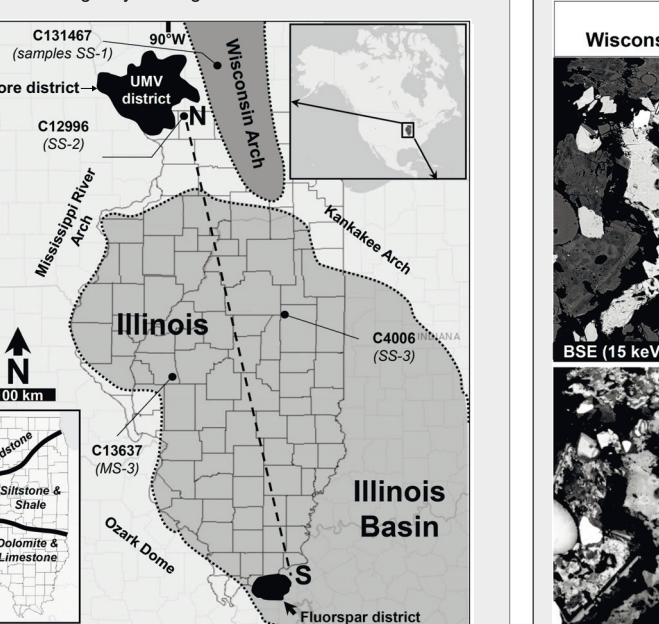
- (1) Focused beam of Cs^+ ions bombards sample ('sputtering')
- (2) Impact causes sample ionization (i.e., production of $^{18}\text{O}^+$ & $^{16}\text{O}^+$ ions, $^{13}\text{C}^+$ & $^{12}\text{C}^+$ ions)
- (3) Ions of interest collected, counted and ratios of different isotopes calculated (e.g., $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$)
- (4) Isotope ratios converted to conventional 'δ-values' by comparison to international reference standards

(3) To detector

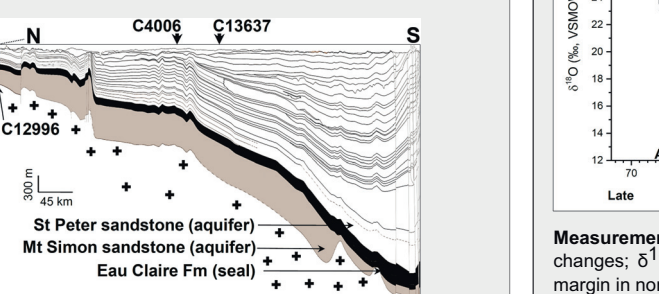


Study Area

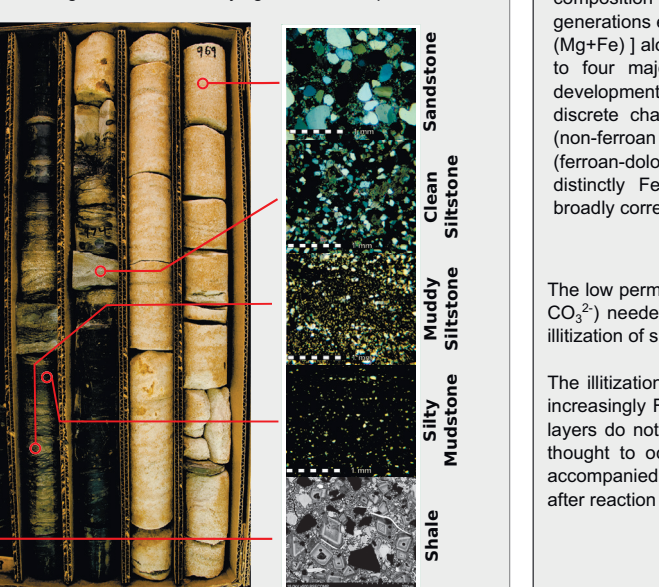
Focus on the lithologically heterogeneous Late Cambrian Eau Claire Fm



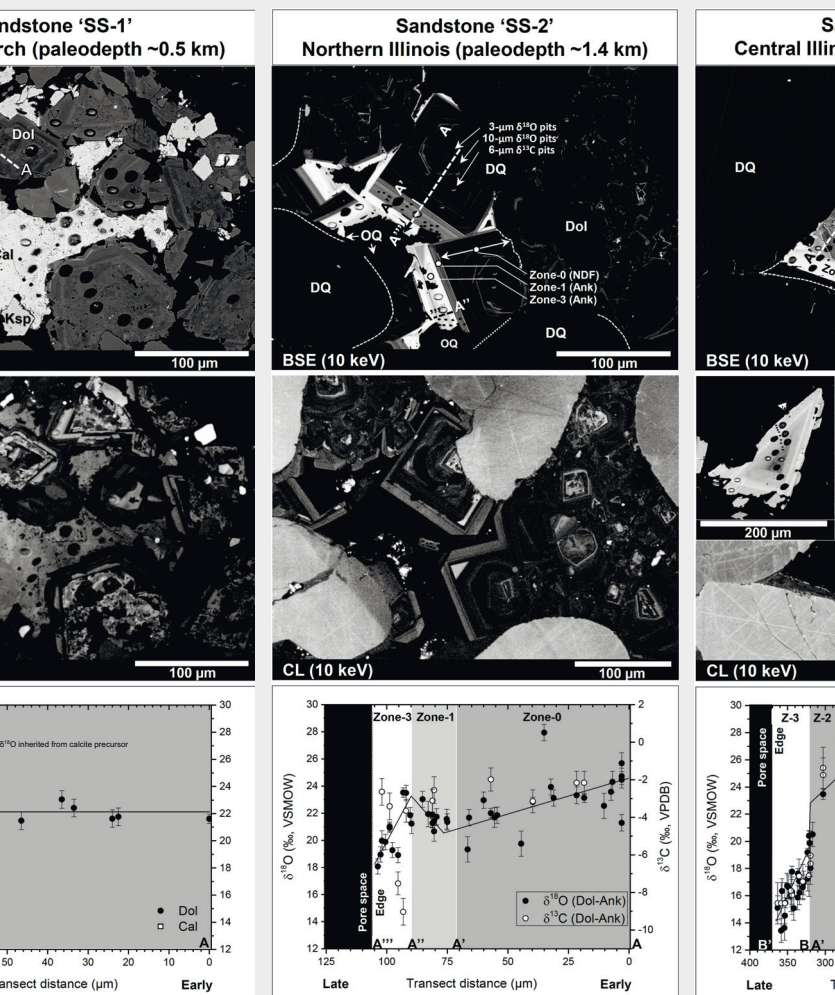
Hydrothermal heating associated with the emplacement of early to mid-Permian MVT ore bodies in SW Wisconsin and Southern Illinois is an important component in understanding the thermal evolution of the Illinois Basin and the anomalously advanced diagenetic maturity of its strata relative to present day or reconstructed maximum burial depths [7].



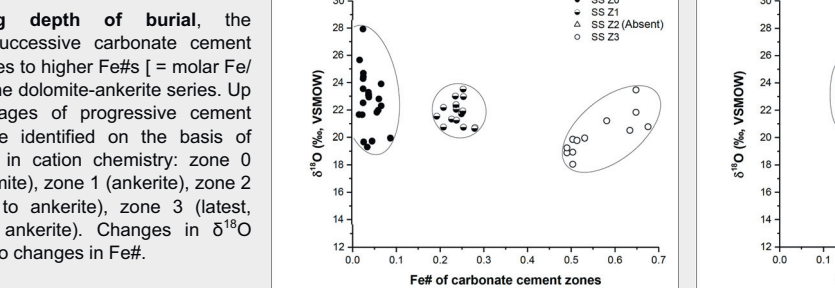
Due to its generally low-permeability [8], the pore fluids of the Eau Claire Formation likely remained isolated from direct contact with the hot mineralizing brines (~100-175°C) that migrated through under- and overlying sandstone aquifers.



Chemo-isotopic evolution of carbonate cements



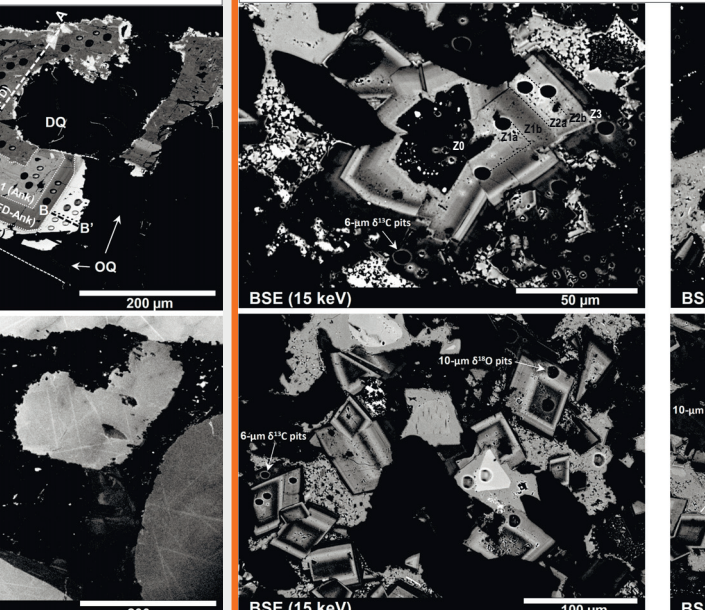
Measurements of $\delta^{18}\text{O}$ in transects (100-500- μm scale) extending from early to late carbonate cement generations reveal systematic, cross-basin changes; $\delta^{18}\text{O}(\text{cement})$ evolves towards lower values with increasing paleodepth, grading from 25‰ to 18‰ (VSMOW) in cements of the basin margin in northern Illinois (sample SS-2), and decreasing further to 14‰ in the central Illinois Basin (sample SS-3).



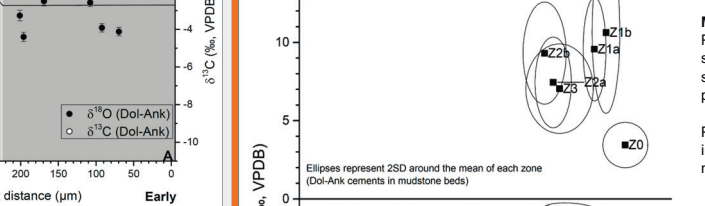
The low permeability of the Eau Claire Fm [8] excludes the through-flow of external fluids as a likely source of the dissolved ions (Ca^{2+} , Fe^{2+} , Mg^{2+} and CO_3^{2-}) needed for carbonate cement authigenesis in the sandstone beds of the Eau Claire Fm. Probable internal sources include the progressive illitization of smectitic clays and organic matter diagenesis within the interbedded mudstone beds, in addition to the dissolution of early calcite cements.

The illitization of smectite is of particular importance in sandstone-shale systems as a source of dissolved Fe^{2+} , Mg^{2+} and Ca^{2+} for the formation of increasingly Fe-rich dolomite and ankerite cements during progressive sediment burial and heating [9]. It is thought that Fe- and/or Mg-rich smectite layers do not react as readily to form illite as do the more aluminous and Ca-rich smectite compositions; the large-scale illitization of the former is thought to occur near the upper end (~125°C, e.g., [9]) of the temperature range proposed for the reaction (60-140°C; e.g. [10]), and to be accompanied by the release of large quantities of aqueous Fe^{2+} and Mg^{2+} into pore fluids (approx. 4 moles of Fe^{2+} and Mg^{2+} for each mole of smectite; after reaction 2 of [9]).

The contrasting evolution of carbonate cement $\delta^{13}\text{C}$ in sandstone vs. mudstone beds



Mudstone beds: Presence of pyrite indicates that mudstone beds were sufficiently TOC-rich to allow for the establishment of sulfate-reducing conditions during diagenesis (at present TOC < 0.5%).



Sandstone beds: A predominant lack of pyrite indicates that sulfate-reducing conditions were not firmly established, likely owing to low TOC content of the sandstone beds.

The near 0‰ $\delta^{13}\text{C}$ values of dolomite-ankerite cement zones 0, 1 and 2 in the sampled sandstone beds are consistent with seawater as the dominant source of dissolved C for carbonate cementation.

The modestly negative $\delta^{13}\text{C}$ values of the latest ankerite cement (zone 3, ~9‰) indicate that CO_2 derived from an organic source was at least partially involved in its formation. The oxidation of CH_4 gas escaping from adjacent mudstones is a plausible source.

A brief review of the trends in the $\delta^{13}\text{C}$ of CO_2 associated with different stages of microbial organic matter recycling

The decomposition of sedimentary organic matter (OM) by microbial communities during diagenesis proceeds sequentially through several different characteristic stages, all of which release CO_2 into porewaters: aerobic oxidation, followed by the reduction of nitrate, Fe- & Mn-oxides (+ Fe/Mn-oxide) and sulfate, and lastly fermentation (bacterial methanogenesis, to a temperature of ~75°C [e.g., 11]).

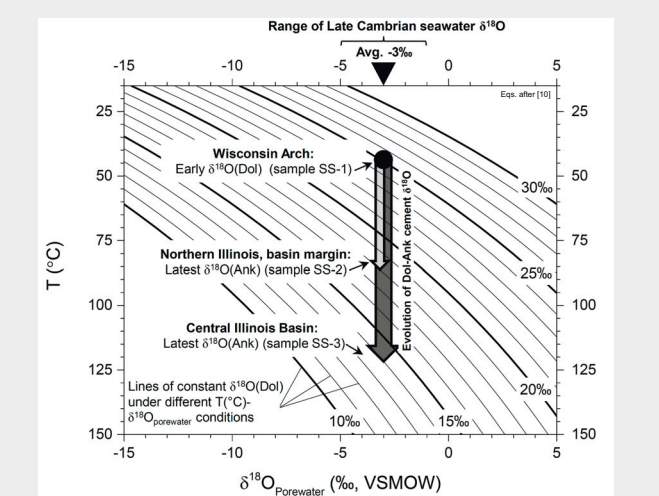
The first three stages produce CO_2 (which equilibrates to HCO_3^- and CO_3^{2-}) with $\delta^{13}\text{C}$ values that resemble that of the bulk organic matter (~25‰ on average). Thus, the $\delta^{13}\text{C}$ of carbon dissolved in porewaters will tend towards ~25‰ (depending on volume of OM-derived CO_2 generated). Carbonate cements that precipitate during these stages will take on negative $\delta^{13}\text{C}$ values. For example: If $\delta^{13}\text{C}$ of porewater CO_2 = -25‰, the $\delta^{13}\text{C}$ of dolomite will be -16.5‰ at 50°C and -21.5‰ at 120°C [e.g., 11,12].

In contrast, bacterial methanogenesis consumes CO_2 and yields CH_4 gas with exceptionally low negative $\delta^{13}\text{C}$ values (down to ~110‰). The residual CO_2 reservoir thus becomes enriched in ^{13}C , acquiring $\delta^{13}\text{C}$ values that are larger than those of CH_4 by 40-100‰ (values may reach +15-25‰). Carbonate cements that precipitate during this stage may take on positive $\delta^{13}\text{C}$ values (depending on the extent to which CO_2 is enriched). For example: If $\delta^{13}\text{C}$ of porewater CO_2 = +5‰, the $\delta^{13}\text{C}$ of dolomite will be +13.5‰ at 50°C and +8.5‰ at 120°C [11,12,13].

If methane gas migrates away from its source area and reaches sediment beds where porewaters still contain oxidants (e.g., dissolved sulfate, nitrate or oxygen), it will undergo bacterial methane oxidation. The CO_2 thus formed becomes enriched in ^{13}C , with $\delta^{13}\text{C}$ values becoming 5-30‰ lower relative to the CH_4 being consumed; this process thus lowers the $\delta^{13}\text{C}$ of carbon dissolved in porewaters (to an extent that depends on the volume of CO_2 thus produced in relation to the size of the porewater dissolved carbon reservoir) [11,13].

Integration of $\delta^{18}\text{O}$ trends with Illinois Basin burial & thermal history models

Carbonate cement precipitation temperatures were calculated with the same parameters used to model the temperature history of quartz cementation in the Mt Simon and Eau Claire Fms [4,5]: constant porewater $\delta^{18}\text{O}$ = -3‰ (avg. Cambrian seawater), geothermal gradient of 30°C/km with a surface temperature of 20°C, and correction of present-day burial depths to account for uplift/erosion (~1 km within the Illinois Basin and < 0.5 km on the Wisconsin Arch).



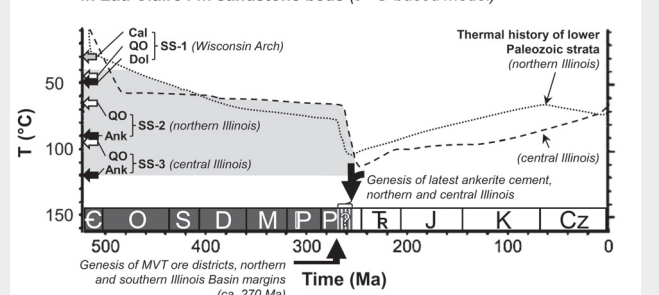
Precipitation temperature estimates based on $\delta^{18}\text{O}$ for the earliest and latest quartz-overgrowth (QOs) and carbonate cements in Eau Claire Fm sandstone beds sampled for this study at three cored localities

Sample name	Max. burial depth (m)	$\delta^{18}\text{O}$ (‰ VSMOW)	Model T(°C)	Latest carbonate cement $\delta^{18}\text{O}$ (‰ VSMOW)	Model T(°C)	Early quartz-overgrowth $\delta^{18}\text{O}$ (‰ VSMOW)	Model T(°C)	Latest quartz-overgrowth $\delta^{18}\text{O}$ (‰ VSMOW)	Model T(°C)	Model T(°C) expected at max. burial
SS-1	<500	25‰ (avg.)	30° (Cal)	N/A	N/A	28-28‰	40-55°	28-28‰	40-55°	35
SS-2	1371	24‰ (avg.)	50° (Dol)	18‰	90° (Ank)	28-28‰	40-55°	24‰	65°	60
SS-3	2178	22‰ (avg.)	50° (Dol)	14‰	120° (Ank)	28-28‰	40-55°	19‰	95°	85

¹ Data from [6].
² Model of [8] integrated with Illinois Basin burial and thermal history models of [7] and [12] (geothermal gradient = 30°C/km, 20°C at the surface).

When integrated with Illinois Basin burial and thermal history models that are independently-constrained [7,15], this range of temperatures indicates that cements began precipitating soon after deposition during Late Cambrian time and continued developing, perhaps intermittently, into the early to mid-Permian (until ca. 270-250 Ma); authigenesis ended before the onset of uplift-related cooling beginning in the late Permian.

Precipitation temperatures of latest quartz and carbonate cements in Eau Claire Fm sandstone beds ($\delta^{18}\text{O}$ -based model)



The basin-wide precipitation of the latest, distinctly Fe-rich ankerite cement (zone 3) is inferred to have occurred (nearly)-contemporaneously with conductive heating of the Eau Claire Fm from under- and overlying sandstone aquifers through which hot Mississippi Valley-Type mineralizing brines migrated at ca. 270 Ma. This inference plausibly explains the anomalously high $\delta^{18}\text{O}$ -based precipitation temperature estimates for this late cement (30-35°C higher than burial model predictions; [15,5]) in the sandstone beds of basin margin in northern Illinois and in the central Illinois Basin.