

CARBONATE, SILICATE, AND SULFIDE MINERAL DIAGENETIC HISTORIES FROM THE BAKKEN AND
TRAVIS PEAK FORMATIONS BY SIMS

By

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General Acknowledgements

The website www.healingwithcrystals.net explains in no uncertain terms that dolomite reduces insomnia and irregular sleep patterns, creates inner tranquility, promotes self-confidence, increases my stamina, and can even thicken my hair. Of all the mineral phases I discuss in the following pages, dolomite is the one I have spent the most time working with and thinking about during my time at the University of Wisconsin-Madison. I can personally attest that dolomite performs none of the functions listed above.

It is the people in my life, not the minerals, that have borne that responsibility.

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Introduction

Diagenesis is “a broad spectrum of physical, chemical and biological post-depositional processes by which original sedimentary assemblages and their interstitial pore waters react in an attempt to reach textural and geochemical equilibrium with their environment” (Figure 0.1) (Worden and Burley, 2003). Put more simply, it is the set of processes by which sediment is turned into sedimentary rock. If the minerals that compose the original sediment may be considered a “primary” record of the surficial environment, then diagenesis comprises the growth of secondary mineralizations and overgrowths that serve to cement the sediment together and turn it into rock. In the process, these cements that form may in turn record in their chemical compositions a record of contemporaneous conditions in the porewater, and overprint primary environmental geochemical signals.

Introduction to $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and $\delta^{34}\text{S}$

Since the pioneering work of Harold Urey and others during the late 1940s and 1950s (e.g. Urey, 1947; Urey, 1948), stable isotope geochemistry has developed into a potent and widely used tool for approaching geological problems (Hoefs, 2009). The light stable isotopes have found a great deal of utility in the sedimentary geochemistry community, as the abundance of these lighter isotopes in the natural system makes their relative abundances in rocks an indicator of global environmental change, and the low surface temperatures at which sedimentary rocks form are conducive to larger and more easily measured isotopic

fractionations. In particular, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and $\delta^{34}\text{S}$ have seen widespread use as tools for the interpretation of sedimentary rocks and environments in Earth's past.

The expected $\delta^{18}\text{O}$ value of a mineral precipitate is a function of temperature and the $\delta^{18}\text{O}$ of the fluid it precipitates from (Friedman and O'Neil, 1977). This allows one to use mineral $\delta^{18}\text{O}$ to infer temperature if the $\delta^{18}\text{O}$ of the precipitating fluid is known, or infer fluid $\delta^{18}\text{O}$ if the temperature is known. As calcite is a direct precipitate from seawater at low temperatures, carbonate rocks have been used to generate records of past temperature and ocean $\delta^{18}\text{O}$ change. Significant variability has been observed in carbonates throughout geologic time (Figure 0.2) (Veizer et al., 1999; Prokoph et al., 2008), but interpreting this variability has challenges. Pore space in carbonate rocks can be filled with diagenetic carbonates grown from non-oceanic fluids at elevated (non-surface) temperatures (Śliwiński et al., 2016; Denny et al., 2017), and carbonate minerals themselves have been known to recrystallize under certain conditions, changing their isotopic value (Swart, 2015). The situation becomes more complex once a rock has undergone enough (≈ 100 s of meters) burial, as water-rock exchange through diagenetic processes will drive porewater $\delta^{18}\text{O}$ compositions away from their starting value (Clayton et al., 1966), which will in turn affect the $\delta^{18}\text{O}$ composition of subsequent mineral precipitates.

In contrast with $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ values of carbonates are less impacted by temperature and are thereby considered better indicators of the $\delta^{13}\text{C}$ composition of the fluid from which they form. Biological processes are tied to the most significant $\delta^{13}\text{C}$ fractionations in nature, with buried organic matter possessing $\delta^{13}\text{C}$ values much lower (by about 25-30‰) than contemporaneous $\delta^{13}\text{C}$ values from carbonate (Hoefs, 2009). Despite the reduced impact of

temperature on fractionations, significant $\delta^{13}\text{C}$ variability can be found in carbonates throughout geologic time, particularly in the Precambrian (Figure 0.3) (Veizer et al., 1999; Prokoph et al., 2008). For this reason, $\delta^{13}\text{C}$ measured in both organic matter and carbonates have been used to infer information about changes to the past global environment, particularly concerning the fluxes into (volcanic activity, methane releases) and out of (organic vs. inorganic carbon burial) the ocean-atmospheric system. However, diagenetic processes can also impact the $\delta^{13}\text{C}$ value of carbonates, mostly through the conversion of low- $\delta^{13}\text{C}$ organic matter into CO_2 by a variety of biogenic and abiogenic processes (Oehlert and Swart, 2014; Bojanowski et al., 2015; Denny et al., 2017). As with $\delta^{18}\text{O}$, the processes of recrystallization and cement precipitation are nontrivial problems for interpreting primary $\delta^{13}\text{C}$ values.

Similar to calcite, sulfate minerals can precipitate directly out of evaporating ocean water. As the fractionation produced during this process is negligible (Raab and Spiro, 1991), sulfate mineral $\delta^{34}\text{S}$ is considered to be good records of seawater $\delta^{34}\text{S}$ sulfate compositions so long as the minerals in question can be demonstrated to be primary. By contrast, formation of pyrite in the sediment is recognized as a purely diagenetic process tied to biogeochemical sulfate reduction, a process which leads to large fractionations and sometimes distillation effects (Fike et al., 2015). The records of both sulfate and sulfide $\delta^{34}\text{S}$ have been studied as a means of understanding changing redox processes, microbial metabolisms, and sulfate availability in Earth's past (Figure 0.4) (Prokoph et al., 2008; Canfield and Farquhar, 2009). However, a growing body of research is showing just how easily sulfide records may be misinterpreted on the basis of bulk values by failing to capture magnitude of μm -scale $\delta^{34}\text{S}$ variability, or by not fully appreciating sulfide formation as integrally linked to sedimentation

rates and biological activity in a potentially restricted environment (Q. Lin et al., 2016; Z. Lin et al., 2016; Pasquier et al., 2017; Cui et al., 2018).

Outstanding Questions

As aforementioned, all of these isotopic systems have tremendous potential for interpreting Earth's past surface environment. However, until we gain a more thorough understanding of how these records are preserved over the course of burial and sediment diagenesis, there will remain a very real risk in assuming that variability in these records fully reflects surficial processes. The terms "sedimentary rock" and "diagenesis" are, by their very definitions, intimately linked. There are hardly any sedimentary rocks that have not undergone diagenesis in some form or degree, for if they had not, they would still be sediment. The only exceptions to this rule would be direct chemical precipitates such as calcite or evaporite minerals, but even these phases are prone to low-temperature recrystallization and other processes that might alter the original chemical composition. If all sedimentary rocks are probably altered to some degree, then the questions we must ask to move forward are these:

- What are the causes of observed μm -scale isotopic variability in diagenetic cements and sediments in general?
- Do the large ($>10\%$) and reproducible isotopic zonations observed in transects of diagenetic minerals more commonly reflect local or regional processes?
- What do observations of μm -scale variability in primary and diagenetic phases indicate about the interpretations of bulk analyses for different rock types?
- How well can the timing of diagenetic cement formation be reasonably constrained?

- How does one best identify which biomineralic or petrographic phases in rocks are most likely to accurately preserve “primary” geochemical signals?
- How can we reconstruct and/or model water-rock interaction chemistry from early through late burial, and can such models provide additional constraints on the interpretation of bulk and μm -scale geochemical analyses?

By allowing for the analysis of individual cements within their full petrographic context, microanalytical techniques offer exciting opportunities to address these issues. By integrating SIMS and EPMA analyses, SEM imagery, and computer modeling, I will explore possible answers to all of these questions in the following chapters.

Overview of Chapters

Chapter 1 focuses on carbonate diagenesis in the middle member of the Bakken Formation, which contains ankerite-series carbonates that show extensive zonation in $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and Fe content. In particular, this chapter examines the extent to which the μm -scale cements left behind by carbonate diagenesis may be tied to processes occurring in the rock across the basin, at scales of 10s to 100s of kilometers. I show that observed zonations can be correlated across the basin, and in doing so I am able to detect preserved geochemical signals of hydrocarbon expulsion and fluid infiltration along basin margins. I also demonstrate that these cements are not forming in response to a single event.

Chapters 2 and 3 tell the story of sulfide $\delta^{34}\text{S}$ in the Bakken, how microanalytical measurements of $\delta^{34}\text{S}$ in sulfides allow for a better understanding of formation processes, and why any bulk analysis $\delta^{34}\text{S}$ study must pay careful attention to the mineral petrography of the

samples in question. Chapter 2 documents a bimodal distribution in Bakken sulfide $\delta^{34}\text{S}$ values that cannot be ascribed to a single process driving sulfide formation, and show that petrography is an effective predictor of which sulfide phases possess what $\delta^{34}\text{S}$ values. Chapter 3 focuses on a subset of this data associated with framboidal pyrite, and examines fundamental questions concerning the origin of these enigmatic features.

Chapter 4 explores the utility of coupling SIMS analyses with fluid inclusion data as a means to extract $\delta^{18}\text{O}_{\text{porewater}}$ information, using samples from fluvial channel sands in the Travis Peak Formation. This is a new method by which detailed coupled histories of temperature- $\delta^{18}\text{O}_{\text{porewater}}$ change in basins might be extracted from the geologic record. I then use this data to test a closed-system model for sandstone water-rock interaction, and in doing so demonstrate 1) that Travis Peak sandstones are not closed systems, and 2) that most quartz sandstones do not significantly contribute to changing $\delta^{18}\text{O}_{\text{porewater}}$ values during low temperature water-rock interaction.

References

- Bojanowski M. J., Bagiński B., Guillermier C. and Franchi I. A. (2015) Carbon and oxygen isotope analysis of hydrate-associated Oligocene authigenic carbonates using NanoSIMS and IRMS. *Chemical Geology* **416**, 51–64.
- Canfield D. E. and Farquhar J. (2009) Animal evolution, bioturbation, and the sulfate concentration of the oceans. *Proceedings of the National Academy of Sciences* **106**, 8123–8127.
- Clayton R. N., Friedman I., Graf D. L., Mayeda T. K., Meents W. F. and Shimp N. F. (1966) The Origin of Saline Formation Waters: 1. Isotopic Composition. *Journal of Geophysical Research* **71**, 3869–3882.
- Cui H., Kitajima K., Spicuzza M. J., Fournelle J. H., Denny A., Ishida A., Zhang F. and Valley J. W. (2018) Questioning the biogenicity of Neoproterozoic superheavy pyrite by SIMS. *American Mineralogist: Journal of Earth and Planetary Materials* **103**, 1362–1400.
- Denny A. C., Kozdon R., Kitajima K. and Valley J. W. (2017) Isotopically zoned carbonate cements in Early Paleozoic sandstones of the Illinois Basin: $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records of burial and fluid flow. *Sedimentary Geology* **361**, 93–110.
- Fike D. A., Bradley A. S. and Rose C. V. (2015) Rethinking the Ancient Sulfur Cycle. *Annual Review of Earth and Planetary Sciences* **43**, 593–622.
- Friedman I. and O'Neil J. R. (1977) Chapter KK. Compilation of Stable Isotope Fractionation Factors of Geochemical Interest. In *Data of Geochemistry* (ed. M. Fleischer). United States Geological Survey Professional Paper 440-KK. pp. 1–12.
- Hoefs J. (2009) *Stable isotope geochemistry*. 6th ed., Springer Science & Business Media. Available at:
https://books.google.com/books?hl=en&lr=&id=8sylR4fIOFEC&oi=fnd&pg=PA1&dq=hoefs&ots=1ZplpsRqSt&sig=2MATQuS6BNF7nBs9MIN_Xbxhg6E [Accessed August 12, 2016].
- Lin Q., Wang J., Algeo T. J., Sun F. and Lin R. (2016) Enhanced framboidal pyrite formation related to anaerobic oxidation of methane in the sulfate-methane transition zone of the northern South China Sea. *Marine Geology* **379**, 100–108.
- Lin Z., Sun X., Peckmann J., Lu Y., Xu L., Strauss H., Zhou H., Gong J., Lu H. and Teichert B. M. A. (2016) How sulfate-driven anaerobic oxidation of methane affects the sulfur isotopic composition of pyrite: A SIMS study from the South China Sea. *Chemical Geology* **440**, 26–41.
- Oehlert A. M. and Swart P. K. (2014) Interpreting carbonate and organic carbon isotope covariance in the sedimentary record. *Nature communications* **5**. Available at:

http://www.nature.com/ncomms/2014/140819/ncomms5672/full/ncomms5672.html?WT.ec_id=NCOMMS-20140820 [Accessed December 15, 2015].

- Pasquier V., Sansjofre P., Rabineau M., Revillon S., Houghton J. and Fike D. A. (2017) Pyrite sulfur isotopes reveal glacial- interglacial environmental changes. *Proceedings of the National Academy of Sciences* **114**, 5941–5945.
- Prokoph A., Shields G. A. and Veizer J. (2008) Compilation and time-series analysis of a marine carbonate $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ database through Earth history. *Earth-Science Reviews* **87**, 113–133.
- Raab M. and Spiro B. (1991) Sulfur isotopic variations during seawater evaporation with fractional crystallization. *Chemical Geology: Isotope Geoscience section* **86**, 323–333.
- Śliwiński M. G., Kozdon R., Kitajima K., Denny A. and Valley J. W. (2016) Microanalysis of carbonate cement $\delta^{18}\text{O}$ in a CO_2 -storage system seal: Insights into the diagenetic history of the Eau Claire Formation (Upper Cambrian), Illinois Basin. *AAPG Bulletin* **100**, 1003–1031.
- Swart P. K. (2015) The geochemistry of carbonate diagenesis: The past, present and future. *Sedimentology* **62**, 1233–1304.
- Urey H. C. (1948) Oxygen Isotopes in Nature and in the Laboratory. *Science* **108**, 489–496.
- Urey H. C. (1947) The thermodynamic properties of isotopic substances. *Journal of the Chemical Society*, 562–581.
- Veizer J., Ala D., Azmy K., Bruckschen P., Buhl D., Bruhn F., Carden G. A. F., Diener A., Ebner S., Godderis Y., Jasper T., Korte C., Pawellek F., Podlaha O. G. and Strauss H. (1999) $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ evolution of Phanerozoic seawater. *Chemical Geology* **161**, 59–88.
- Worden R. H. and Burley S. D. (2003) Sandstone Diagenesis: The Evolution of Sand to Stone. In *Sandstone Diagenesis: Recent and Ancient* (eds. S. D. Burley and R. H. Worden). Blackwell Publishing Ltd., Oxford, UK. pp. 1–44. Available at: <http://onlinelibrary.wiley.com.ezproxy.library.wisc.edu/doi/10.1002/9781444304459.ch/summary>.

Figures

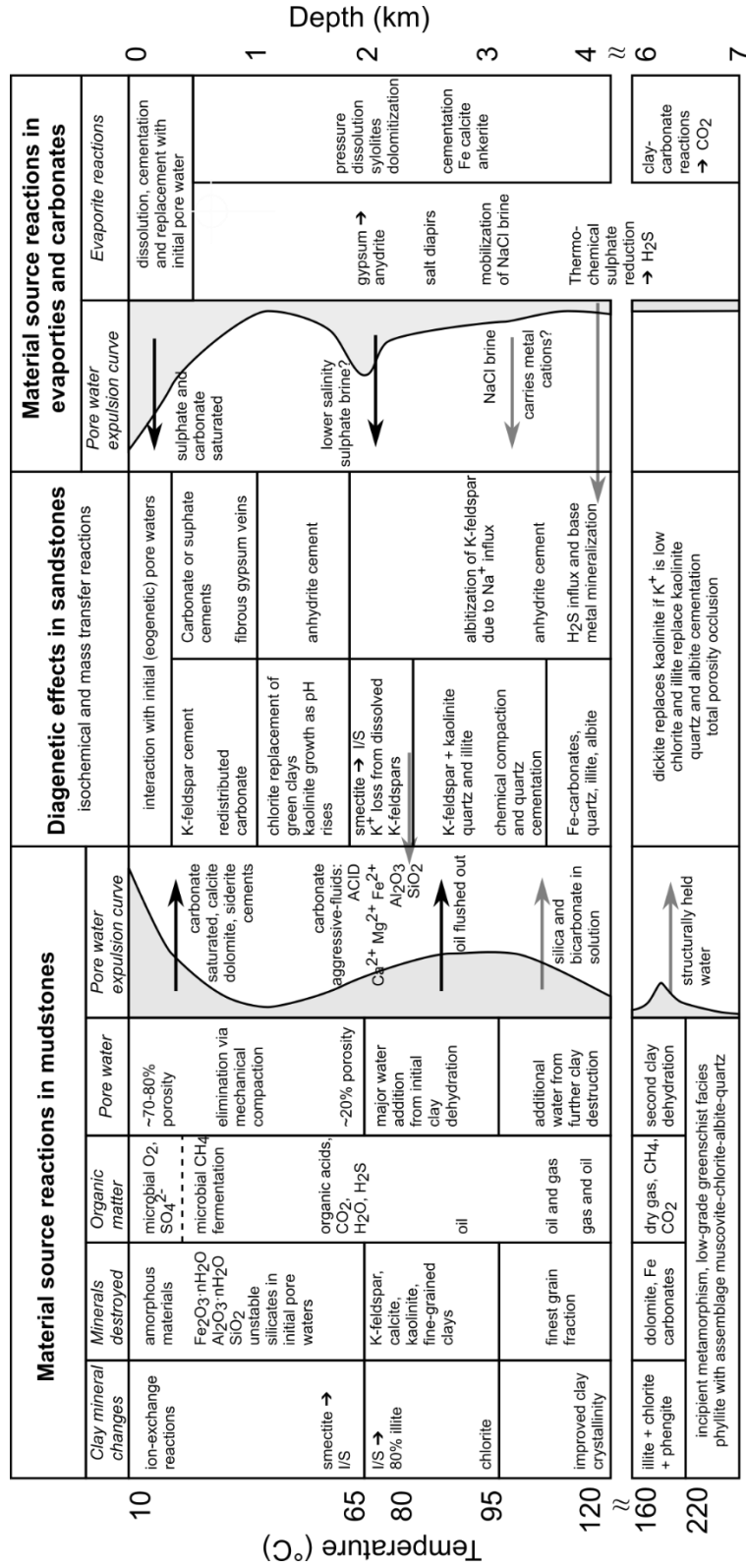


Figure 0.1. Summary of important diagenetic reactions found in sediments, and the approximate depth conditions where they occur. Adapted from Worden and Burley (2003).

Figure 0.2 (next page) Global compilations of $\delta^{18}\text{O}$ carbonate data for **(a)** the Phanerozoic only, and **(b)** with the Precambrian included. Equilibrium temperatures of calcite precipitation from $\delta^{18}\text{O} = 0\text{‰}$ water are provided along the right axis for reference (Friedman and O'Neil, 1977). Data are from Prokoph et al. (2008).

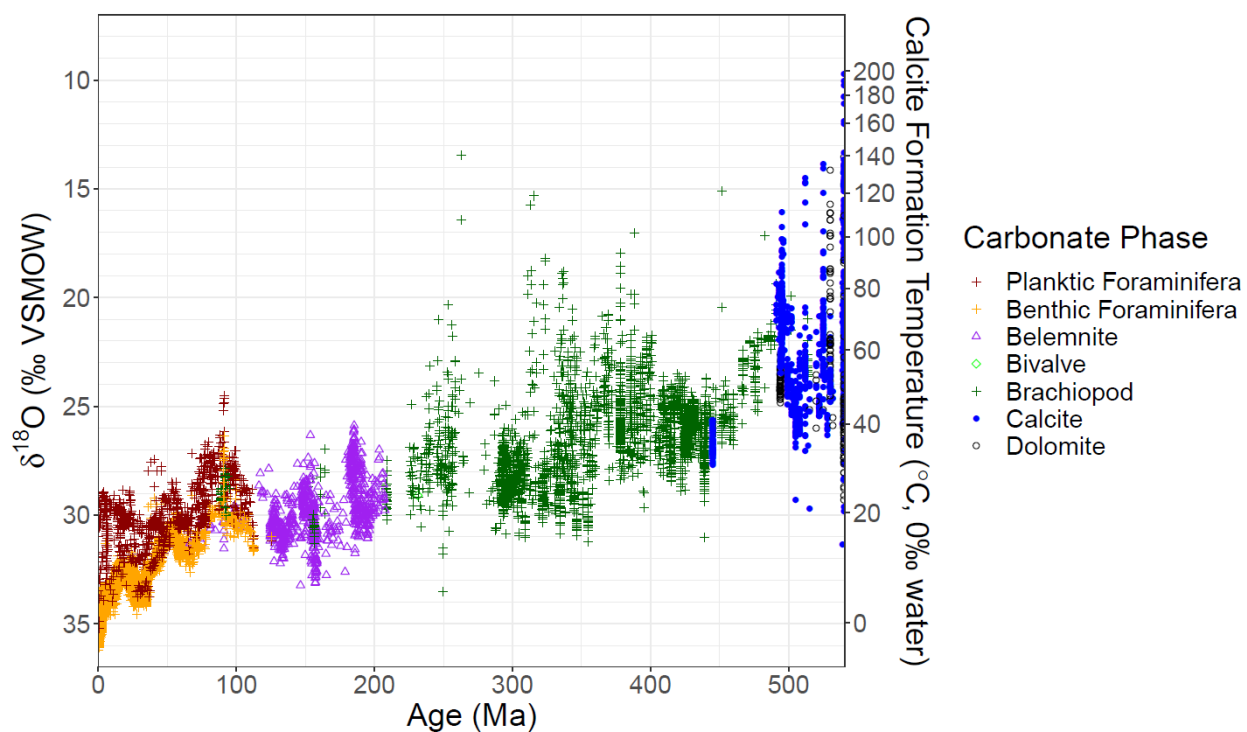
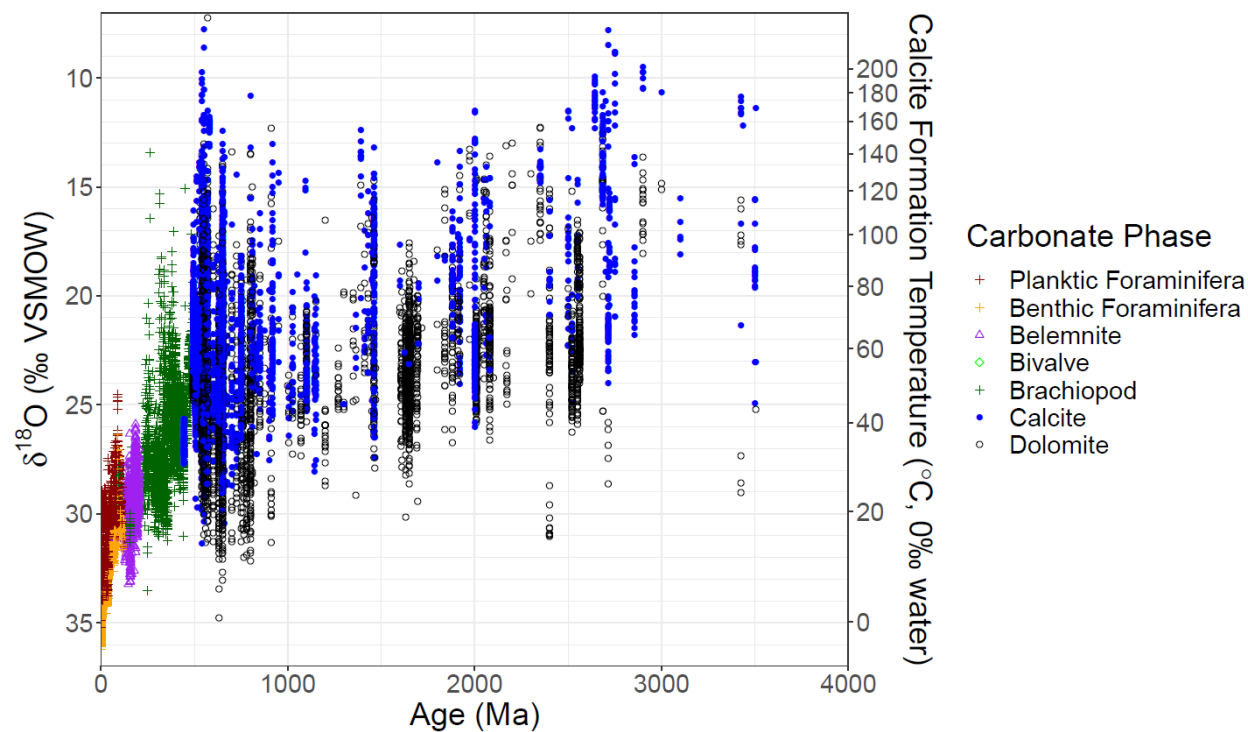
(a) Global $\delta^{18}\text{O}$ Compilation (Phanerozoic Only)(b) Global $\delta^{18}\text{O}$ Compilation (Full Record)

Figure 0.3 (next page) Global compilations of $\delta^{13}\text{C}$ carbonate data for **(a)** the Phanerozoic only, and **(b)** with the Precambrian included. Data are from Prokoph et al. (2008).

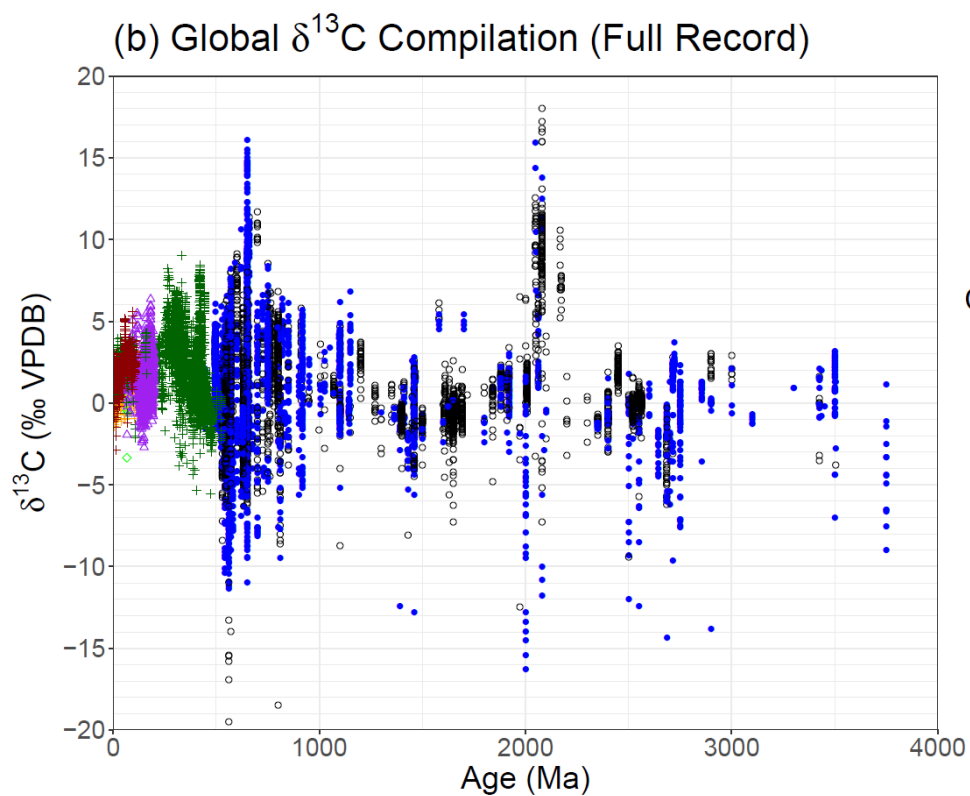
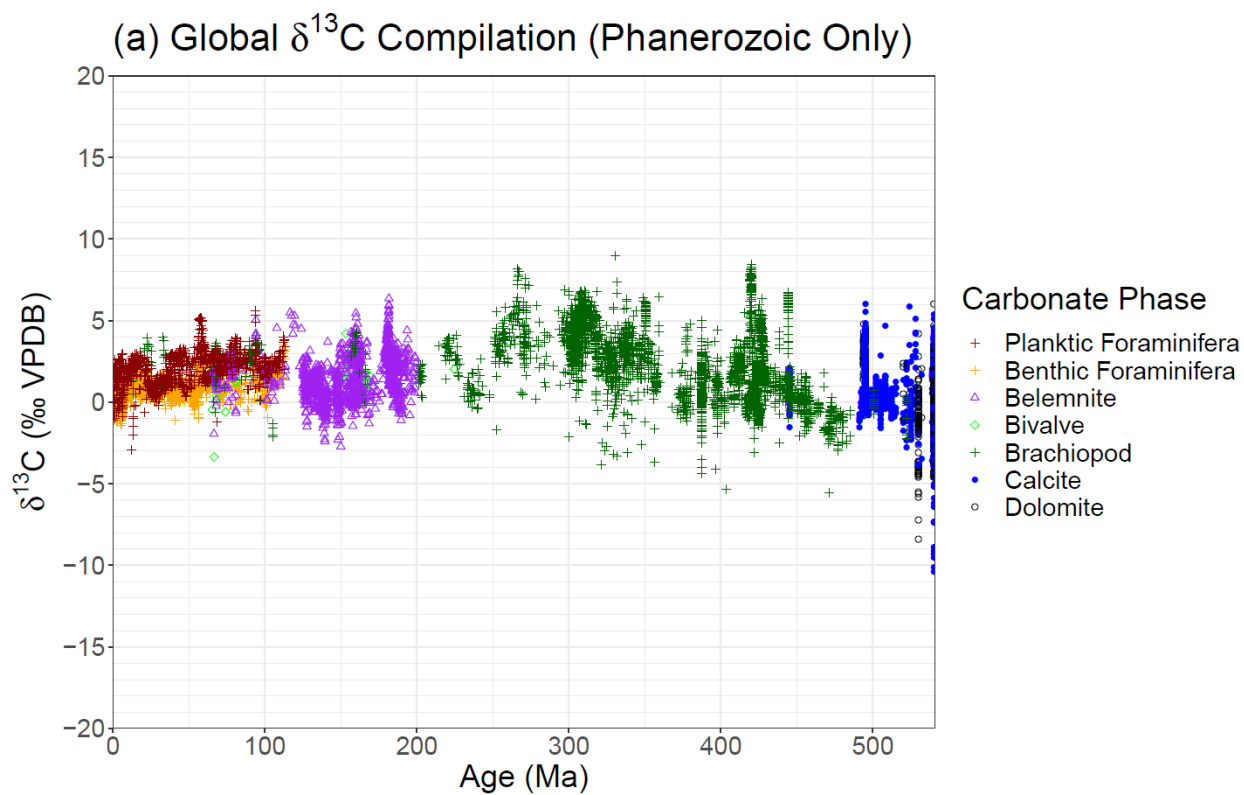
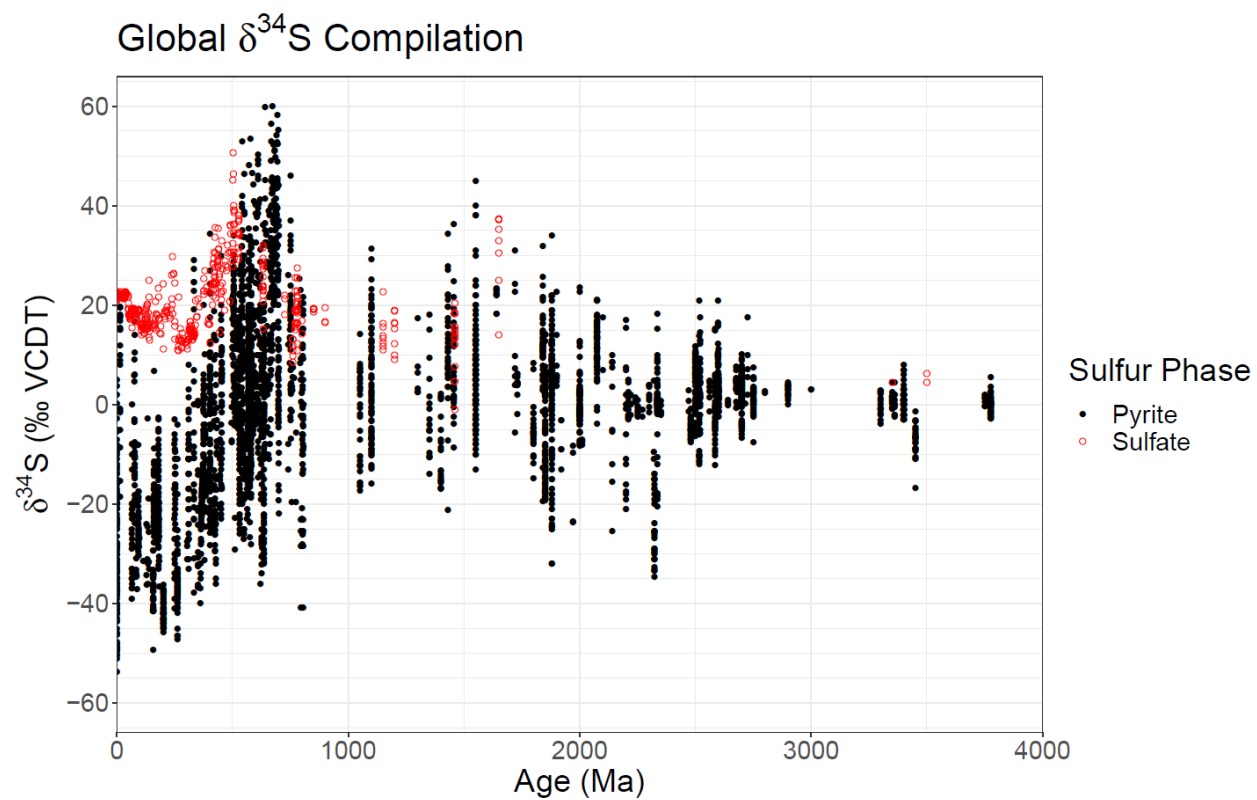


Figure 0.4 Global compilation of $\delta^{34}\text{S}$ data for the last four billion years. Pyrite data are from Canfield and Farquhar (2009), sulfate data are from Prokoph et al. (2008).



CHAPTER 1: Regionally Correlated Oxygen and Carbon Isotope Zonation in Diagenetic Carbonates of the Bakken Formation

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Abstract

Diagenetic minerals preserve records of burial processes that overprint records of seawater chemistry and impact reservoir porosity. The Mississippian-Devonian aged Bakken Formation in the Williston Basin is a reservoir rock of economic importance whose productivity is affected by diagenetic carbonates, particularly dolomite-ankerite-series carbonates. To investigate how diagenetic carbonate alteration manifests in the Bakken and how that might change across the basin, a combined $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope dataset for diagenetic carbonates was collected by in situ SIMS analysis of 10- μm spots from nine drill holes covering a ~ 250 km transect of the middle Bakken member. Observed core-to-rim isotopic variability in these small Fe-zoned dolomites and calcites frequently exceeds 10‰ in both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, indicating significant changes in thermal and chemical conditions during cementation. Individual ankeritic growth bands can be correlated across the basin by systematic similarities in minor-element compositions and isotope ratios. In the central part of the basin, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ trends at sub-mm-scale decline consistently towards the rims of ankerite-series carbonates, which is interpreted to reflect mineral growth coincident with rising temperatures and an increasing organic contribution to inorganic carbon during burial. The most abrupt shifts in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (changes as large as 12‰ for $\delta^{18}\text{O}$ and 6.5‰ for $\delta^{13}\text{C}$ within distances < 15 μm) are observed along the basin margin, and are believed to preserve signals of hydrocarbon expulsion and fluid infiltration along basin margins. Based on the data, we conclude that ankerite-series carbonates preserve records of prolonged thermal and chemical processes that operated basinwide. The isotopic trends presented here show diagenetic rock evolution from shallow dolomite formation to deep burial ankerites, as well as the isotopic responses of carbonates to changing

fluids and availability of organic $\delta^{13}\text{C}$. These results provide important constraints on how carbonate isotope records may be altered during burial in organic-rich sedimentary rocks and emphasize the need for caution in using bulk powder samples for geochemical analysis in carbonate systems.

1. Introduction

Diagenetic carbonate cements are μm -scale mineralizations that can grow throughout the burial and lithification of sedimentary rock under low-temperature and low-pressure conditions (Worden and Burley, 2003). Cementation is ubiquitous in sedimentary rocks, and may be influenced chemically (e.g., aragonite recrystallization to calcite, infiltration of meteoric fluids), mechanically (e.g., cements sourced from pressure solution at grain boundaries), or by thermally controlled processes (e.g., organic maturation reactions, clay alteration reactions). Carbonate diagenesis is of interest to the geochemical community due to its potential overprinting of primary seawater isotopic signals (e.g., Banner, 1995; Banner and Hanson, 1990; Brand and Veizer, 1981; Kozdon et al., 2011; Irwin et al., 1977; Swart, 2015), impact on permeability and porosity (Brodie et al., 2018; Purser et al., 1994; Sarg, 2012; Sun, 1995), relevance to carbon sequestration (Berger et al., 2009; Bowen et al., 2011), and continued uncertainty of the underlying kinetics and conditions of carbonate, particularly dolomite, formation (Warren, 2000). Understanding the timing and factors that control carbonate diagenesis is important not only for predicting porosity preservation and porosity creation, but also for constraining carbonate behavior during an array of organic and inorganic reactions. Furthermore, understanding how geochemical processes in the subsurface result in the dissolution and precipitation of carbonates is of paramount importance to understanding fluid

flow, both for resource development and for optimizing carbon sequestration, where diagenetic reactions are the primary mechanism by which CO₂ will be stored.

Because diagenetic minerals develop under temperature, pressure, and fluid conditions that are commonly present across large areas of basins, it is important that diagenetic studies should attempt to correlate changes in individual μm -scale growth bands laterally through rocks that have experienced different environmental or thermal histories. Secondary Ion Mass Spectrometry (SIMS) is a powerful tool for reconstructing such diagenetic histories, as it can accurately measure isotopic ratios at the μm scale, and reveal isotopic heterogeneities in minerals that might otherwise be homogenized by more traditional bulk analyses (Cammack et al., 2018; Denny et al., 2017; Harwood et al., 2013; Hyodo et al., 2014; Pollington et al., 2011; Śliwiński et al., 2017a; Teboul et al., 2019).

Presented here are μm -scale diagenetic carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data of samples collected from a ~ 250 km transect of the organic-rich, low-porosity middle Bakken member. This study's main goals were: 1) To determine the degree of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variability preserved at sub-mm-scale in the rock, 2) To determine if carbonate isotopic zonation may be correlated across the basin, and 3) To constrain the formation conditions of early dolomite cements. The results provide insight into how carbonate diagenesis responds to changes in depth, thermal history, and maturity of adjacent petroleum source rocks.

2. Geological Background

2.1 Bakken Formation, Middle Member

The Bakken Formation was deposited in the Williston Basin of present-day North Dakota, Montana, and southern Saskatchewan (Figure 1.1). It is Devonian-Mississippian in age (Figure 1.2a), and is overlain by the Lodgepole Limestone and underlain by the Three Forks Formation (Figure 1.2b). The Bakken Formation is divided into a middle, mixed carbonate-siliciclastic member surrounded by upper and lower organic-rich shale members. In the United States the shales have reported average total organic carbon of 8 to 11 weight percent (LeFever et al., 2011; Smith and Bustin, 2000; Sonnenberg, 2011a). The Bakken does not intersect the surface, and all direct study of the formation must be performed using drill core and well logs. It formed in a shallow restricted basin, with the middle Bakken thought to reflect shallower and more oxic conditions than the shales, which were deposited in oxygen-poor conditions (Borcovsky et al., 2017). All three members show a high degree of regional continuity; some authors argue that individual parasequences within the Bakken may be traced laterally over distances exceeding 150 km (Egenhoff et al., 2011).

In recent years the Bakken Formation has become a prolific source of oil and gas in North America, and there is much resource potential still to be explored—a 2013 assessment by the USGS estimated total unrecovered oil resources to be in excess of seven billion barrels (Gaswirth et al., 2013; Gaswirth and Marra, 2015). The middle member is a significant reservoir for hydrocarbons produced in the adjacent shales despite low porosities ranging from 1 to 11% and an average permeability of 0.0042 mD (Simenson et al., 2011). It is regarded to be an unconventional reservoir, and hydraulic fracturing is used heavily in resource extraction (Sonnenberg et al., 2011b). Carbonate diagenesis had an important impact on present-day

porosity, with porous dolomitized zones and fracture distributions contributing significantly to reservoir potential (Pitman et al., 2001; Simenson et al., 2011; Śliwiński et al., 2019).

3. Methods

3.1 Sample Collection and Preparation

Seventy-four samples were collected from ten drill cores stored at the North Dakota Geological Survey (NDGS) Wilson M. Laird Core and Sample Library. Cores were chosen that intersected the middle Bakken Formation and cover a ~250 km transect from immature source rock conditions along the northeast margin of the basin to mature source rocks in the basin center (Figure 1.1). Maximum burial temperatures are estimated to range from ~75 °C on the basin margin sample to ~160 °C in the basin center (Kuhn et al., 2012). All cores and samples were initially described using the lithofacies architecture defined by Egenhoff et al. (2011) (Figure 1.2b). Samples were polished and imaged in backscattered electron (BSE) mode using a Hitachi S3400-N scanning electron microscope (SEM) in variable pressure mode; this was found to be the most efficient and effective way of quickly identifying and evaluating the quality of μm -scale ankerite-series zonation. One sample per core was selected to be prepared for SIMS analysis, as determined by which sample in each core showed the thickest zoned ankerite-series cements in the middle Bakken, and therefore would yield the highest resolution isotopic records by SIMS; one sample, from NDGS core #21706 (not shown in Figure 1.1), later proved too friable to produce a good quality polish and was not analyzed further. In preparation for SIMS analysis, 1-2 cm chips were cut from sample rock and cast in Buehler epoxy in 2.54 cm-diameter round molds. In the center of each was mounted the UW-6220 dolomite standard

(Valley et al., 2009; Śliwiński et al., 2016a,b). Mounts were then polished to a final grit of 0.25 μm with a diamond suspension and checked for flatness using a reflected light microscope. In total, 11 mounts covering 9 cores were prepared and analyzed by SIMS. To simplify discussion, these cores will hereafter be numbered 1 through 9 (Table 1.1) from the shallow NE basin margin (core 1) to the deep basin center in the SW (core 9; see Figure 1.1). Two samples each were prepared in two cores (21668 and 22493) to compare two endmembers of Fe-banded dolomite formation (sandstone dolomites vs. conspicuous fracture or vug dolomites).

3.2 SIMS Procedure

Values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ were measured on a CAMECA IMS 1280 large-radius, multi-collector secondary ion mass spectrometer (SIMS) at the University of Wisconsin-Madison WiscSIMS laboratory using established sample preparation and analysis procedures (Kita et al., 2009; Valley and Kita, 2009). Samples were analyzed using a focused $^{133}\text{Cs}^+$ primary beam with a 10 kV accelerating voltage and 20 keV impact energy. The impact of the $^{133}\text{Cs}^+$ atoms sputters ions off of the sample surface and excavates a pit. Pit dimensions were $\sim 11 \times 8 \mu\text{m}$ for $\delta^{18}\text{O}$ analyses and $\sim 9 \times 6 \mu\text{m}$ for $\delta^{13}\text{C}$ analyses; pit depths are estimated to be 2 μm . Charge neutralization is performed with an electron flood gun and a 60 nm gold coat. Sputtered ions are accelerated into a double-focusing mass spectrometer where they are sorted by mass/charge before reaching an array of detectors; $\delta^{18}\text{O}$ measurements were made with an array of 3 Faraday cup detectors (for $^{16}\text{O}^-$, $^{18}\text{O}^-$, and $^{16}\text{O}^1\text{H}^-$) (Wang et al., 2014) and $\delta^{13}\text{C}$ measurements were made using one Faraday cup and two electron multiplier detectors (measuring $^{12}\text{C}^-$, $^{13}\text{C}^-$, and $^{13}\text{C}^1\text{H}^-$, respectively). In this study, all SIMS analyses of unknowns were made using dolomite UW-6220 as a running standard (Valley and Kita, 2009), which involves

bracketing groups of 8-16 analyses of unknowns with eight analyses on the dolomite standard (4 before the unknowns and 4 after). This bracketing allows users to monitor and correct for small amounts of instrumental drift. Analytical precision for unknowns is typically reported as two standard deviations of the 8 bracketing standard analyses, and is typically $\pm 0.3\%$ for $\delta^{18}\text{O}$ and $\pm 0.7\%$ for $\delta^{13}\text{C}$ data reported here (Appendices 1.1, 1.2).

The raw isotope ratios obtained by SIMS are affected by an instrumental mass fractionation (IMF) or bias that can vary in magnitude depending on isotopic system, instrumental conditions, mineralogy, and sample composition (Valley and Kita, 2009; Śliwiński et al., 2016a,b, 2017b). IMF is monitored and corrected through the repeated analysis of standards of known composition. It is most sensitive to the concentration of Fe in the carbonate, such that for the conditions of this study, ankerite-series IMFs range by more than 10‰ for $\delta^{18}\text{O}$ using 10 μm diameter analysis pits, and may range in excess of 5‰ for $\delta^{13}\text{C}$. This effect is particularly pronounced towards dolomitic compositions, where a compositional shift from 0% ankerite (endmember dolomite) to 1.5% ankerite can change the $\delta^{18}\text{O}$ IMF by 1.5‰.

To address the effect of variable Fe/Mg on analytical IMF, a suite of standards along the ankerite-series are analyzed at the start of each session and used to generate a calibration curve relative to running standard UW-6220 (Śliwiński et al. 2016a,b). After SIMS analysis, this calibration curve is used to determine the composition-specific IMF using an electron microprobe (see EPMA Procedure, below) to determine the Fe concentration ($\text{Fe\#} = \text{Fe}/[\text{Fe}+\text{Mg}]$) of each SIMS pit that lies on the ankerite-series.

SIMS analyses were monitored for internal error (2SE of individual analyses) or OH or CH ion count rates ($^{16}\text{O}^1\text{H}$ for $\delta^{18}\text{O}$ sessions and $^{13}\text{C}^1\text{H}$ for $\delta^{13}\text{C}$ sessions) that were significantly above bracketing standard measurements; these analyses were excluded from later discussion of the data. SEM imagery was also acquired of all SIMS pits, and analyses that were observed to intersect large inclusions or other mineral phases were not included in data discussion. Quartz and calcite data were corrected using standards UWQ-1 quartz (Kelly et al., 2007) and UWC-3 calcite (Kozdon et al., 2009), respectively. All SIMS data are available in Appendices 1.1 and 1.2.

3.3 Electron Probe Microanalysis

Chemical compositions for Ca, Mg, Fe, Mn, and Sr were determined by Electron Probe Micro-Analysis (EPMA) for each carbonate SIMS pit using the CAMECA SX-51 in the Cameron Electron Microprobe Lab at the University of Wisconsin-Madison. Data were collected over two analytical sessions with a ~120 second analysis time and a 15 keV, 20 nA beam, which was defocused to a 5 μm diameter in an attempt to minimize sample damage. Data were processed in the Probe for EPMA software (Donovan, 2018), and background correction was performed using the Mean Atomic Number (MAN) procedure (Donovan and Tingle, 1996). As changes over time in measured intensities are common for EPMA measurements in carbonates, particularly for the element Ca, a self-fitted Time Dependent Intensity (TDI) correction was applied for all elements (Donovan, 2018).

As reliable EPMA measurements cannot be obtained from uneven surfaces, it was necessary that measurements be made at least half the EPMA beam diameter from SIMS pits. Previously acquired SEM-BSE imagery was used to aid in targeting EPMA analysis locations

along the same compositional growth bands as SIMS analyses, such that EPMA analyses measure areas compositionally equivalent to that of the SIMS analysis pit. SEM-SE (secondary electron) imaging was made of regions post-EPMA as an additional verification that EPMA analyses were properly located, and compared to SEM-BSE imaged zonation to verify that SIMS-equivalent chemistries were obtained. Two to four analyses were made adjacent to each SIMS analysis pit and their chemistries were averaged. If an EPMA analysis was found by SEM imaging to have analyzed a growth band different from the SIMS analysis, or if elemental totals for an EPMA analysis fell outside of the 98 to 101% range, then it was not included in the calculation of the chemistry at each SIMS analysis.

4. Results

The following sections describe the SIMS data, first concerning the overall trends observable in the data basinwide, and then as it relates to middle Bakken petrography on a sample-specific basis. Readers wishing to see the data broken down in detail should proceed to Section 4.2. All $\delta^{18}\text{O}$ data are reported in ‰ VSMOW, and $\delta^{13}\text{C}$ data are reported in ‰ VPDB. Equivalent values of $\delta^{18}\text{O}$ are provided on the VPDB scale in Appendix 1.1. To simplify discussion, the term “dolomite” will only be used to describe non-ferroan, near-stoichiometric $(\text{Ca,Mg})\text{CO}_3$ carbonates ($\text{Fe\#} < \sim 0.02$), whereas carbonates which are on the dolomite-ankerite solid solution and contain iron will be referred to as “ankerite-series carbonates”. Unless otherwise noted, ankerite-series Fe contents will be reported as Fe# (mol. Fe/[Fe+Mg]).

4.1 Overview of Mineral $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ Data

4.1.1 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ Distributions in Minerals

Banded ankerite-series cements and calcite both show large variability in $\delta^{18}\text{O}$ (Figure 1.3) and $\delta^{13}\text{C}$ (Figure 1.4) (Table 1.2). This variability is often larger than 10‰ across banded carbonates (some < 100 μm wide) and is reproducible from grain to grain within an individual sample. This systematic zonation of ankerite-series cements in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ parallels zonation in Fe#. Because SEM-BSE imaging of Fe-zonation aided in the identification of all growth stages of ankerite-series carbonates in each sample, the ranges of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ present in these histograms reflects the true isotopic range present in each sample at the μm scale. With the exception of the two samples from the margin of the basin (Wells 1 and 2), there is a basin-wide correlation between increasing Fe content, decreasing $\delta^{18}\text{O}$, and decreasing $\delta^{13}\text{C}$ from core to rim in ankerite-series cements (Figure 1.5a). Note that stable isotope variability at this scale could not be measured by other techniques; data measured by conventional acid dissolution yield average values and do not record distinct burial events.

Calcite also shows large (often >10‰) variability in $\delta^{18}\text{O}$ (Figure 1.3) and $\delta^{13}\text{C}$ (Figure 1.4) values, and the range of values for calcite overlaps closely with ankerite-series carbonate ranges in most samples (Figure 1.6). Unlike Fe-banded ankerite-series carbonates, SEM imaging of calcite does not readily show compositional zonation at this scale, either by BSE or CL, which makes the selection of analysis spots that represent the full isotopic spectrum of calcite more challenging, especially in fine-grained rocks. Because growth sequence could not be imaged, calcite was analyzed less often than ankerite-series carbonates (for which Fe-zonation patterns are apparent).

On the whole, quartz overgrowths >10 μm thick appear to be rare in the middle Bakken, although locally-significant diagenetic quartz growth may still occur. Quartz $\delta^{18}\text{O}$ values were analyzed in 23 spots from core 3 (Figure 1.3c), which contained large and pervasive quartz overgrowths. Classifying all quartz analyses according to whether they were made on detrital grains or overgrowth (as evaluated by SEM-CL imagery) reveals a bimodal distribution, with detrital grains clustering towards $\delta^{18}\text{O} = 10\text{‰}$ and overgrowths clustering towards 30‰ (Figure 1.7). This bimodality indicates a dominantly high-temperature igneous and metamorphic origin for the detrital quartz grains and low temperatures of cementation for quartz overgrowths. These observations are consistent with previous studies (Denny et al., 2017; Graham et al., 1996; Harwood et al., 2013; Hyodo et al., 2014; Pollington et al., 2011, 2016; Williams et al., 1997). Very little evidence of $\delta^{18}\text{O}$ zonation was detected within individual quartz overgrowths, though this is likely in part due to the small width of overgrowths relative to the spot size.

4.1.2 Growth Zones of Ankerite-series Cement

To aid classification and facilitate discussion of analyzed dolomite and ankerite cements, ankerite-series cements are qualitatively divided into 3 growth zones based on a pervasive pattern of zonation observed repeatedly by SEM-BSE. As schematically illustrated in Figure 1.8, each successive zone of the cement is delineated by a stepped increase in Fe-content along a traverse from core to rim. Figure 1.5b and Figure 1.9 show the distribution of Zones 1, 2, and 3 in plots of $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$.

Zone 1 is defined as the earliest-formed dolomite ($\text{Fe\#} = 0.00$) cores that make up the center of most of the ankerite-series cements observed in the middle Bakken. Subsequent generations of carbonate are delineated from the dolomite cores by increases in Fe#. In places,

this increase occurs along a non-euhedral boundary that is indicative of dissolution or abrasion, while elsewhere in the same sample other dolomite cores might show euhedral morphologies indicative of formation in place. A comparison of the isotopic values between rounded and euhedral dolomites basinwide demonstrates that morphology is not a predictor of chemistry (Figure 1.10).

Zones 2 and 3 surround Zone 1 and have higher Fe#s. Zone 2 is defined here as the first significant relative rise in Fe content. Zone 2 Fe#s typically fall in the 0.02-0.1 range. Zone 3 starts at the second sharp rise in Fe content, and includes the last carbonate rims to grow. The Zone 2 to 3 transition tends to occur when Fe#s approach 0.1, but this changeover may occur at Fe#s as low as 0.05 in shallow samples. Zone 2 commonly contains at least one, and in places two, visible (by SEM-BSE) Fe-poor bands (e.g., Figure 1.11a) that may even mark a brief return to dolomitic compositions, but will frequently return to Fe#s more typical of Zone 2 before Zone 3 compositions are encountered.

Other studies have reported isotopic zonation in the Bakken, and the 3 zones discussed here may be correlated to the work of others as follows. We use the Zone 1, 2, and 3 nomenclature of Śliwiński et al. (2019), but their Zone 4 is not always present and has been consolidated here into Zone 3 to simplify discussion. Zones 1 and 2 correlate to the Phases 1 and 2 described by Staruiala et al. (2013); an Fe-rich equivalent to Zone 3 is present in the samples examined by Staruiala et al., but was not thick enough to sample by SIMS.

4.2 Sample-Specific Petrography and Geochemistry

This section will present sample-specific descriptions of the observed petrography and geochemistry for each SIMS mount. Mounts are labeled with a “Core number – depth in feet” nomenclature for accurate comparison with other NDGS core records (that are measured in feet); equivalent depths below the surface in meters are provided with each sample name. Samples are presented in order as they would fall along a NE-SW transect starting at the NE shallow basin margin and working towards the deepest part of the basin in the SW. Grain sizes are described under the Wentworth classification scheme (Wentworth, 1922), using the terms medium silt (16 to 31 μm), coarse silt (31 to 63 μm), very fine sand (63 to 125 μm), and fine sand (125 to 250 μm).

Figures 1.11 through 1.15 show petrography, SIMS pit locations and stable isotope values for selected sample regions. These images will be referenced in concert with the following results and discussion. SIMS mount maps were created by integrating SEM-BSE imagery, SIMS analyses, and EPMA data in the QGIS software environment (Linzmeier et al., 2018), and additional images showing the locations and values of all SIMS $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ analyses in each mount are available in Appendix 1.3.

4.2.1 Well 1, Sample 24883-3743.4 (1141 m)

The shallowest and northeastern-most sample was collected from a predominantly carbonate grain-supported rock at a depth of 1141 m (3743.4 ft.), and was made into a single SIMS mount (Appendix 1.3.01). Both medium to fine sand-sized calcite grains (some ooids) and fine to very fine sand-sized quartz grains are present. Calcite cement is present between most calcite grains. Ankerite-series cements are predominantly found either growing into large uncemented pore spaces in the rock, or growing within a 0.5 to 1 mm wide vertical fracture

running through the sample. In hand sample, this fracture is predominantly filled with anhydrite, except in a few places (one of which was incorporated into the mount) where 3-4 mm wide diagenetic pyrites are located within the fracture and appear to have replaced surrounding carbonates leaving silicate grains largely unaffected (Appendix 1.3.01). Calcite $\delta^{18}\text{O}$ values range from 20.1 to 29.2‰ (n = 13) and $\delta^{13}\text{C}$ ranges from -7.4 to 2.6‰ (n = 13). Ankerite-series $\delta^{18}\text{O}$ values range from 19.2 to 38.2‰ (n = 36) and $\delta^{13}\text{C}$ ranges from -8.3 to 4.8‰ (n = 31).

In the banded ankerite-series carbonates, the innermost carbonate core (Zone 1) is dolomite (Fe# = 0.00); $\delta^{18}\text{O}$ values range from 24.9 to 27.2‰, and $\delta^{13}\text{C}$ values range from -0.3 to 3.7‰ (Figures 1.11a, 1.11b, Appendix 1.3.01). These dolomite cores are surrounded by a euhedral band of carbonate (Zone 2) with Fe#s in the ~0.02-0.04 range (Figure 1.11c), slightly higher $\delta^{18}\text{O}$ values showing a range of 26.4-29.9‰, and $\delta^{13}\text{C}$ values showing a range of -1.9 to 4.8‰, with $\delta^{13}\text{C}$ values declining towards the rim. This band is ringed by a double euhedral band of dolomite (Fe# = 0.00) across which $\delta^{18}\text{O}$ values spike (from 24.8 to 38.2) and $\delta^{13}\text{C}$ values decline abruptly (from -0.7 to -5.9‰). This is surrounded by a broad Fe-rich band (Zone 3) with a semi-euhedral boundary and increasing Fe content (Fe#s from 0.08 to 0.16), a narrow $\delta^{18}\text{O}$ range (30.5 to 31.8‰), and very low $\delta^{13}\text{C}$ values (-6.6 to -8.3‰) (Figures 1.11d, 1.11e, 1.11f). The final, outermost band consists of rapidly rising Fe concentrations (Fe#s from 0.01 to 0.12), with $\delta^{18}\text{O}$ steadily increasing from 19.2 to 22.9‰ and $\delta^{13}\text{C}$ ranging from -2.1 to -0.8. This final band is thin and truncated in fracture carbonates but broad and correlatable within rock pores, suggesting that it formed coincident with or after the precipitation of anhydrite within the fracture.

4.2.2 Well 2, Sample 20249-6013.4 (1833 m)

This sample was collected from a sandstone intercalated with laminated siltstones at a depth of 1833 m (6013.4 ft.), and was made into two SIMS mounts displaying similar petrography (Appendices 1.3.02, 1.3.03). Fine to very fine sand-sized quartz and fine sand-sized calcite grains are surrounded by significant volumes of banded ankerite-series carbonate and anhydrite. No fractures or other structural features were observed. Calcite $\delta^{18}\text{O}$ ranges from 27.6 to 29.7‰ (n = 6) and $\delta^{13}\text{C}$ ranges from -0.7 to 0.8‰ (n = 5). Ankerite-series $\delta^{18}\text{O}$ ranges from 23.1 to 35.2‰ (n=63) and $\delta^{13}\text{C}$ ranges from -3.2 to 4.0‰ (n = 40).

In the banded ankerite-series carbonates, the innermost carbonate (Zone 1) is dolomite with Fe#s of 0.00, $\delta^{18}\text{O}$ values showing a range of 23.1 to 28.2‰, and $\delta^{13}\text{C}$ values showing a range of -1.8 to 4.0‰. These dolomite cores commonly show rounded morphologies and internal banding, though others show euhedral morphologies indicative of formation in place. Surrounding the dolomite core is a band of carbonate (Zone 2) with higher Fe#s (~0.04), $\delta^{18}\text{O}$ values ranging from 25.0 to 26.3‰, and $\delta^{13}\text{C}$ ranging from 0.6 to 4.0‰ (Figures 1.12a, 1.12b). This band is in turn surrounded by a double band of more Fe-poor carbonate (Fe#s 0.02 to 0.03), similar to that in C24883, with $\delta^{18}\text{O}$ values spiking from 26.3 up to 35.2‰ (Figure 1.12b), and a range of $\delta^{13}\text{C}$ values between 0.0 to 3.8‰. This is surrounded by a final region more enriched in Fe (Fe#s 0.05 to 0.10) with $\delta^{18}\text{O}$ values ranging from 27.7 to 30.6 and $\delta^{13}\text{C}$ ranging from -3.2 to 1.2‰. This final band typically ends in a euhedral rim.

4.2.3 Well 3, Sample 17272-7591.5 (2314 m)

This sample was collected from a sandstone at a depth of 2314 m (7591.5 ft.), and was made into a single SIMS mount (Appendix 1.3.04). Fine to very fine sand-sized quartz forms the

majority of the grains, but fine to very fine sand-sized calcite grains are also present. Euhedral quartz overgrowths are present around most detrital quartz grains. Banded ankerite-series carbonates are sparse but evenly distributed through the rock, and are large in diameter ($> 100 \mu\text{m}$). No fractures or other structural features are present. Quartz $\delta^{18}\text{O}$ values range from 9.2 to 31.5‰ (n = 22, detrital and overgrowth). Calcite $\delta^{18}\text{O}$ values range from 23.2 to 31.3‰ (n = 10) and $\delta^{13}\text{C}$ ranges from -4.2 to 5.7‰ (n = 11). Ankerite-series $\delta^{18}\text{O}$ values range from 23.4 to 29.8‰ (n = 31) and $\delta^{13}\text{C}$ ranges from -7.2 to 2.6‰ (n=30).

In the banded ankerite-series carbonates, the innermost carbonate (Zone 1) is dolomite with Fe#s of 0.00 to 0.01, $\delta^{18}\text{O}$ values of 23.7 to 28.1‰, and $\delta^{13}\text{C}$ values of -0.8 to 2.2‰. The dolomite cores commonly show rounded morphologies (Figures 1.13a, 1.13c), and some show partial recrystallization and higher Fe#s (up to 0.03). Surrounding these dolomite cores is a band of carbonate (Zone 2) with higher Fe#s (0.03-0.05), declining $\delta^{18}\text{O}$ values from 29.8 to 24.5‰, and declining $\delta^{13}\text{C}$ values from 1.1 to -4.5‰. This band is in turn surrounded by a final band of carbonate (Zone 3) with increasing Fe#s from 0.10 to 0.22, $\delta^{18}\text{O}$ values in the 23.4 to 25.3‰ range, and rising $\delta^{13}\text{C}$ values from -7.2 to -1.9‰ (Figures 1.13a, 1.13d, 1.13e). This final band possesses a euhedral rim in some locations, but not where it impinges upon calcite grains.

4.2.4 Well 4, Sample 17676-8738.4 (2663 m)

This sample was collected from an isolated ~2-cm thick carbonate-rich shell bed that was isolated in a predominantly sandstone layer intercalated with siltstone at a depth of 2663 m (8738.4 ft.), and was made into a single SIMS mount (Figures 1.14a, 1.14b, Appendix 1.3.05). The sample matrix is predominantly composed of microcrystalline calcite and coarse to medium silt-sized ankerite-series carbonates and quartz. Larger banded ankerite-series carbonates have

grown in porosity associated with skeletal calcite (Appendix 1.3.05). These ankerite-series cements were the main target for SIMS analysis. No fractures or other structural features are present. Quartz $\delta^{18}\text{O}$ data range from 16.0 to 27.3‰ (n = 3). Calcite $\delta^{18}\text{O}$ values range from 24.5 to 32.1‰ (n = 15) and $\delta^{13}\text{C}$ values from -10.3 to 4.8‰ (n = 17). Ankerite-series $\delta^{18}\text{O}$ values range from 21.8 to 28.5‰ (n = 32) and $\delta^{13}\text{C}$ ranges from -8.8 to 1.4 (n = 37).

In the banded ankerite-series carbonates, the innermost carbonate (Zone 1) is dolomite with Fe#s of 0.00, $\delta^{18}\text{O}$ values in the 26.3 to 28.5‰ range, and $\delta^{13}\text{C}$ values in the -0.9 to 1.4‰ range. These dolomite cores are euhedral in shape and do not generally show evidence of rounding or recrystallization (Figure 1.14a). Surrounding the dolomite cores is a band of carbonate (Zone 2) with higher Fe#s (0.03-0.05), $\delta^{18}\text{O}$ values in the 25.8 to 27.3‰ range, and $\delta^{13}\text{C}$ values in the -3.7 to -0.9‰ range. This band is in turn surrounded by a final band of carbonate (Zone 3) with increasing Fe#s from 0.10 to 0.15, $\delta^{18}\text{O}$ values in the 21.8 to 25.2‰ range, and rising $\delta^{13}\text{C}$ values from -8.6 to -4.4‰. This final band possesses a euhedral rim in most locations, but not where it impinges upon skeletal calcites (e.g., 14b).

4.2.5 Well 5, Sample 16586-9812.5 (2991 m)

This sample was collected from a carbonate grain-supported rock from a depth of 2991 m (9812.5 ft.), and was made into a single SIMS mount (Figures 1.15a, 1.15b, Appendix 1.3.06). The sample is mainly composed of fine sand-sized calcite grains, with very-fine sand-sized detrital quartz grains being less predominant. Banded ankerite-series carbonates are sparse, but where present tend to be large (100 to 200 μm) when measured from rim to rim. No fractures or other structural features were observed. Calcite $\delta^{18}\text{O}$ values range from 24.5 to

28.0 (n = 7) and $\delta^{13}\text{C}$ ranges from -2.0 to 5.2‰ (n = 10). Ankerite-series $\delta^{18}\text{O}$ values range from 21.7 to 29.5‰ (n = 32) and $\delta^{13}\text{C}$ ranges from -5.9 to 3.3‰ (n = 39).

In the banded ankerite-series carbonates, the innermost carbonate (Zone 1) is near to endmember dolomite with Fe#s of 0.01 to 0.02, $\delta^{18}\text{O}$ values in the 24.2 to 26.4‰ range, and $\delta^{13}\text{C}$ values in the -0.7 to 2.4‰ range. These carbonate cores have a rounded, anhedral contact with subsequent, higher-Fe growth bands, texturally indicative of mechanical abrasion or dissolution. Surrounding these cores is a thin band of carbonate (Zone 2) with higher Fe#s (~0.06), higher $\delta^{18}\text{O}$ values (25.7 to 29.4‰), and heavier $\delta^{13}\text{C}$ values (-0.1 to 3.3‰). A thin Fe-poor (Fe#s 0.01 to 0.03) band is next, with $\delta^{18}\text{O}$ ~27.0‰ and $\delta^{13}\text{C}$ ~-1.1‰. Surrounding this thin Fe-poor band is a broad band with increasing Fe#s (0.05 to 0.09), $\delta^{18}\text{O}$ values in the 24.9 to 26.4‰ range, and declining $\delta^{13}\text{C}$ values from -0.6 to -4.0‰. Two narrow high-Fe bands follow (Zone 3), the first with Fe#s in the 0.18 to 0.23 range, $\delta^{18}\text{O}$ values in the 21.7 to 22.3‰ range, and $\delta^{13}\text{C}$ in the -2.9 to -2.9‰ range; the second and final band has Fe#s around 0.38, $\delta^{18}\text{O}$ values of ~23‰, and $\delta^{13}\text{C}$ values of ~-5‰. These last two Fe-rich bands are not present in many of the sample's banded ankerite-series carbonates (e.g., present in Figure 1.15a vs. absent in Figure 1.15b), and where they are present they show intermittently anhedral rims suggestive of partial recrystallization to calcite.

4.2.6 Well 6, Sample 17015-10354.4 (3156 m)

This sample was collected from the horizontally laminated siltstone facies at a depth of 2991 m (9812.5 ft.), and was made into a single SIMS mount (Figures 1.15c, 1.15d, Appendix 1.3.07). The rock is supported by rounded calcite, quartz, banded ankerite-series carbonate, and feldspar grains in the very fine sand to course silt-size range. Both the feldspars and the

ankerite-series carbonate commonly possess euhedral overgrowths; it is difficult to determine based on textural evidence if dolomite was originally grain supporting or if it is replacive after calcite. No fractures or other structural features are present. Quartz $\delta^{18}\text{O}$ data range from 10.4 to 17.1‰ (n = 5, detrital and overgrowth). Calcite $\delta^{18}\text{O}$ values range from 22.7 to 25.3‰ (n = 17) and $\delta^{13}\text{C}$ ranges from -2.2 to 7.5‰ (n = 17). Ankerite-series $\delta^{18}\text{O}$ values range from 22.3 to 29.5‰ (n = 47) and $\delta^{13}\text{C}$ ranges from -5.5 to 5.1‰ (n = 51).

In the banded ankerite-series carbonates, the innermost carbonate (Zone 1) is near to endmember dolomite; however, while individual near-endmember dolomite cores are homogenous in Fe#, the range of Fe#s varies from grain to grain, from 0.00 to 0.03. These cores also have a wide range of $\delta^{18}\text{O}$ values (23.4 to 29.5‰), and $\delta^{13}\text{C}$ values in the -2.3 to 3.1‰ range. These carbonate cores commonly show partially anhedral boundaries with surrounding generations, as well as isolated interior pockets containing higher Fe compositions, both of which argue for partial dissolution/recrystallization. Two main bands of different Fe content lie between these cores and the ankerite-series carbonate rim. The first of these (Zone 2) has Fe#s in the 0.06 to 0.12 range, $\delta^{18}\text{O}$ values in the 22.6 to 26.6‰ range, and $\delta^{13}\text{C}$ values in the -5.2 to 3.9‰ range. The second and final high-Fe band (Zone 3) has Fe#s in the 0.23 to 0.36 range, $\delta^{18}\text{O}$ values in the 22.3 to 23.6‰ range, and $\delta^{13}\text{C}$ values in the -5.5 to -1.4‰ range. This final band is extremely thin or not present in a portion of the ankerite-series.

4.2.7 Well 7, Sample 21668-10225.8 (3117 m)

This sample was collected from skeletal mudstone at a depth of 3117 m (10225.8 ft.), and was combined with underlying sample C21668-10233.5 into a single SIMS mount (Figures 1.15e, 1.15f, Appendix 1.3.08). The rock matrix is dominated by coarse to medium silt-sized

silicates and carbonates, and surrounds large (up to 1 cm) skeletal calcites. Skeletal calcite is partially silicified in places, and parts of the sample where skeletal cavities once preserved porosity are now completely infilled with microcrystalline calcite. Grown into one of the larger cavities is a ~1mm diameter fractured banded ankerite-series carbonates, which was main target for SIMS. Calcite $\delta^{18}\text{O}$ values range from 20.4 to 30.8‰ (n = 9) and $\delta^{13}\text{C}$ ranges from -6.3 to 6.1‰ (n = 9). Ankerite-series $\delta^{18}\text{O}$ values range from 19.3 to 27.7‰ (n = 11) and $\delta^{13}\text{C}$ ranges from -8.3 to -0.2‰ (n = 15).

The innermost region of this banded carbonate (Zone 1) is dolomite with an Fe# of 0.00, $\delta^{18}\text{O}$ values of 24.6 to 28.0‰, and $\delta^{13}\text{C}$ values of -3.1 to -0.3. This is surrounded by a broad band (Zone 2) of more Fe-rich carbonate (Fe#s from 0.04 to 0.10), declining $\delta^{18}\text{O}$ values (24.9 to 21.4‰), and $\delta^{13}\text{C}$ values in the -7.6 to -3.1‰ range. At this stage of ankerite-series carbonate growth, the mineral was fractured in several places by an unknown mechanism. This fracturing precedes the final, most Fe-rich band (Zone 3, Fe#s of 0.17 to 0.24), which has $\delta^{18}\text{O}$ values in the 19.5 to 19.8‰ range and $\delta^{13}\text{C}$ values in the -8.2 to -6.7‰ range.

4.2.8 Well 7, Sample 21668-10233.5 (3119 m)

This sample was collected from an oolitic sandstone at a depth of 3119 m (10233.5 ft.), and was combined with overlying sample C21668-10225.8 into a single SIMS mount (Figures 1.15g, 1.15h, 1.15i, Appendix 1.3.08). Rounded calcite grains are medium to fine sand-size, and quartz detrital grains are fine sand to coarse silt- size. Banded ankerite-series carbonates are present throughout. Calcite $\delta^{18}\text{O}$ values range from 26.4 to 28.1 (n = 4) and $\delta^{13}\text{C}$ ranges from -0.7 to 5.5‰ (n = 4). Ankerite-series $\delta^{18}\text{O}$ values range from 22.4 to 30.0‰ (n = 19) and $\delta^{13}\text{C}$ ranges from -4.6. to 2.5‰ (n = 16).

The innermost region of this banded carbonate (Zone 1) is dolomite with an Fe# of 0.00, $\delta^{18}\text{O}$ values of 23.1 to 30.2‰, and $\delta^{13}\text{C}$ values of 0.2 to 2.5‰. Subsequent Fe-compositional zonation in these ankerite-series carbonates is more complex than in other samples. There is a general overall trend of increasing Fe# from core (innermost dolomite) to rim, but these banded ankerite-series carbonates also in places show regions of higher Fe concentration that are not evenly or concentrically distributed about dolomite cores (e.g., Figure 1.15i), indicating that they did not form through concentric outward growth of ankerite-series carbonates, and likely result from recrystallization processes. There are two major bins into which Fe#s may be placed. The first (Zone 2) has Fe#s in the range of 0.04-0.08 ($\delta^{18}\text{O}$ from 23.0 to 25.2‰ and $\delta^{13}\text{C}$ from -3.8 to 0.5‰, and the second (Zone 3) has Fe#s > 0.12 ($\delta^{18}\text{O}$ from 22.5 to 23.2‰ and $\delta^{13}\text{C}$ from -4.5 to -2.1‰).

4.2.9 Well 8, Sample 12785-11315.5 (3449 m)

This sample was collected from a calcite-filled fracture in a rock with a mixed carbonate-siliciclastic matrix at a depth of 3449 m (11315.5 ft.), and was made into a single SIMS mount (Figures 1.15j, 1.15k, 1.15l, Appendix 1.3.09). The rock matrix is predominantly calcite grains and diagenetic calcite pore-fill, with some detrital quartz; grains are very fine sand-sized. Banded ankerite-series carbonates are sparse in the rock matrix and entirely absent from the fracture itself. Calcite $\delta^{18}\text{O}$ values range from 22.9 to 27.0‰ (n=18) and $\delta^{13}\text{C}$ ranges from -4.1 to 5.9‰ (n=19). Ankerite-series $\delta^{18}\text{O}$ values range from 20.2 to 27.2‰ (n = 20) and $\delta^{13}\text{C}$ ranges from -6.1 to 5.2‰ (n = 21).

In the banded ankerite-series carbonates, the innermost carbonate (Zone 1) is dolomite with Fe#s of 0.00, $\delta^{18}\text{O}$ values showing a range of 24.9 to 27.2‰, and $\delta^{13}\text{C}$ values showing a

range of 1.3 to 2.8‰. These dolomite cores show euhedral morphologies indicative of formation in place. Surrounding many of these dolomite cores is a complex series of bands of carbonate with increasing Fe#s (0.04 up to 0.24), declining $\delta^{18}\text{O}$ values (26.2 down to 20.2‰), and fluctuating $\delta^{13}\text{C}$ values (-6.1 to 5.2‰). Some of these bands do not appear to correlate between individual ankerite-series carbonates, and in some cases no Fe-enriched bands are found around the 0.00 Fe# dolomite (e.g., Figure 1.15l).

4.2.10 Well 9, Sample 22493-11122.9 (3390 m)

This sample was collected from a sandstone at a depth of 3390 m (11122.9 ft.), and was made into a single SIMS mount (Figures 1.15m, 1.15n, Appendix 1.3.10). The rock is supported by detrital quartz, detrital calcite, banded ankerite-series carbonate, and feldspar grains in the very fine sand to coarse silt-size range. Both the feldspars and the ankerite-series carbonates commonly possess overgrowths; it is difficult to determine based on textural evidence if dolomite was originally grain supporting or if it is replacive after calcite. No fractures or other structural features are present. Calcite $\delta^{18}\text{O}$ data range from 24.0 to 24.6‰ ($n = 3$) and $\delta^{13}\text{C}$ data range from -2.1 to 1.1‰ ($n = 2$). Ankerite-series $\delta^{18}\text{O}$ values range from 22.3 to 30.4‰ ($n = 34$) and $\delta^{13}\text{C}$ ranges from -5.6 to 5.3‰ ($n = 37$).

The innermost band in the ankerite-series carbonates (Zone 1) is dolomite with an Fe# of 0.00, $\delta^{18}\text{O}$ values of 22.3 to 28.2‰, and $\delta^{13}\text{C}$ values in the -0.3 to 4.1‰ range. These dolomite cores commonly show rounded morphologies, and some show partial recrystallization to higher Fe#s (up to 0.18) (e.g., Figure 1.15n). Subsequent Fe-compositional zonation in these ankerite-series carbonates is more complex than in other samples, but shares certain textural parallels with C21668-10354.4. There is an overall trend of increasing Fe# from core (innermost

dolomite) to rim, but these banded ankerite-series carbonates also in places show regions of higher Fe concentration that are not evenly or concentrically distributed about dolomite cores (e.g., Figure 1.15n), suggesting that they did not form through concentric outward growth of ankerite-series carbonates, interpreted to result from recrystallization. There are two major bins into which Fe#s may be placed. The first (Zone 2) has broadly increasing Fe#s in the range of 0.02-0.08 (with declining $\delta^{18}\text{O}$ values from 30.3 to 22.8‰ and $\delta^{13}\text{C}$ values declining rapidly from 5.3 to -5.6), and the second (Zone 3) has Fe#s > 0.12 (with $\delta^{18}\text{O}$ in the 22.4 to 22.9‰ range and $\delta^{13}\text{C}$ from -2.1 to -1.0‰).

4.2.11 Well 9, Sample 22493-11159 (3401 m)

This sample was collected from the lower Bakken at a depth of 3401 m (11159 ft.), and was made into a single SIMS mount (Figures 1.15o, 1.15p, Appendix 1.3.11). This is the only sample analyzed that was not from the middle Bakken member; the rock was sampled due to the presence of a conspicuous 7 mm-wide fracture bounded by bands of pyrite and containing macroscopic ankerite-series carbonate rhombs. The fracture is in a predominantly calcite rock matrix, with individual crystals in the matrix falling in the 20-50 μm size range. Infilling the fracture is the following growth sequence of minerals: a thin 0.1 mm calcite band, a 0.5 mm band of pyrite, a thick layer of euhedral calcite crystals whose points can stretch 2 mm from tip to base, large fracture-spanning banded ankerite-series carbonate rhombs showing the curved euhedral growth bands typical of ‘saddle dolomite’ (Radke and Mathis, 1980), and finally, anhydrite filling in the remaining fracture space.

Matrix calcite has $\delta^{18}\text{O}$ values ranging 26.5 to 29.5‰ ($n = 5$) and very negative $\delta^{13}\text{C}$ values ranging -17.4 to -12.6‰ ($n = 8$). Fracture infill calcite shows a $\delta^{18}\text{O}$ values in the 23.1 to

26.5‰ range ($n = 10$), and $\delta^{13}\text{C}$ starts low and climbs towards higher values towards the calcite spar tips, from -15.7 up to $\sim -2\text{‰}$ ($n = 12$). Banded ankerite-series carbonates (all Zone 3) show increasing Fe#s as towards the rim (from 0.13 up to 0.30), declining $\delta^{18}\text{O}$ values (from 26.6 to 21.9‰, $n = 15$), and declining $\delta^{13}\text{C}$ values (from -1.8 to -10.3‰, $n = 25$).

5. Discussion

5.1 Dolomite Zone 1

Zone 1 dolomites commonly show rounded boundaries and non-euhedral internal textures that are suggestive of euhedral growth being interrupted by some additional process (e.g., 13c, 15b). Such textures suggest either that rounded dolomites formed from abrasion in a clastic environment on the seafloor, or that a period of dissolution that occurred within the sediment before carbonate precipitation resumed with ankerite-series compositions. The former interpretation would require dolomite to have formed at or near the sediment-water interface so as to be accessible to mechanical processes on the sea floor. Importantly, not all Zone 1 dolomites within an individual sample show rounded morphologies, indicating that the process was selective and did not affect all grains equally. If there is a mechanism by which heterogeneous dissolution can occur on dolomites at this scale, it is not immediately evident from petrographic observations. Values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ from Zone 1 show a fair degree of isotopic uniformity if compared between cores across the basin (Figures 1.9 and 1.16a), which could be used to argue for formation from water with nearly constant composition at a narrow range in temperatures, as one would expect if dolomite formed near the sediment-seawater interface or during early burial (Figure 1.17a).

The range of $\delta^{18}\text{O}$ values of dolomite in Zone 1 (most are 24-29‰) presents an interesting interpretational problem, however. If near-surface temperatures ($\sim 25^\circ\text{C}$) are assumed, the $\delta^{18}\text{O}$ of water from which the dolomite precipitated was in the -3 to -8‰ range (Horita, 2014) (Figure 1.16a). This is low for marine conditions; estimates for seawater $\delta^{18}\text{O}$ at this time are substantially higher at -1.5‰ (Hudson and Anderson, 1989; van Geldern et al., 2006). Three plausible explanations exist for these observations: 1) Basin waters had very low $\delta^{18}\text{O}$ values at this time and did not reflect global seawater values, 2) Zone 1 dolomites precipitated from -1.5‰ porewater derived from seawater at around 50°C , and 3) Petrographic textures reflect early metastable dolomite precipitation near the sediment-seawater interface (25°C) and their isotopic geochemistry was reset when these dolomites recrystallized at higher temperatures.

If the Williston depocenter was sufficiently restricted at this time, it is conceivable that local water may have been driven to lower $\delta^{18}\text{O}$ values by meteoric input from either enhanced precipitation or riverine input. Such an interpretation would remove the necessity of invoking elevated temperatures to explain the range of low $\delta^{18}\text{O}$ values of these dolomites, and allow for dolomite to form near enough to the surface to allow the grains to be eroded in a clastic environment. However, a variable meteoric contribution cannot sufficiently explain the sizeable spread of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values ($\sim 5\text{‰}$) observed in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements of these dolomites *within the same sample*, as such fluids might be expected to be relatively homogenous across these length scales during early dolomite formation.

If, however, precipitation of Zone 1 dolomite occurred from water with a $\delta^{18}\text{O}$ value that was no lower than $\delta^{18}\text{O} = -1.5\text{‰}$ for the Devonian-Mississippian ocean, then dolomite $\delta^{18}\text{O}$

values represent either initial precipitation or recrystallization at higher temperatures of ~50 °C. In the precipitation case, rounded textures would be indicative of dissolution, rather than abrasion, and that dissolution occurred nonuniformly from dolomite grain to dolomite grain. Under this interpretation, the earliest growth phase in these ankerite-series carbonates precipitated at or above 50 °C and no detrital dolomites were present in the Bakken. By contrast, the recrystallization case allows rounded petrographic textures to originate as detrital dolomite, but also necessitates that dolomites recrystallized from metastable precursors at or above 50 °C, resetting their isotope ratios.

With the prevalence of recognizable recrystallization textures in some of the dolomite and ankerite-series carbonates, particularly in the deeper and higher temperature parts of the basin, it is evident that recrystallization has played a role in determining the final isotopic composition of some of these carbonates. Regardless of the origin of rounded dolomite textures, we think that dolomite $\delta^{18}\text{O}$ values reflect recrystallization in sediments at ~50°C, a process that has been recognized in other locations (Jones, 2008; Reinhold, 1998). This interpretation is in agreement with fluid inclusion measurements, which indicate that this zone formed below 70°C (Śliwiński et al., 2019).

5.2 Ankerite-series Zones 2 and 3

Zones 2 and 3 formed subsequent to Zone 1 and broadly follow a progression from Zone 1 values towards enriched Fe content and lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values (Figure 1.5a), and are interpreted as forming along the path towards maximum burial temperatures. Fluid inclusion analyses on early Zone 3 cements from a core along the western basin margin indicate

temperatures of formation of $\sim 115\text{--}125^\circ\text{C}$ (Śliwiński et al., 2019), which is close to maximum temperatures modeled for that location by Kuhn et al. (2012). Temperature changes have an effect on the dolomite-water fractionation for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, and the line plotted in Figures 1.5a and 1.5b shows the trajectory that a purely temperature-derived isotopic trend will follow if the composition of fluids is constant. The degree of deviation from this line shows that isotopic values in dolomite and ankerite cannot be ascribed solely to changes in temperature, indicating that source pore water $\delta^{18}\text{O}$ values increased and/or $\delta^{13}\text{C}_{\text{CO}_2}$ declined over the course of ankerite-series cement precipitation. Thus, ankerite-series cements precipitated over a sufficient period of time to generate changes in temperature and porewater chemistry. The observation that pore water $\delta^{18}\text{O}$ increased with time as ankerite-series cements grew is consistent with pore water $\delta^{18}\text{O}$ trends observed to occur in other basins in response to water-rock interaction (Clayton et al., 1966). Brines in the middle Bakken today can have $\delta^{18}\text{O}$ values in excess of 5‰ (Peterman et al., 2017), and $\delta^{18}\text{O}$ in excess of 9.4‰ has been reported for brines from the Devonian Duperow aquifer, which lies below the Bakken (Rostron and Holmden, 2000, 2003).

The progressive trend of dolomite towards lower $\delta^{18}\text{O}$ values observed to occur across Zones 2 and 3 is interpreted to be primarily temperature-driven, but temperature effects were partly offset by changing pore water $\delta^{18}\text{O}$. Values of $\delta^{13}\text{C}$ also decline across Zones 2 and 3, with the lowest $\delta^{13}\text{C}$ values generally being associated with the highest Fe#s. This is consistent with increasing interaction of pore waters with low- $\delta^{13}\text{C}$ organic matter present in adjacent shales, as CO_2 is produced during the breakdown of organic matter and during hydrocarbon maturation (Surdam et al., 1989). If Zone 3 grew relatively late in the burial history and at near-

maximum temperatures, as is suggested by its more ankeritic compositions and low $\delta^{13}\text{C}$ values, then one would also expect Zone 3 data to parallel equilibrium fractionation lines for positive $\delta^{18}\text{O}_{\text{water}}$ values at near maximum burial. Indeed, there is a progressive trend from Zone 1 to Zone 3 towards equilibrium with a +5 to +10‰ $\delta^{18}\text{O}$ basinal brine (Figures 1.16b, 1.16c).

5.3 Late Ankerite in Shallow Cores

Samples collected towards the margin of the basin (Wells 1 and 2) diverge from the above-mentioned trends in some key ways. Fe-poor dolomitic bands present within Zone 2 and correlatable between the two samples are closely associated with high $\delta^{18}\text{O}$ values (>30‰). In Well 2 there is no significant correlation of $\delta^{13}\text{C}$ with this change in $\delta^{18}\text{O}$, but in Well 1 these Fe-poor bands are followed by a thick Fe-rich zone containing $\delta^{18}\text{O}$ values ~30‰ and $\delta^{13}\text{C}$ values ~-7‰, which require the unusual combination of high $\delta^{18}\text{O}$ or low-temperature fluids that have also seen significant conversion of organic to inorganic carbon. The final, Zone 3 growth band in Well 1 contains low $\delta^{18}\text{O}$ (~20‰) and $\delta^{13}\text{C}$ near 0‰, indicative of high temperature or meteoric fluids that have interacted with carbonates. This last band only appears where porosity is still preserved today, and does not develop any significant thickness in an anhydrite-filled fracture, indicating that it is contemporaneous or post-dates the introduction of anhydrite into the fracture. These isotopic trends necessitate the movement of fluids of significantly different composition from those that precipitated Zone 1 and early Zone 2 ankerite-series carbonates. We propose that the initial ~30‰ band resulted from fluids that migrated out of the deeper parts of the basin during hydrocarbon expulsion, as is known to have occurred along the NE margin of the Williston Basin (Webster, 2011). The final band in Zone 3 must result from low-

$\delta^{18}\text{O}$ meteoric waters post-expulsion (Figure 1.16c), likely associated with hypothesized fresh water influx during the Pleistocene glaciation (Grasby and Betcher, 2000).

5.4 Calcite Cements

Calcite and ankerite-series carbonates show similar magnitudes of variability in both $\delta^{18}\text{O}$ (Figure 1.3) and $\delta^{13}\text{C}$ (Figure 1.4). This may indicate that, for some samples (e.g., Well 3), both calcite and ankerite-series carbonate grew or recrystallized under the same range of conditions (Figure 1.6). However, not all of the isotope data suggest that diagenetic calcites in the middle Bakken Formation resulted from the same processes as ankerite-series cements. Most of the calcite values in sample 22493-11159 (Well 9) do not parallel the dolomite trend in Figure 1.6i. These cements petrographically predate those of the zoned ankerite-series (Appendix 1.3.11), and likely resulted from low-temperature methanogenesis in the shallowly buried mud-rich sediments of the lower Bakken member. Indeed, the fracture in sample 22493-11159 (Well 9) bears comparison to septarian concretions for its extremely low $\delta^{13}\text{C}$ values of both rock matrix and fracture-filling calcites (Siegel et al., 1987; Thyne and Boles, 1989). Despite forming in a shale surrounded by calcites with very negative $\delta^{13}\text{C}$ values, the ankerites that have formed within the cracks of the concretion fall along the same trajectory as the other Well 9 sample taken from the middle Bakken. This strongly suggests that the same fluid and temperature trends were driving parallel crystallization of ankerite throughout the formation.

6. Conclusions

SIMS analyses in zoned carbonates from nine middle Bakken cores demonstrate remarkably large isotopic variability (often > 10‰) for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ on the sub-mm scale, that

would otherwise be lost using gas-source mass spectrometry and acid dissolution of bulk powder samples. These zonations are correlatable across a ~250 km transect through the Bakken formation, cover a wide range of burial temperatures, and preserve a history of diagenetic rock evolution from the formation of early dolomites in the shallow sediment on through to deep burial. This indicates that diagenetic processes affecting the middle Bakken carbonates are regional in scope, and that individual growth bands in cements developed in response to diagenetic conditions inherent to the middle Bakken and its neighboring units. Overall trends in ankerite-series minerals strongly indicate a progressive bias of bulk carbonate $\delta^{13}\text{C}$ values due to prolonged organic/inorganic mineral interaction. Cements along the basin margin have also recorded fluid movements into and out of the basin, associated with hydrocarbon expulsion and meteoric water infiltration. Carbonate minerals are sometimes assumed to control the isotope ratio in diagenetic fluids in the subsurface, but the large isotopic variability present in diagenetic carbonates at the micron scale in these samples demonstrates that such rock control cannot be taken for granted in bulk isotopic studies, especially if grain-boundary ion diffusion rates are sufficiently high and carbonate reprecipitation rates are sufficiently low.

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Appendices

Appendix 1.1 – Condensed SIMS dataset (.xlsx)

Appendix 1.2 – Full SIMS datasets w/ standards and IMF corrections (.xlsx)

Appendix 1.3 – Mount maps of SIMS data

1.3.01 – SIMS mount 24883-3743.4 (.pdf)

1.3.02 – SIMS mount 20249-6013.4 (.pdf)

1.3.03 – SIMS mount 20249-6013.4B (.pdf)

1.3.04 – SIMS mount 17272-7591.5 (.pdf)

1.3.05 – SIMS mount 17676-8738.4 (.pdf)

1.3.06 – SIMS mount 16586-9812.5 (.pdf)

1.3.07 – SIMS mount 17015-10354.4 (.pdf)

1.3.08 – SIMS mount 21668-10233.5, 10225.8 (.pdf)

1.3.09 – SIMS mount 12785-11315.5 (.pdf)

1.3.10 – SIMS mount 22493-11122.9 (.pdf)

1.3.11 – SIMS mount 22493-11159 (.pdf)

References

- Banner, J.L., 1995. Application of the trace element and isotope geochemistry of strontium to studies of carbonate diagenesis. *Sedimentology* 42, 805–824.
- Banner, J.L., Hanson, G.N., 1990. Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. *Geochimica et Cosmochimica Acta* 54, 3123–3137. [https://doi.org/10.1016/0016-7037\(90\)90128-8](https://doi.org/10.1016/0016-7037(90)90128-8)
- Berger, P.M., Roy, W.R., Mehnert, E., 2009. Geochemical Modeling of Carbon Sequestration, MMV, and EOR in the Illinois Basin. *Energy Procedia* 1, 3437–3444.
- Borcovsky, D., Egenhoff, S., Fishman, N., Maletz, J., Boelhke, A., Lowers, H., 2017. Sedimentology, facies architecture, and sequence stratigraphy of a Mississippian black mudstone succession—The upper member of the Bakken Formation, North Dakota, United States. *American Association of Petroleum Geologists Bulletin* 101, 1625–1673. <https://doi.org/10.1306/01111715183>
- Bowen, B.B., Ochoa, R.I., Wilkens, N.D., Brophy, J., Lovell, T.R., Fischietto, N., Medina, C.R., Rupp, J.A., 2011. Depositional and diagenetic variability within the Cambrian Mount Simon Sandstone: Implications for carbon dioxide sequestration. *Environmental Geosciences* 18, 69–89.
- Brand, U., Veizer, J., 1981. Chemical diagenesis of a multicomponent carbonate system; 2, Stable isotopes. *Journal of Sedimentary Research* 51, 987–997.
- Brodie, M.W., Aplin, A.C., Hart, B., Orland, I.J., Valley, J.W., Boyce, A.J., 2018. Oxygen Isotope Microanalysis by Secondary Ion Mass Spectrometry Suggests Continuous 300-million-year History of Calcite Cementation and Dolomitization in the Devonian Bakken Formation. *Journal of Sedimentary Research* 88, 91–104. <https://doi.org/10.2110/jsr.2018.1>
- Cammack, J.N., Spicuzza, M.J., Cavosie, A.J., Van Kranendonk, M.J., Hickman, A.H., Kozdon, R., Orland, I.J., Kitajima, K., Valley, J.W., 2018. SIMS microanalysis of the Strelley Pool Formation cherts and the implications for the secular-temporal oxygen-isotope trend of cherts. *Precambrian Research* 304, 125–139. <https://doi.org/10.1016/j.precamres.2017.11.005>
- Clayton, R.N., Friedman, I., Graf, D.L., Mayeda, T.K., Meents, W.F., Shimp, N.F., 1966. The Origin of Saline Formation Waters: 1. Isotopic Composition. *Journal of Geophysical Research* 71, 3869–3882.

- Denny, A.C., Kozdon, R., Kitajima, K., Valley, J.W., 2017. Isotopically zoned carbonate cements in Early Paleozoic sandstones of the Illinois Basin: $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records of burial and fluid flow. *Sedimentary Geology* 361, 93–110. <https://doi.org/10.1016/j.sedgeo.2017.09.004>
- Donovan, J.J., 2018. Probe for EPMA User's Guide and Reference Manual. Probe Software.
- Donovan, J.J., Tingle, T.N., 1996. An improved mean atomic number background correction for quantitative microanalysis. *Microscopy and Microanalysis* 2, 1–7.
- Egenhoff, S., Dolah, A.V., Jaffri, A., Maletz, J., 2011. Chapter 2: Facies Architecture and Sequence Stratigraphy of the Middle Bakken Member, North Dakota, in: Robinson, J.W., LeFever, J.A., Gaswirth, S.B. (Eds.), *The Bakken–Three Forks Petroleum System in the Williston Basin*. Rocky Mountain Association of Geologists, Denver, Colorado, pp. 27–47.
- Gaswirth, S.B., Marra, K.R., 2015. U.S. Geological Survey 2013 assessment of undiscovered resources in the Bakken and Three Forks Formations of the U.S. Williston Basin Province. *American Association of Petroleum Geologists Bulletin* 99, 639–660. <https://doi.org/10.1306/08131414051>
- Gaswirth, S.B., Marra, K.R., Cook, T.A., Charpentier, R.R., Gautier, D.L., Higley, D.K., Klett, T.R., Lewan, M.D., Lillis, P.G., Schenk, C.J., 2013. Assessment of Undiscovered Oil resources in the Bakken and Three Forks Formations, Williston Basin Province, Montana, North Dakota, and South Dakota, 2013 (USGS Fact Sheet No. 2013–3013).
- Grasby, S.E., Betcher, R., 2000. Pleistocene recharge and flow reversal in the Williston basin, central North America. *Journal of Geochemical Exploration* 69–70, 403–407. [https://doi.org/10.1016/S0375-6742\(00\)00092-3](https://doi.org/10.1016/S0375-6742(00)00092-3)
- 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. *Journal of Sedimentary Research* 83, 522–530.
- Horita, J., 2014. Oxygen and carbon isotope fractionation in the system dolomite–water– CO_2 to elevated temperatures. *Geochimica et Cosmochimica Acta* 129, 111–124. <https://doi.org/10.1016/j.gca.2013.12.027>
- Huberty, J.M., Kita, N.T., Kozdon, R., Heck, P.R., Fournelle, J.H., Spicuzza, M.J., Xu, H., Valley, J.W., 2010. Crystal orientation effects in $\delta^{18}\text{O}$ for magnetite and hematite by SIMS. *Chemical Geology* 276, 269–283. <https://doi.org/10.1016/j.chemgeo.2010.06.012>
- Hudson, J.D., Anderson, T.F., 1989. Ocean temperatures and isotopic compositions through time. *Earth and Environmental Science Transactions of The Royal Society of Edinburgh* 80, 183–192. <https://doi.org/10.1017/S0263593300028625>
- Hyodo, A., Kozdon, R., Pollington, A.D., Valley, J.W., 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, 168–180.
<https://doi.org/10.1016/j.chemgeo.2014.06.021>
- Irwin, H., Curtis, C., Coleman, M., 1977. Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. *Nature* 269, 209–213.
- Jones, B., 2007. Inside-Out Dolomite. *Journal of Sedimentary Research* 77, 539–551.
<https://doi.org/10.2110/jsr.2007.056>
- 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. *Geochimica et Cosmochimica Acta* 71, 3812–3832.
- Kita, N.T., Ushikubo, T., Fu, B., Valley, J.W., 2009. High precision SIMS oxygen isotope analysis and the effect of sample topography. *Chemical Geology* 264, 43–57.
<https://doi.org/10.1016/j.chemgeo.2009.02.012>
- Kozdon, R., Kelly, D.C., Kita, N.T., Fournelle, J.H., Valley, J.W., 2011. Planktonic foraminiferal oxygen isotope analysis by ion microprobe technique suggests warm tropical sea surface temperatures during the Early Paleogene. *Paleoceanography* 26.
- Kozdon, R., Ushikubo, T., Kita, N.T., Spicuzza, M., Valley, J.W., 2009. Intratest oxygen isotope variability in the planktonic foraminifer *N. pachyderma*: Real vs. apparent vital effects by ion microprobe. *Chemical Geology* 258, 327–337.
- Kuhn, P.P., di Primio, R., Hill, R., Lawrence, J.R., Horsfield, B., 2012. Three-dimensional modeling study of the low-permeability petroleum system of the Bakken Formation. *American Association of Petroleum Geologists Bulletin* 96, 1867–1897.
<https://doi.org/10.1306/03261211063>
- LeFever, J.A., Fever, R.D.L., Nordeng, S.H., 2011. Chapter 1: Revised Nomenclature for the Bakken Formation (Mississippian-Devonian), North Dakota, in: Robinson, J.W., Lefever, J.A., Gaswirth, S.B. (Eds.), *The Bakken–Three Forks Petroleum System in the Williston Basin*. Rocky Mountain Association of Geologists, Denver, Colorado, pp. 11–26.
- Linzmeier, B.J., Kitajima, K., Denny, A.C., Cammack, J.N., 2018. Making maps on a micrometer scale. *Eos* 99, 24–28.
- Peterman, Z., Thamke, J.N., Futa, K., Oliver, T.A., 2017. Characterization and origin of brines from the Bakken-Three Forks petroleum system in the Williston Basin, USA. *Mountain Geologist* 54, 203–221.
- Pitman, J.K., Price, L.C., LeFever, J.A., 2001. Diagenesis and fracture development in the Bakken Formation, Williston Basin: Implications for reservoir quality in the middle member (No. 1653), U.S. Geological Survey Professional Paper.

- Pollington, A.D., Kozdon, R., Anovitz, L.M., Georg, R.B., Spicuzza, M.J., Valley, J.W., 2016. Experimental calibration of silicon and oxygen isotope fractionation between quartz and water at 250°C by in situ microanalysis of experimental products and application to natural samples. *Chemical Geology* 421: 127–142.
- Pollington, A.D., Kozdon, R., Valley, J.W., 2011. Evolution of quartz cementation during burial of the Cambrian Mount Simon Sandstone, Illinois Basin: In situ microanalysis of $\delta^{18}\text{O}$. *Geology* 39, 1119–1122.
- Purser, B.H., Brown, A., Aissaoui, D.M., 1994. Nature, Origins and Evolution of Porosity in Dolomites, in: Purser, B., Tucker, M., Zenger, D. (Eds.), *Dolomites*. Blackwell Publishing Ltd., pp. 281–308.
- Radke, B.M., Mathis, R.L., 1980. On the Formation and Occurrence of Saddle Dolomite. *Journal of Sedimentary Research* 50, 1149–1168.
- Reinhold, C., 1998. Multiple episodes of dolomitization and dolomite recrystallization during shallow burial in Upper Jurassic shelf carbonates: eastern Swabian Alb, southern Germany. *Sedimentary Geology* 121, 71–95. [https://doi.org/10.1016/S0037-0738\(98\)00077-3](https://doi.org/10.1016/S0037-0738(98)00077-3)
- Rostron, B.J., Holmden, C., 2003. Regional variations in oxygen isotopic compositions in the Yeoman and Duperow aquifers, Williston basin (Canada-USA). *Journal of Geochemical Exploration, Proceedings of Geofluids Fourth International Conference on Fluid Evolution, Migration and Interaction in Sedimentary Basins and Orogenic Belts* 78–79, 337–341. [https://doi.org/10.1016/S0375-6742\(03\)00086-4](https://doi.org/10.1016/S0375-6742(03)00086-4)
- Rostron, B.J., Holmden, C., 2000. Fingerprinting formation-waters using stable isotopes, Midale Area, Williston Basin, Canada. *Journal of Geochemical Exploration* 69–70, 219–223. [https://doi.org/10.1016/S0375-6742\(00\)00024-8](https://doi.org/10.1016/S0375-6742(00)00024-8)
- Siegel, D.I., Chamberlain, S.C., Dossert, W.P., 1987. The isotopic and chemical evolution of mineralization in sepiarian concretions: Evidence for episodic paleohydrogeologic methanogenesis. *Geological Society of America Bulletin* 99, 385–394. [https://doi.org/10.1130/0016-7606\(1987\)99<385:TIACEO>2.0.CO;2](https://doi.org/10.1130/0016-7606(1987)99<385:TIACEO>2.0.CO;2)
- Simenson, A.L., Sonnenberg, S.A., Cluff, R.M., 2011. Chapter 3: Depositional Facies and Petrophysical Analysis of the Bakken Formation, Parshall Field and Surrounding Area, Mountrail County, North Dakota, in: Robinson, J.W., LeFever, J.A., Gaswirth, S.B. (Eds.), *The Bakken–Three Forks Petroleum System in the Williston Basin*. Rocky Mountain Association of Geologists, Denver, Colorado, pp. 48–101.
- Śliwiński, M.G., Kitajima, K., Kozdon, R., Spicuzza, M.J., Denny, A., Valley, J.W., 2017a. In situ $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ microanalysis by SIMS: A method for characterizing the carbonate

- components of natural and engineered CO₂-reservoirs. *International Journal of Greenhouse Gas Control* 57, 116–133. <https://doi.org/10.1016/j.ijggc.2016.12.013>
- Śliwiński, M.G., Kitajima, K., Kozdon, R., Spicuzza, M.J., Fournelle, J.H., Denny, A.C., Valley, J.W., 2016a. Secondary Ion Mass Spectrometry Bias on Isotope Ratios in Dolomite–Ankerite, Part I: $\delta^{18}\text{O}$ Matrix Effects. *Geostandards and Geoanalytical Research* 40, 157–172. <https://doi.org/10.1111/j.1751-908X.2015.00364.x>
- Śliwiński, M.G., Kitajima, K., Kozdon, R., Spicuzza, M.J., Fournelle, J.H., Denny, A.C., Valley, J.W., 2016b. Secondary Ion Mass Spectrometry Bias on Isotope Ratios in Dolomite–Ankerite, Part II: $\delta^{13}\text{C}$ Matrix Effects. *Geostandards and Geoanalytical Research* 40, 173–184. <https://doi.org/10.1111/j.1751-908X.2015.00380.x>
- Śliwiński, M.G., Kitajima, K., Spicuzza, M.J., Orland, I.J., Ishida, A., Fournelle, J.H., Valley, J.W., 2017b. SIMS Bias on Isotope Ratios in Ca-Mg-Fe Carbonates (Part III): $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ Matrix Effects Along the Magnesite–Siderite Solid-Solution Series. *Geostandards and Geoanalytical Research* 42, 49–76. <https://doi.org/10.1111/ggr.12194>
- Śliwiński, M.G., Schreiber, B.C., Ishida, A., Haroldson, E., Kuhn, P.P., Salazar-Jaramillo, S., Denny, A.C., Barnes, B.D., Spicuzza, M.J., Kitajima, K., Peters, S.E., Valley, J.W., 2019. Dolomitization of the Middle Bakken Tight-oil Reservoir (Late Devonian – Early Mississippian, Williston Basin), 47. http://www.geology.wisc.edu/homepages/wiscsims/public_html/pdfs/Sliwinski_Unpub2019.pdf
- Smith, M.G., Bustin, R.M., 2000. Late Devonian and Early Mississippian Bakken and Exshaw black shale source rocks, Western Canada sedimentary basin: a sequence stratigraphic interpretation. *American Association of Petroleum Geologists Bulletin* 84, 940–960.
- Sonnenberg, S.A., 2011a. Chapter 11: TOC and Pyrolysis Data for the Bakken Shales, Williston Basin, North Dakota and Montana, in: Robinson, J.W., LeFever, J.A., Gaswirth, S.B. (Eds.), *The Bakken–Three Forks Petroleum System in the Williston Basin*. The Rocky Mountain Association of Geologists, Denver, Colorado, pp. 308–331.
- Sonnenberg, S.A., LeFever, J.A., Hill, R.J., 2011b. Chapter 15: Fracturing in the Bakken Petroleum System, Williston Basin, in: Robinson, J.W., LeFever, J.A., Gaswirth, S.B. (Eds.), *The Bakken–Three Forks Petroleum System in the Williston Basin*. The Rocky Mountain Association of Geologists, Denver, Colorado, pp. 393–417.
- Staruiala, A., Qing, H., Chi, G., Stern, R., Petts, D., 2013. Dolomite petrography and stable isotope geochemistry of the Bakken Formation, southeastern Saskatchewan, in: *Summary of Investigations, Volume 1, Saskatchewan Geological Survey, Saskatchewan Ministry of the Economy, Miscellaneous Report 2013-4.1, Paper A-8*, 10 p.

- Sun, S.Q., 1995. Dolomite Reservoirs: Porosity Evolution and Reservoir Characteristics. *American Association of Petroleum Geologists Bulletin* 79, 186–204.
- Surdam, R.C., Crossey, L.J., Hagen, E.S., Heasler, H.P., 1989. Organic-Inorganic Interactions and Sandstone Diagenesis. *American Association of Petroleum Geologists Bulletin* 73, 1–23.
- Swart, P.K., 2015. The geochemistry of carbonate diagenesis: The past, present and future. *Sedimentology* 62, 1233–1304. <https://doi.org/10.1111/sed.12205>
- Teboul, P.-A., Durlet, C., Girard, J.-P., Dubois, L., San Miguel, G., Virgone, A., Gaucher, E.C., Camoin, G., 2019. Diversity and origin of quartz cements in continental carbonates: Example from the Lower Cretaceous rift deposits of the South Atlantic margin. *Applied Geochemistry* 100, 22–41. <https://doi.org/10.1016/j.apgeochem.2018.10.019>
- Thyne, G.D., Boles, J.R., 1989. Isotopic evidence for origin of the Moeraki septarian concretions, New Zealand. *Journal of Sedimentary Research* 59, 272–279. <https://doi.org/10.1306/212F8F6C-2B24-11D7-8648000102C1865D>
- Valley, J.W., Kita, N.T., 2009. In situ oxygen isotope geochemistry by ion microprobe. *Mineralogical Association of Canada Short Course* 41, 19–63.
- van Geldern, R., Joachimski, M.M., Day, J., Jansen, U., Alvarez, F., Yolkin, E.A., Ma, X.-P., 2006. Carbon, oxygen and strontium isotope records of Devonian brachiopod shell calcite. *Palaeogeography, Palaeoclimatology, Palaeoecology, Evolution of the System Earth in the Late Palaeozoic: Clues from Sedimentary Geochemistry* 240, 47–67. <https://doi.org/10.1016/j.palaeo.2006.03.045>
- Wang, X.-L., Coble, M.A., Valley, J.W., Shu, X.-J., Kitajima, K., Spicuzza, M.J., Sun, T., 2014. Influence of radiation damage on Late Jurassic zircon from southern China: Evidence from in situ measurements of oxygen isotopes, laser Raman, U–Pb ages, and trace elements. *Chemical Geology* 389, 122–136. <https://doi.org/10.1016/j.chemgeo.2014.09.013>
- Warren, J., 2000. Dolomite: occurrence, evolution and economically important associations. *Earth-Science Reviews* 52, 1–81. [https://doi.org/10.1016/S0012-8252\(00\)00022-2](https://doi.org/10.1016/S0012-8252(00)00022-2)
- Webster, R.L., 2011. Chapter 19: Petroleum Source Rocks and Stratigraphy of the Bakken Formation in North Dakota, in: Robinson, J.W., LeFever, J.A., Gaswirth, S.B. (Eds.), *The Bakken–Three Forks Petroleum System in the Williston Basin*. The Rocky Mountain Association of Geologists, Denver, Colorado, pp. 490–507.
- Wentworth, C.K., 1922. A scale of grade and class terms for clastic sediments. *The Journal of Geology* 30, 377–392.
- Williams, L.B., Hervig, R.L., Dutton, S.P., 1997. Constraints on Paleofluid Compositions in the Travis Peak Formation, East Texas: Evidence from Microanalyses of Oxygen Isotopes in

Diagenetic Quartz, in: Basin-Wide Diagenetic Patterns: Integrated Petrologic, Geochemical, and Hydrologic Considerations, SEPM Special Publication. pp. 269–280.

Worden, R.H., Burley, S.D., 2003. Sandstone Diagenesis: The Evolution of Sand to Stone, in: Burley, S.D., Worden, R.H. (Eds.), Sandstone Diagenesis: Recent and Ancient. Blackwell Publishing Ltd., Oxford, UK, pp. 1–44.

Figures

Table 1.1. Name, depth, and location information for the 9 cores sampled.

Transect Name	NDGS Well #, API #	Original Operator	Well Name	Latitude, Longitude	Depth of SIMS sample (ft from surface)	Depth of SIMS sample (~m from surface)
Well 1	24883, 33009023020000	CORINTHIAN EXPLORATION (USA) CORP	2-BRENDEN 9- 33 1-M	48.9856084102176, -100.64720876165	3743.4	1141
Well 2	20249, 33075014170000	MUREX PETROLEUM CORPORATION	HEATHER LYNNE 1	48.862857 -101.826943	6013.4	1833
Well 3	17272, 33101004730000	HESS CORPORATION	IM-SHORTY- 159-88- 0805H-1	48.604914 -102.061986	7591.5	2314
Well 4	17676, 33061008840000	EOG RESOURCES, INC.	SIDONIA 1- 06H	48.533032 -102.344392	8738.4	2663
Well 5	16586, 33061005300000	EOG RESOURCES, INC.	BURES 1-17H	48.340544 -102.545948	9812.5	2991
Well 6	17015, 33105016670000	HEADINGTON OIL COMPANY LLC	NESSON STATE 42X-36	48.291365 -102.828463	10354.4	3156
Well 7	21668, 33053038190000	BURLINGTON RESOURCES OIL & GAS COMPANY LP	UBERWACHEN 22-34	48.033330 -102.886133	10225.8/10233.5	3117/3119
Well 8	12785, 33025004470000	MAXUS EXPLORATION CO.	CARUS FEE #21-19	47.542727, -102.963685	11315.5	3449
Well 9	22493, 33053040110000	NEWFIELD PRODUCTION COMPANY	BERNICE 150- 99-20-17-2H	47.791458 -103.373165	11122.9/11159	3390/3401

Table 1.2. Ranges of isotopic data observed in each sample. A more detailed breakdown of isotopic trends in each sample may be found in the text.

Sample	Ankerite-series carbonate		Calcite	
	$\delta^{18}\text{O}$ range (VSMOW)	$\delta^{13}\text{C}$ range (VPDB)	$\delta^{18}\text{O}$ range (VSMOW)	$\delta^{13}\text{C}$ range (VPDB)
Well 1, 24883-3743.4	19.2 to 38.2‰ (n = 36)	-8.3 to 4.8‰ (n = 31)	20.1 to 29.2 (n = 13)	-7.4 to 2.6‰ (n = 13)
Well 2, 20249-6013.4	23.1 to 35.2‰ (n=63)	-3.2 to 4.0‰ (n = 40)	27.6 to 29.7‰ (n = 6)	-0.7 to 0.8‰ (n = 5)
Well 3, 17272-7591.5	23.4 to 29.8‰ (n = 31)	-7.2 to 2.6‰ (n=30)	23.2 to 31.3‰ (n = 10)	-4.2 to 5.7‰ (n = 11)
Well 4, 17676-8738.4	21.8 to 28.5‰ (n = 32)	-8.8 to 1.4‰ (n = 37)	24.5 to 32.1‰ (n = 15)	-10.3 to 4.8‰ (n = 17)
Well 5, 16586-9812.5	21.7 to 29.5‰ (n = 32)	-5.9 to 3.3‰ (n = 39)	24.5 to 28.0‰ (n = 7)	-2.0 to 5.2‰ (n = 10)
Well 6, 17015-10354.4	22.3 to 29.5‰ (n = 47)	-5.5 to 5.1‰ (n = 51)	22.7 to 25.3‰ (n = 17)	-2.2 to 7.5‰ (n = 17)
Well 7, 21668-10225.8	19.3 to 27.7‰ (n = 11)	-8.3 to -0.2‰ (n = 15)	20.4 to 30.8‰ (n = 9)	-6.3 to 6.1‰ (n = 9)
Well 7, 21668-10233.5	22.4 to 30.0‰ (n = 19)	-4.6. to 2.5‰ (n = 16)	26.4 to 28.1‰ (n = 4)	-0.7 to 5.5‰ (n = 4)
Well 8, 12785-11315.5	20.2 to 27.2‰ (n = 20)	-6.1 to 5.2‰ (n = 21)	22.9 to 27.0‰ (n=18)	-4.1 to 5.9‰ (n=19)
Well 9, 22493-11122.9	22.3 to 30.4‰ (n = 34)	-5.6 to 5.3‰ (n = 37)	24.0 to 24.6‰ (n = 3)	-2.1 to 1.1‰ (n = 2)
Well 9, 22493-11159	21.9 to 26.6 ‰ (n = 15)	-10.3 to -1.8‰ (n = 25)	23.1 to 29.5‰ (n = 15)	-17.4 to -1.8‰ (n = 20)

Figure 1.1. Map of structure-depth contours for the Bakken Formation in western North Dakota, with the locations of drill core samples analyzed in this paper marked by stars. Note that contours displayed here are measured relative to sea level so as to best convey the basin's structure; all other depths reported in this paper are relative to the local surface elevation. The subsurface extent of the Bakken formation is marked with a dashed line. MT = Montana, ND = North Dakota. Figure modified from Sonnenberg et al., 2011a. See Table 1.1 for more information about sampling locations.

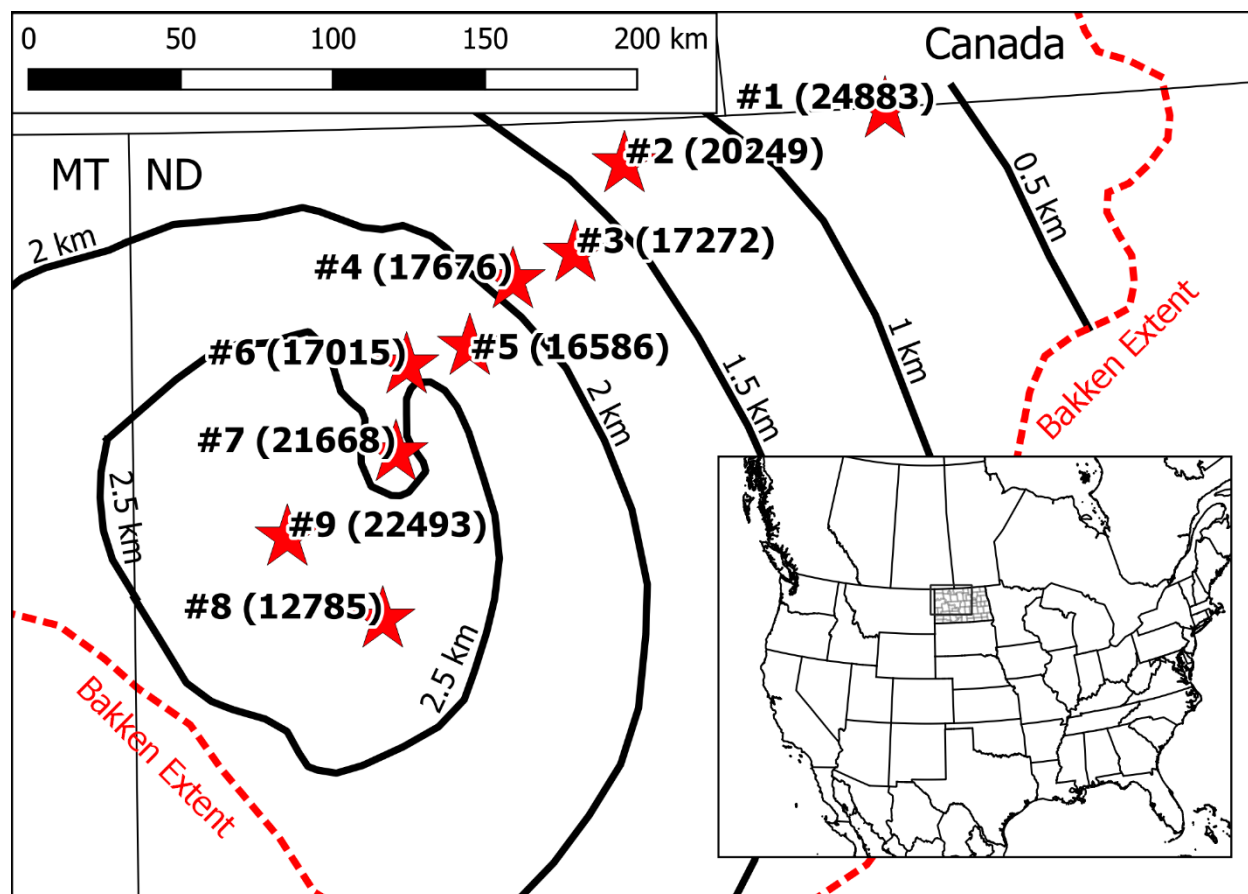


Figure 1.2. (a) Generalized stratigraphy of the Williston Basin, modified from Borcovsky et al. (2017). **(b)** Facies of the Bakken in studied drill cores, using the classification scheme of Egenhoff et al. (2011). Red dots denote the locations of samples selected for SIMS analysis. Color available in online version.

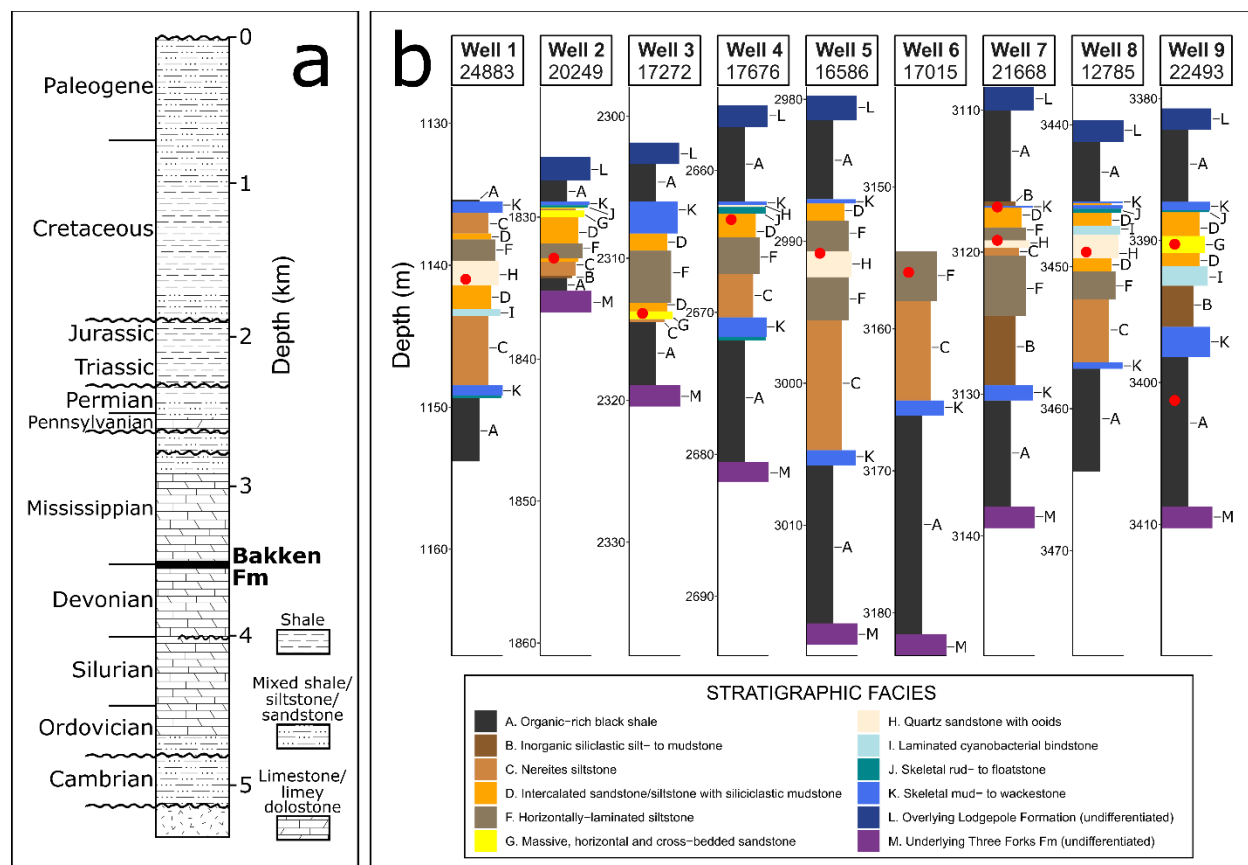


Figure 1.3. Histograms showing the distribution of all SIMS $\delta^{18}\text{O}$ analyses for each core. Plots are arranged from upper left to bottom right in the order from shallow to deep as described in the text. Bars are shaded by mineral.

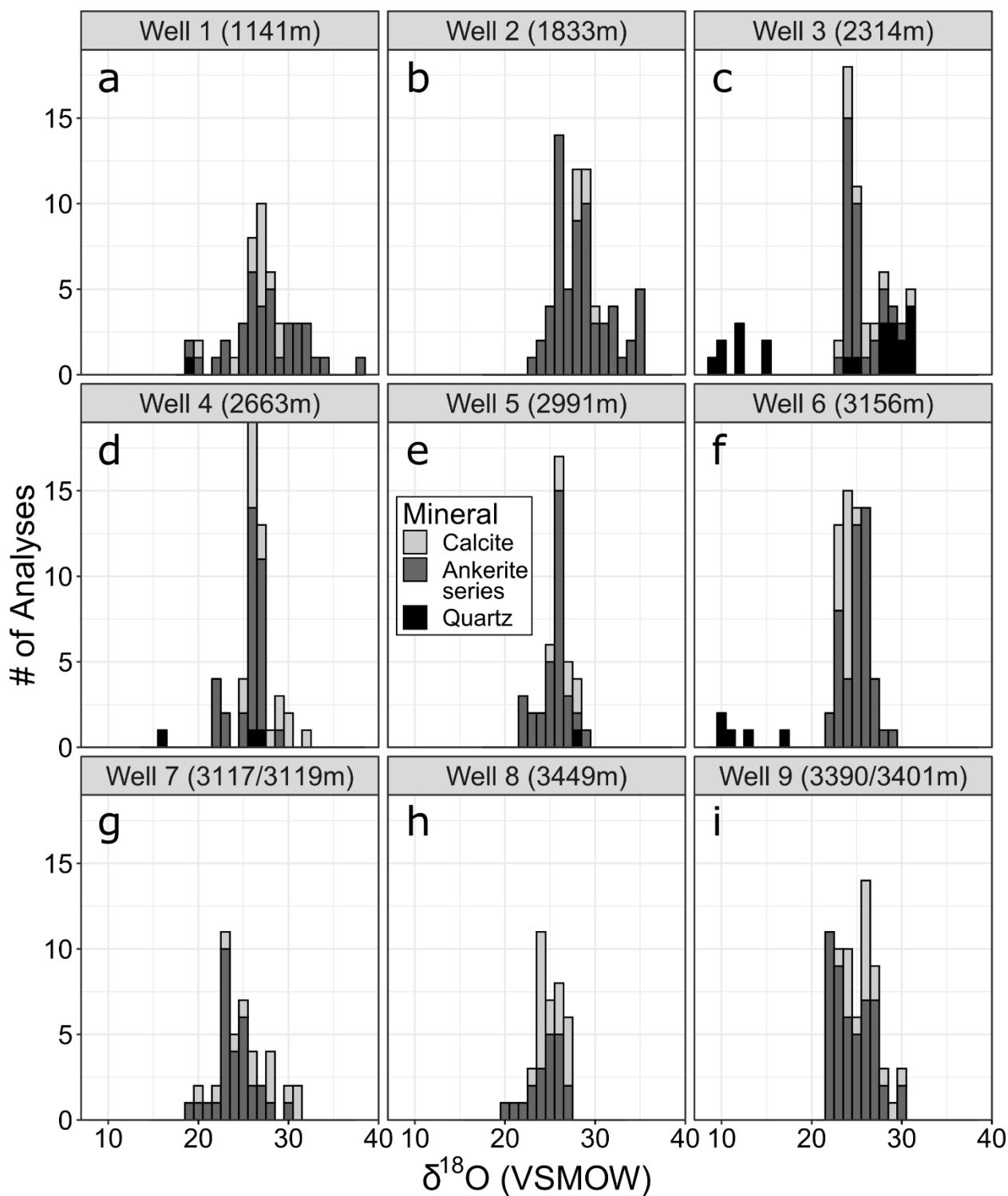


Figure 1.4. Histograms showing the distribution of all SIMS $\delta^{13}\text{C}$ analyses for each core. Plots are arranged from upper left to bottom right in the order described in the text. Bars are shaded by mineral.

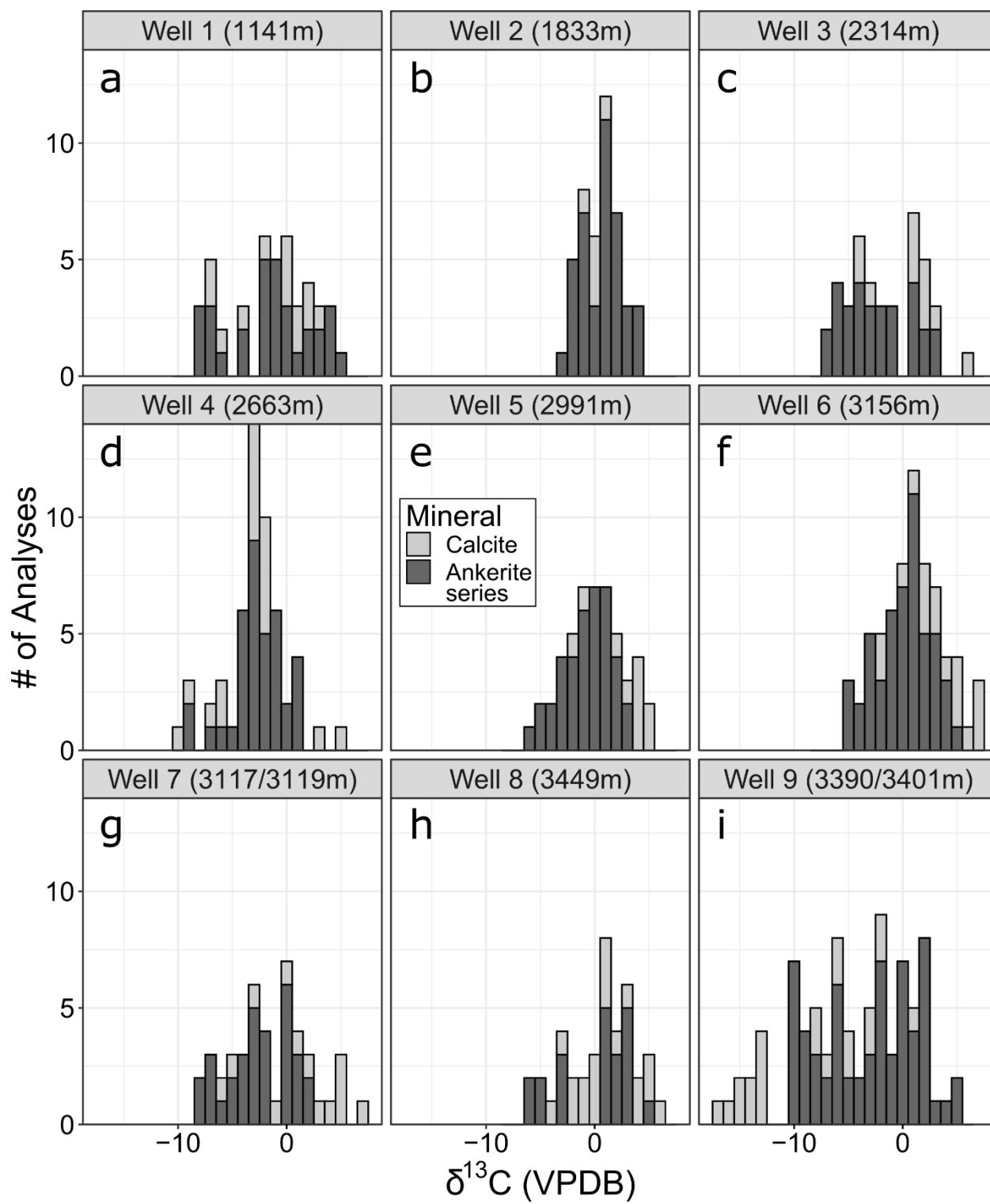


Figure 1.5. Crossplot for Bakken zoned ankerite-series cement SIMS data, showing paired $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ carbonate analyses that are colored **(a)** by Fe#, and **(b)** by growth zone. Only adjacent analyses were paired, making this dataset a subset of that presented in Figures 1.3 and 1.4. The reference line shows the equilibrium dolomite compositions for variable temperature, if $\delta^{18}\text{O}_{\text{water}} = 0\text{‰}$ and $\delta^{13}\text{C}_{\text{CO}_2} = -7\text{‰}$ (Horita, 2014). Color available in online version.

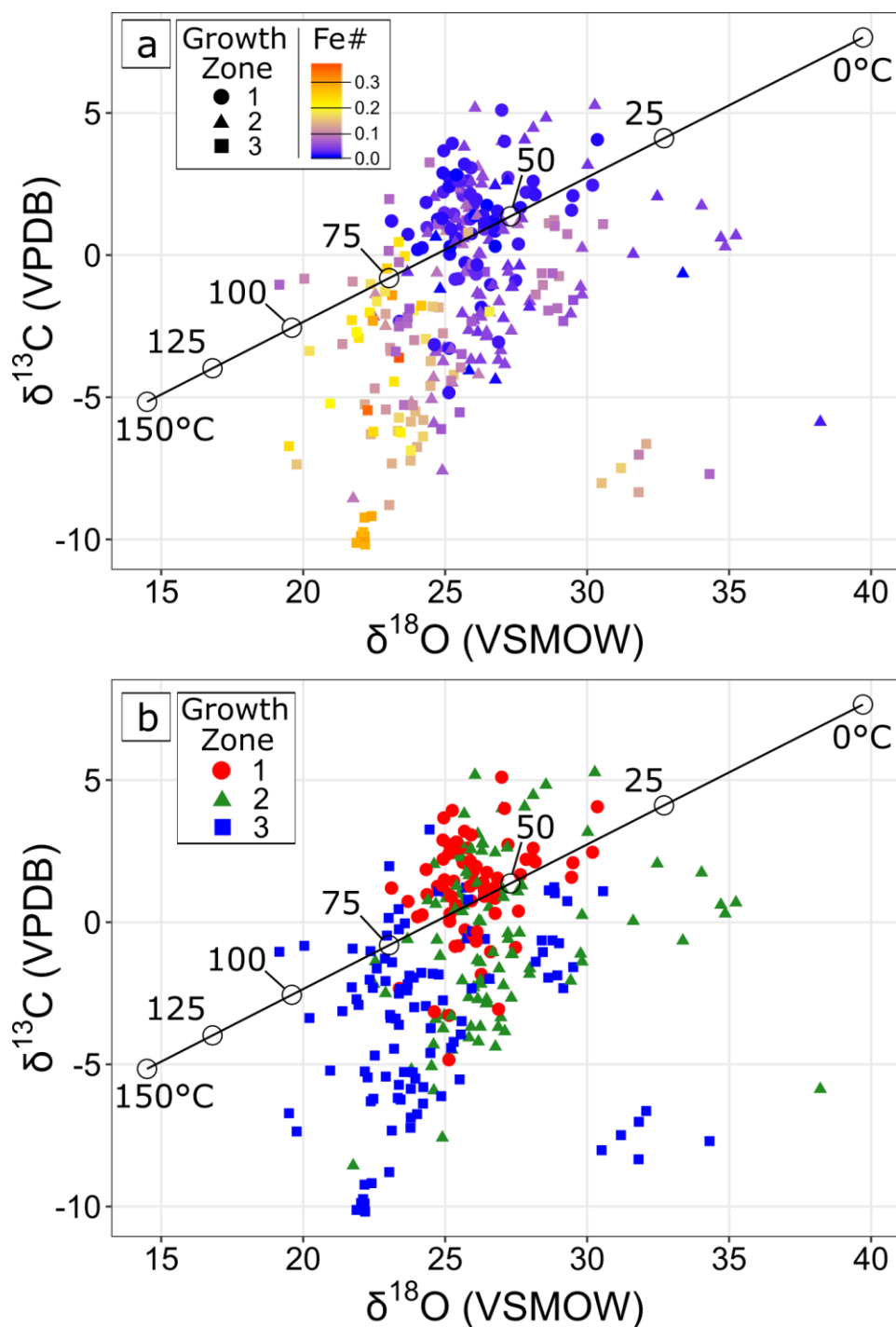


Figure 1.6. Crossplots, one for each core, showing the distributions of paired $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ analyses for both dolomite and calcite. Filled dots correspond to dolomite analyses and are shaded by Fe#; open grey dots correspond to calcite analyses. Only adjacent analyses were paired; this dataset is a subset of that presented in Figures 1.3 and 1.4. Plots are arranged from upper left to bottom right in the order described in the text. Sample depths are indicated in each panel. Error bars are the 2SD precision measured on bracketing dolomite standard UW-6220. Color available in online version.

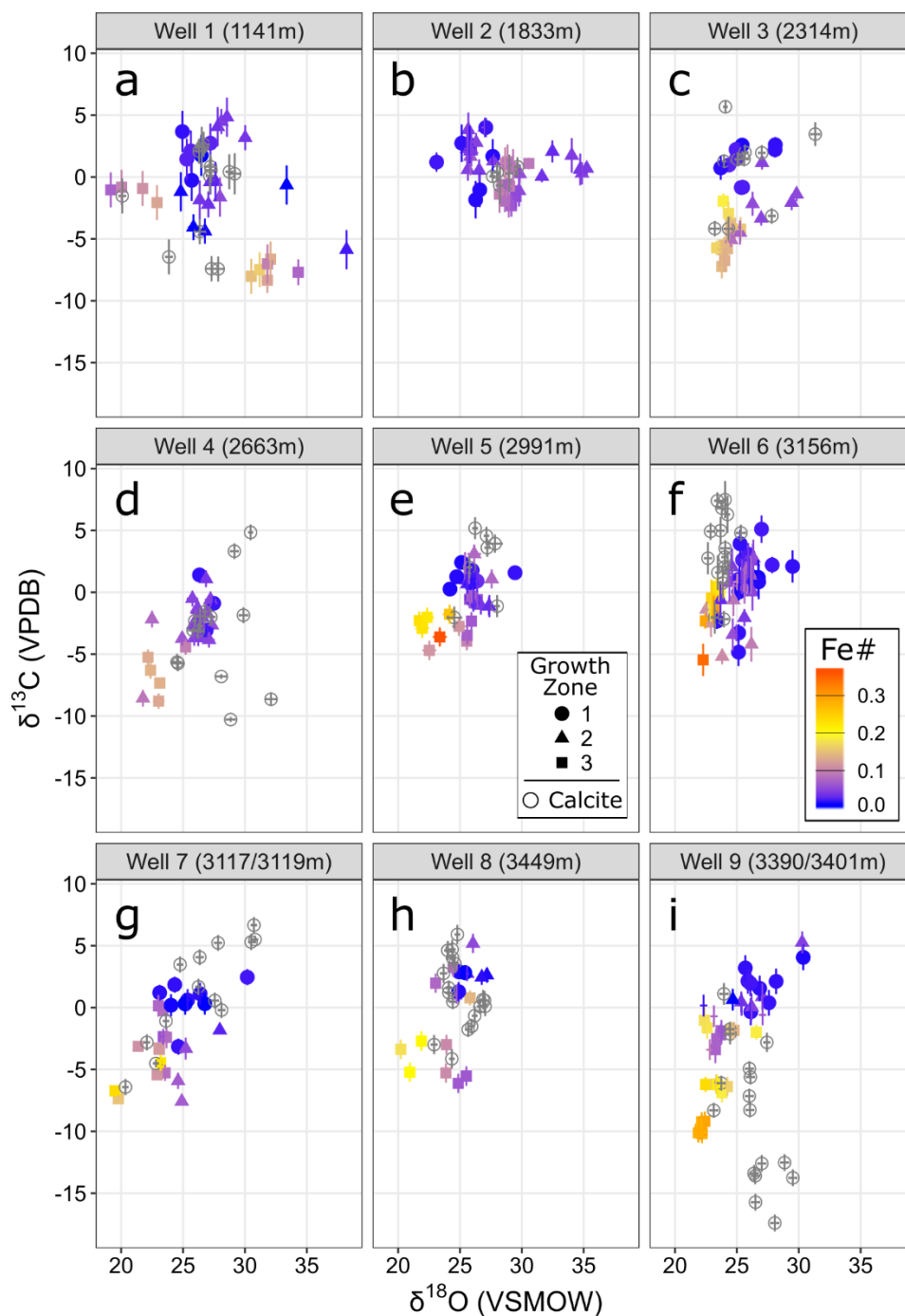


Figure 1.7. Histogram showing the distribution of SIMS $\delta^{18}\text{O}$ quartz analyses, classified using cathodoluminescence according to whether the analysis was made on detrital grains or quartz overgrowths.

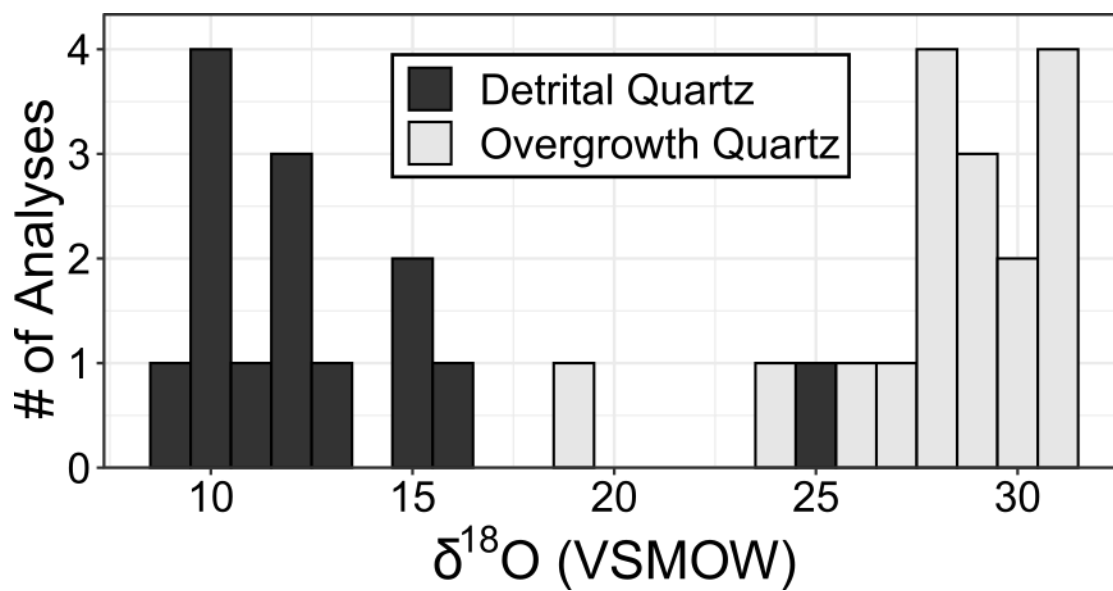


Figure 1.8. Schematic ankerite-series crystal showing the three zones discussed in this paper. Darker grey indicates lower Fe/Mg. The Zone 1 to Zone 2 boundary can be either euhedral or rounded. See text for details.

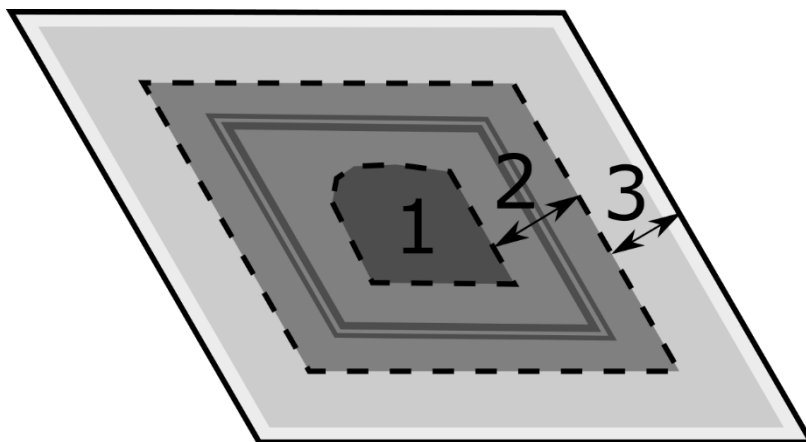


Figure 1.9. Crossplots showing the distributions of paired $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ analyses (ankerite-series only) for each core, and colored by growth zone. Only adjacent analyses were paired, making this dataset a subset of that presented in Figures 1.3 and 1.4. Plots are arranged from upper left to bottom right in the order described in the text. Sample depths are indicated in each panel. Arrows have been added to generalize changes in isotopic values from core out to the rim. Color available in online version.

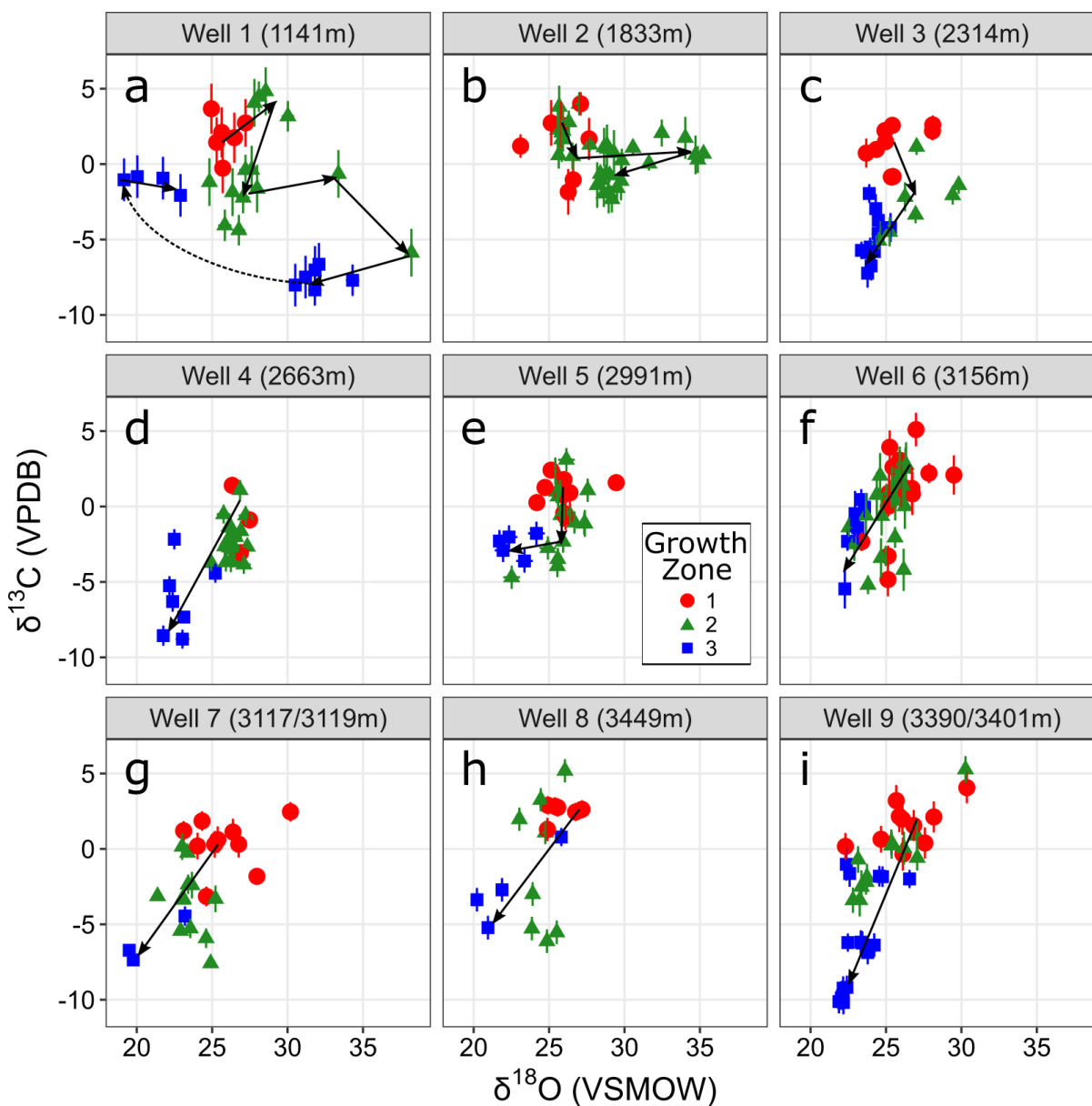


Figure 1.10. Histogram showing the distribution of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for Zone 1 dolomite cores classified according to the type of boundary they have with Zone 2.

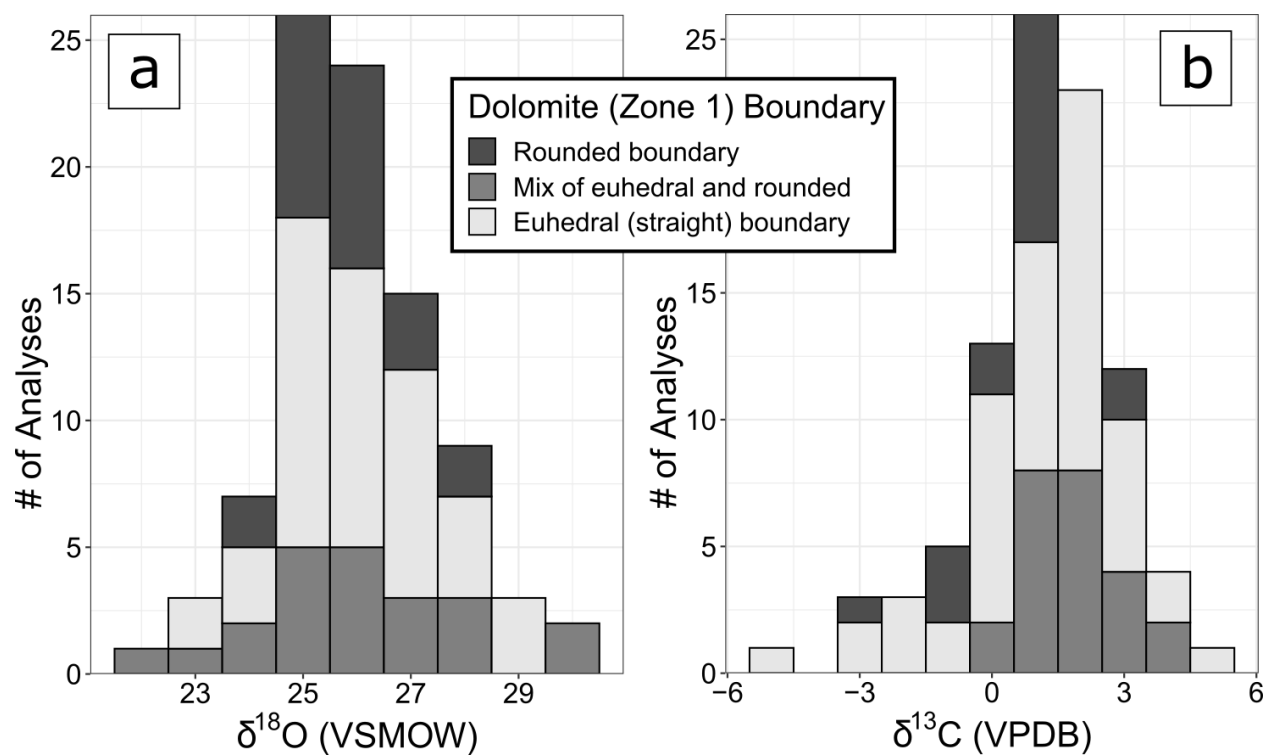


Figure 1.11. SEM-BSE imagery overlain with SIMS analysis-pit locations for Well 1 (core 24883). SIMS pits are represented by ovals and are the size and shape of actual analysis pits; $\delta^{18}\text{O}$ pits are light pink and $\delta^{13}\text{C}$ pits are dark blue. Minerals are labeled as follows: Dol = Dolomite (endmember compositions), Ank = Ankerite-series carbonates, DQ = Detrital Quartz, Anh = Anhydrite. Boundaries between growth Zones 1, 2, and 3 are shown in representative locations. Detailed discussion of petrography for each sample is in the text. **(a)** Transect through an analyzed area of Well 1, with isotopic data **(b)** and Fe# **(c)** plotted. **(d)** Transect through an analyzed area of Well 1, with isotopic data **(e)** and Fe# **(f)** plotted.

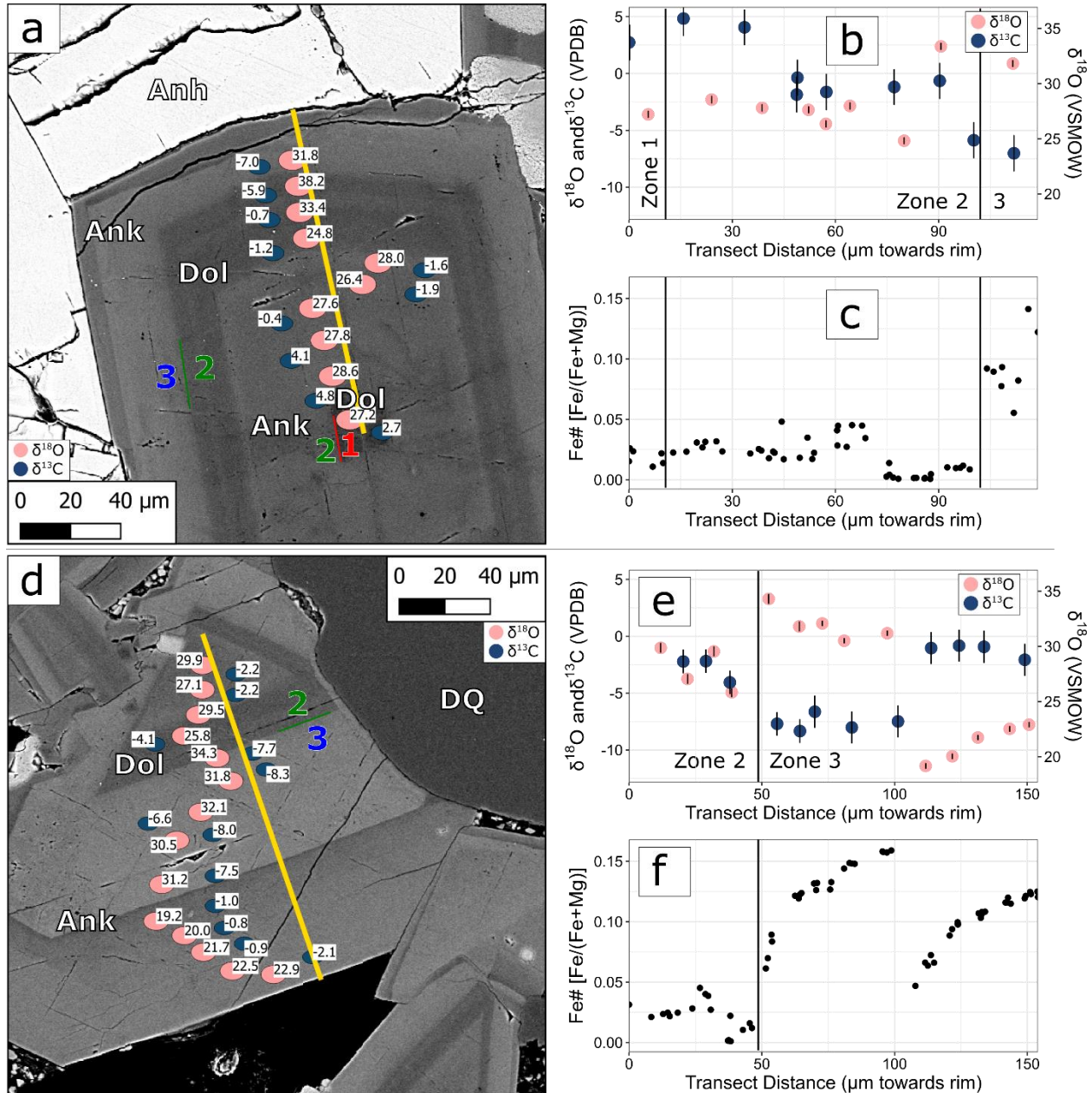


Figure 1.12. SEM-BSE imagery overlain with SIMS analysis-pit locations for Well 2 (core 20249). SIMS pits are represented by ovals and are the size and shape of actual analysis pits; $\delta^{18}\text{O}$ pits are light pink and $\delta^{13}\text{C}$ pits are dark blue. Minerals are labeled as follows: Dol = Dolomite (endmember compositions), Ank = Ankerite-series carbonates, Cal = Calcite, Anh = Anhydrite. Boundaries between growth Zones 1, 2, and 3 are shown in representative locations. Detailed discussion of petrography for each sample is in the text, and more sample imagery may be found in Appendix 1.3. **(a)** Transect through an analyzed area of Well 2, with isotopic data **(b)** and Fe# **(c)** plotted.

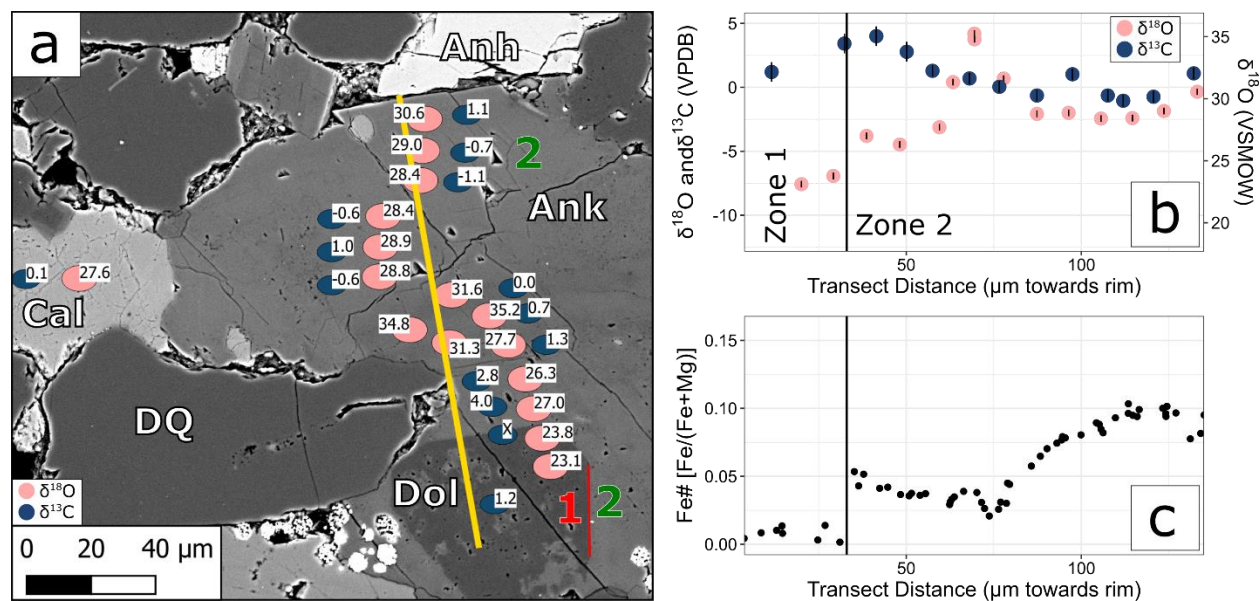


Figure 1.13. SEM-BSE imagery overlain with SIMS analysis-pit locations for Well 3 (core 17272). SIMS pits are represented by ovals and are the size and shape of actual analysis pits; $\delta^{18}\text{O}$ pits are light pink and $\delta^{13}\text{C}$ pits are dark blue. Minerals are labeled as follows: Dol = Dolomite (endmember compositions), Ank = Ankerite-series carbonates, Cal = Calcite, OQ = Overgrowth (diagenetic) Quartz, DQ = Detrital Quartz. Boundaries between growth Zones 1, 2, and 3 are shown in representative locations. Detailed discussion of petrography for each sample is in the text, and more sample imagery may be found in Appendix 1.3. **(a,b)** Analyzed ankerite-series carbonates from Well 3. **(c)** Transect through an analyzed area of Well 3, with isotopic data **(d)** and Fe# **(e)** plotted.

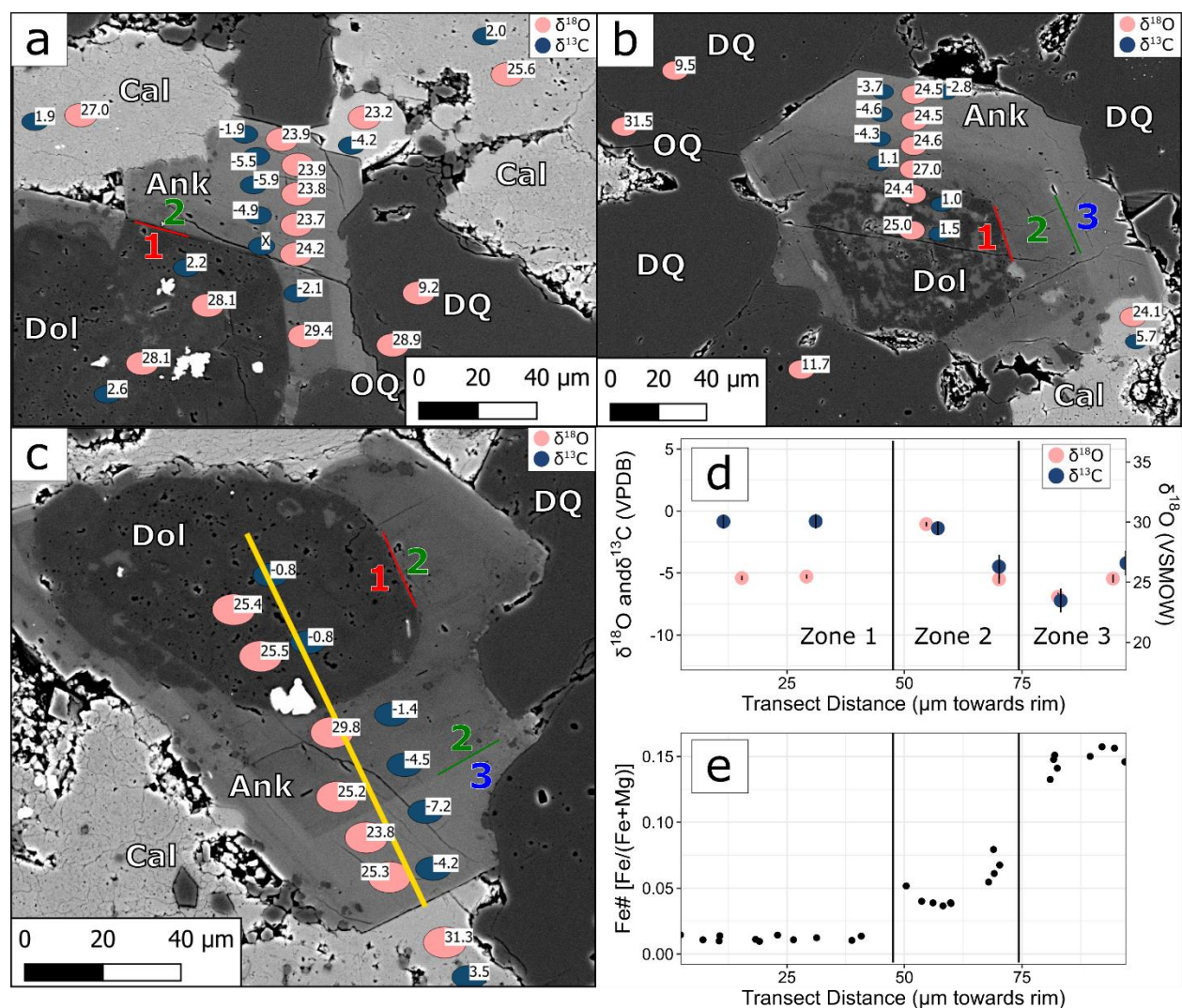


Figure 1.14. SEM-BSE imagery overlain with SIMS analysis-pit locations for Well 4 (core 17676). SIMS pits are represented by ovals and are the size and shape of actual analysis pits; $\delta^{18}\text{O}$ pits are light pink and $\delta^{13}\text{C}$ pits are dark blue. Minerals are labeled as follows: Dol = Dolomite (endmember compositions), Ank = Ankerite-series carbonates, Cal = Calcite, OQ = Overgrowth (diagenetic) Quartz. Boundaries between growth Zones 1, 2, and 3 are shown in representative locations. Detailed discussion of petrography for each sample is in the text, and more sample imagery may be found in Appendix 1.3. **(a,b)** Analyzed ankerite-series carbonates from Well 4.

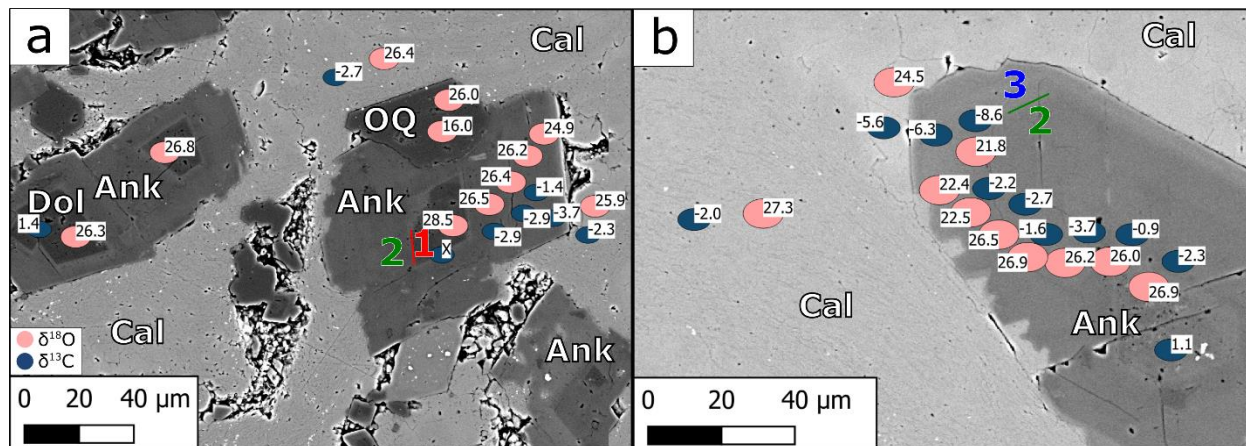


Figure 1.15a-i. (next page, additional sample petrography, part 1 of 2, images a-i) Examples of sample SEM-BSE imagery overlain with SIMS analysis-pit locations. SIMS pits are represented by ovals and are the size and shape of actual analysis pits; $\delta^{18}\text{O}$ pits are light pink and $\delta^{13}\text{C}$ pits are dark blue. Minerals are labeled as follows: Dol = Dolomite (endmember compositions), Ank = Ankerite-series carbonates, Cal = Calcite, DQ = Detrital Quartz. Boundaries between growth Zones 1, 2, and 3 are shown in representative locations. Detailed discussion of petrography for each sample is in the text, and more sample imagery may be found in Appendix 1.3. **(a,b)** Well 5 (core C16586), sampled at 2991 m. **(c,d)** Well 6 (core 17015), sampled at 3156 m. **(e,f,g,h,i)** Well 7 (core C21668), sampled at 3117 m (e,f) and 3119 m (g,h,i).

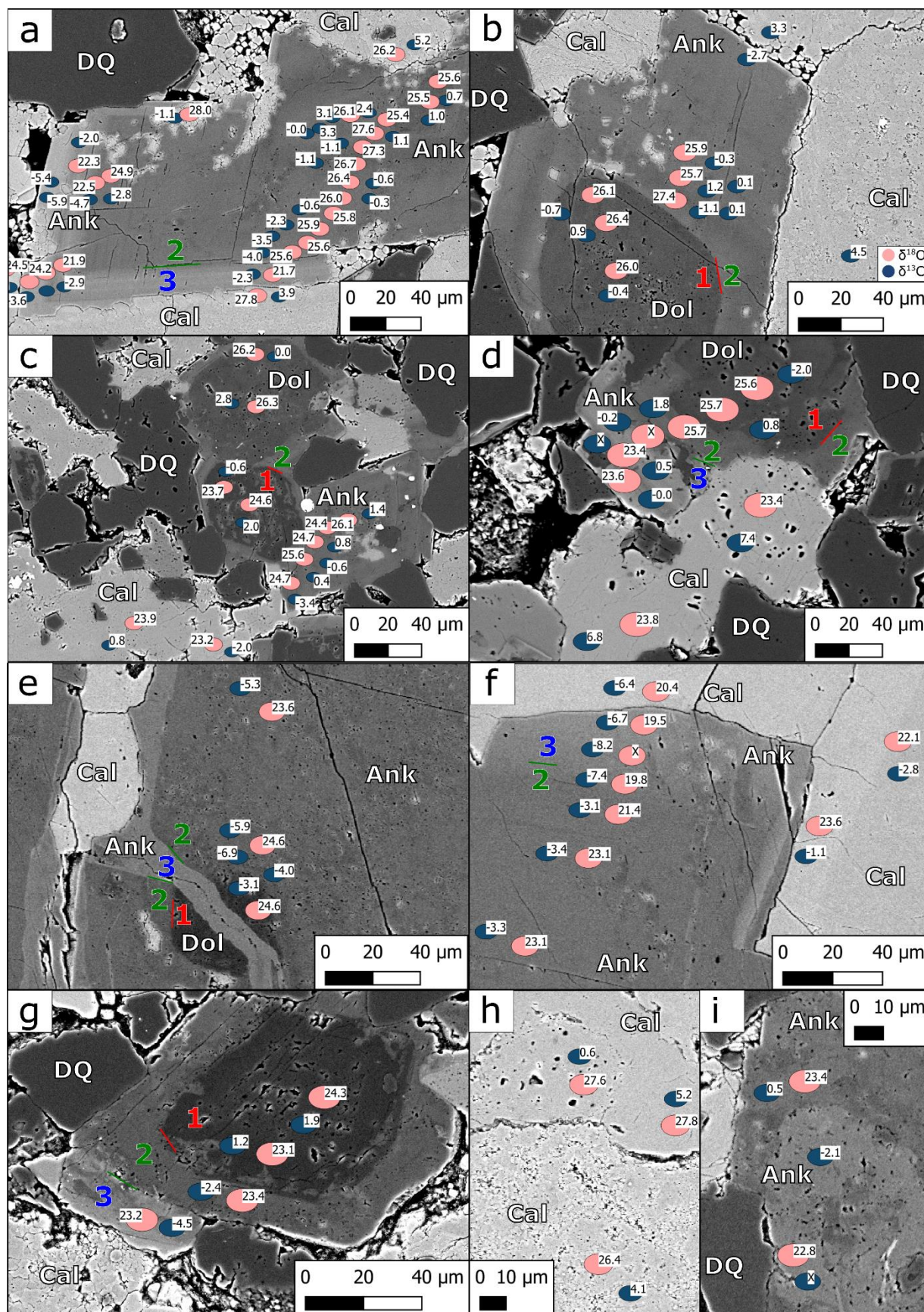


Figure 1.15j-p. (next page, additional sample petrography, part 2 of 2, images j-p) Examples of sample SEM-BSE imagery overlain with SIMS analysis-pit locations. SIMS pits are represented by ovals and are the size and shape of actual analysis pits; $\delta^{18}\text{O}$ pits are light pink and $\delta^{13}\text{C}$ pits are dark blue. Minerals are labeled as follows: Dol = Dolomite (endmember compositions), Ank = Ankerite-series carbonates, Cal = Calcite, DQ = Detrital Quartz, OQ = Overgrowth (diagenetic) Quartz, Anh = Anhydrite, Py = Pyrite. Boundaries between growth Zones 1, 2, and 3 are shown in representative locations. Detailed discussion of petrography for each sample is in the text, and more sample imagery may be found in Appendix 1.3. **(j,k,l)** Well 8 (core 12785), sampled at 3449 m. Small round holes in (j) are locations where qualitative SEM-EDS measurements have damaged calcite. **(m,n,o,p)** Well 9 (core 22493), sampled at 3390 m (m,n) and 3401 m (o,p). Image (o) is a zoomed in region of (p).

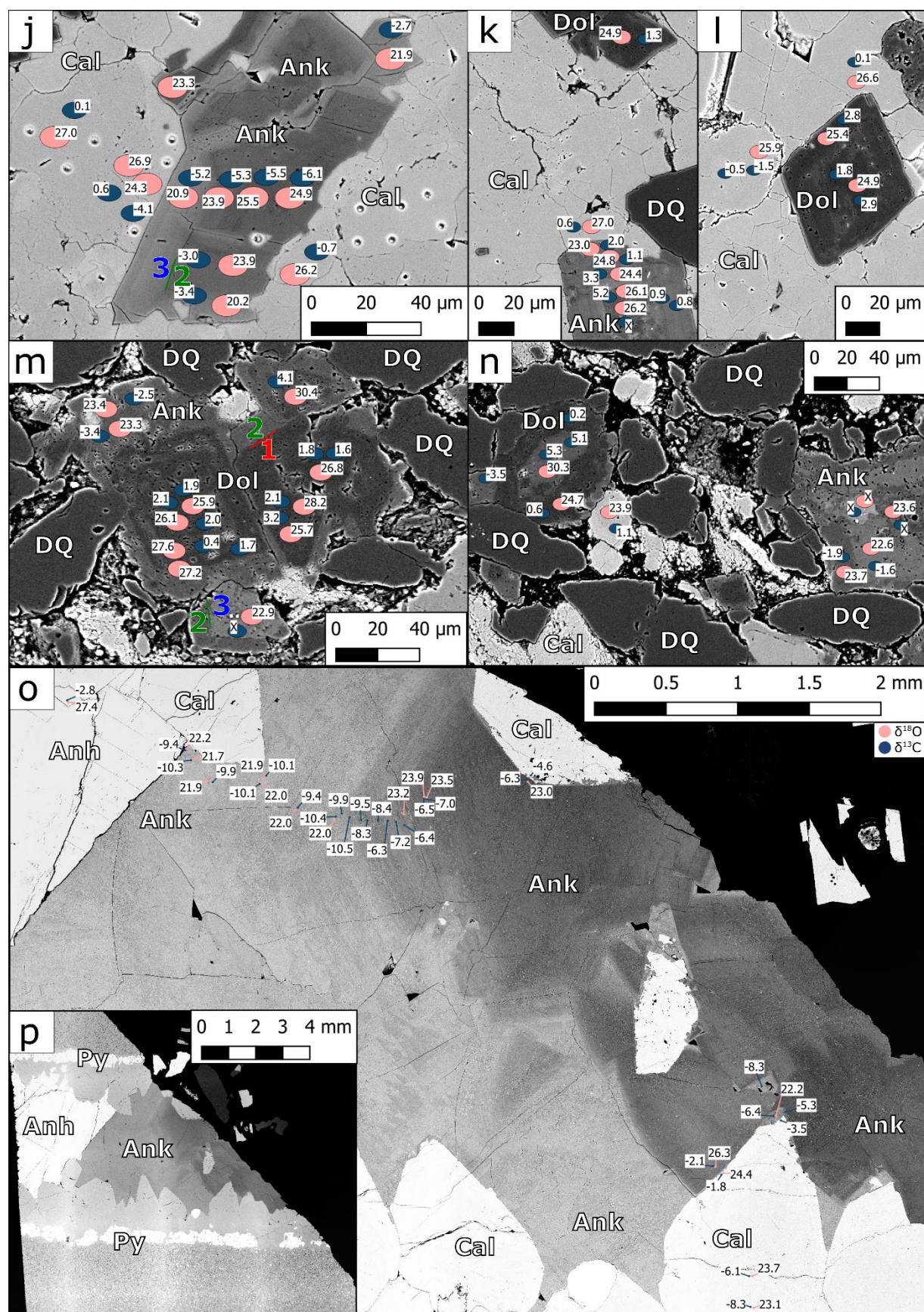


Figure 1.16. Values of $\delta^{18}\text{O}$ for ankerite-series cements, colored by zone, and plotted by the maximum temperature each sample experienced as determined from burial models; plotted temperatures are not necessarily the temperatures that each cement stage grew at (Kuhn et al., 2012). Lines represent $\delta^{18}\text{O}$ water in equilibrium with dolomite at variable $\delta^{18}\text{O}$ and temperature (Horita, 2014); modern porewater possesses $\delta^{18}\text{O}$ values $>5\text{‰}$ (Peterman et al., 2017). Color available in online version. **(a)** Zone 1 dolomites show a similar spread of $\delta^{18}\text{O}$ values regardless of depth, indicating that they formed early in burial under similar temperature and fluid conditions. Assuming seawater fluid compositions at -1.5‰ yields a temperature range of Zone 1 formation of ~ 30 to 75°C . **(b)** Zone 2 dolomite $\delta^{18}\text{O}$ values develop a slant that shows similarity to curves for high- $\delta^{18}\text{O}$ water, presumably as burial and water-rock interaction advance. **(c)** Zone 3 dolomite continues the Zone 2 trend at depth, but Well 1 shows a sequence of chemical zonation indicative of fluid passage (see text for discussion).

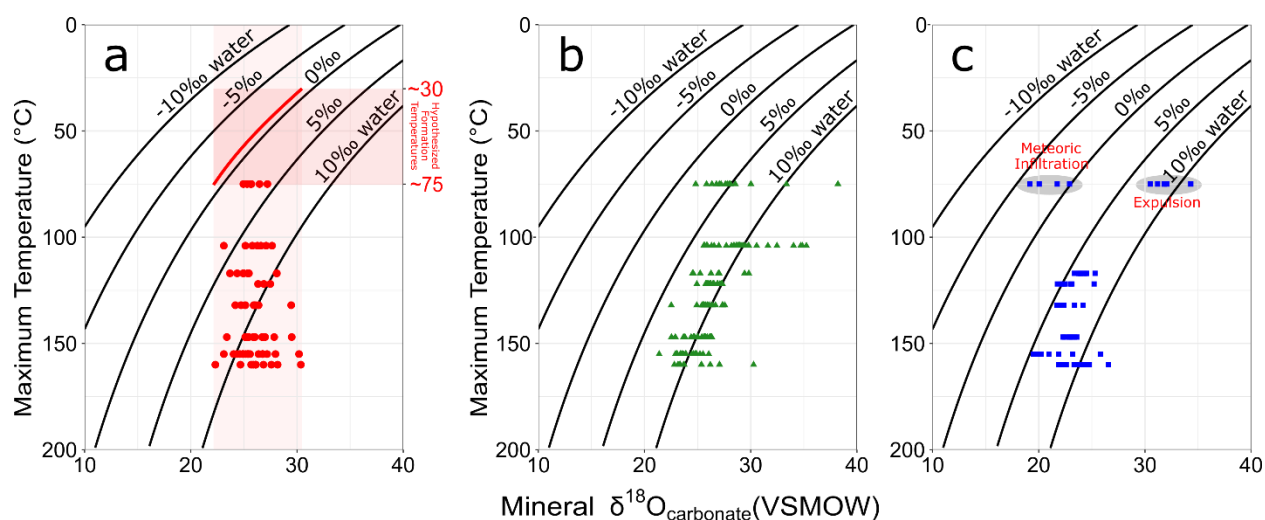
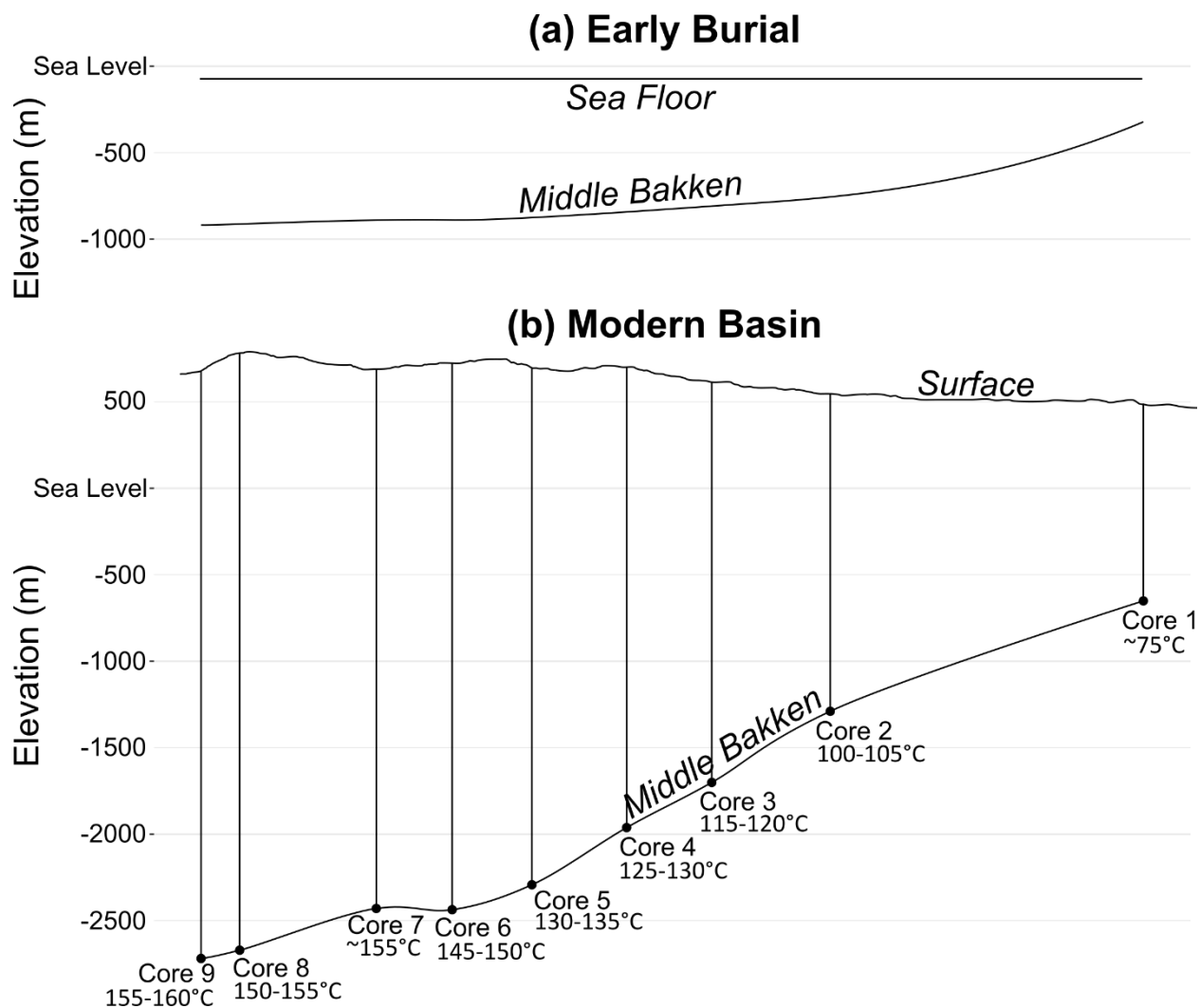


Figure 1.17. (a) Basin configuration during early burial, by which point Zone 1 dolomites are interpreted to have locked in their $\delta^{18}\text{O}$ values. **(b)** Modern basin configuration, with maximum burial temperatures listed under each core as reported by Kuhn et al. (2012).



CHAPTER 2: Mind the Gap: Bimodal Sulfur Isotope Distributions from the Bakken Formation

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CONTRIBUTIONS: Samples were acquired from the North Dakota Geologic Survey and the United States Geological Survey core repositories in collaboration with staff there. Benjamin Barnes and Maciej Śliwiński provided additional assistance with sample collection. Bil Schneider provided instrument support on the SEM. Instrumental support in the WiscSIMS lab was provided Kouki Kitajima, Aki Ishida, and Noriko Kita. Chapter contents were reviewed and edited by John Valley, Clay Kelly, Alan Carroll, Stephen Meyers, and Matthew Ginder-Vogel.

Abstract

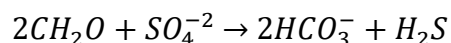
In situ SIMS-SEM analysis of pyrite and sphalerite from 5 drillcores intersecting Devonian to Mississippian-aged Bakken Formation shales in the central Williston Basin shows a bimodal distribution of $\delta^{34}\text{S}$ values. This distribution is present in all samples, and the petrographic expression of each mode is unique enough to allow for the general prediction of sulfide $\delta^{34}\text{S}$ based purely on petrographic observations. Framboidal sulfides fall in the -45 to -25‰ range, indicating strong open-system H_2S behavior and formation at the sea floor in an oxygen poor environment. By contrast, replacive sulfides fall above $\delta^{34}\text{S} \approx -20\text{‰}$ and are found closely associated with skeletal carbonates, silicified microfossils, and individual dolomite crystals. The bimodal distribution indicates either a) a large change in $\delta^{34}\text{S}$ of precipitating sulfides due to vital effects or pulsed formation during early burial, or b) two temporally separate periods of growth, one in the sediment during or shortly after deposition, and one at $>100^\circ\text{C}$ during thermochemical sulfate reduction. Integrated geochemistry and petrographic observations argue more strongly for the latter hypothesis. This study verifies the existence of strong sediment and mineral controls on both early and late sulfide formation in Bakken organic-rich shales, demonstrating that careful petrographic evaluation of sample mineralogies and sulfide phases is a must for any $\delta^{34}\text{S}$ studies.

1. Introduction

The petrographic expressions and $\delta^{34}\text{S}$ values of sedimentary sulfide are powerful tools for interpreting and understanding paleoclimate and redox conditions in Earth's past (Farquhar and Wing, 2003; Bottrell and Newton, 2006; Johnston, 2011; Fike et al., 2015; Pasquier et al., 2017). However, studies using careful petrographic work and microanalytical techniques have demonstrated strong diagenetic controls and large μm -scale variability for $\delta^{34}\text{S}$, which can complicate interpretations of the rock record (Ushikubo et al., 2014; Lin et al., 2016; Cui et al., 2018). This paper presents a $\delta^{34}\text{S}$ dataset measured *in situ* at μm -scale by SIMS from Devonian-Mississippian black shales that not only demonstrates that there are additional mineralogical controls on where within a formation late high- $\delta^{34}\text{S}$ sulfides precipitate, but also suggests a petrographic blueprint by which sulfide growth sequences might be interpreted for rocks from similar environments.

1.1 Controls on Sedimentary Sulfide $\delta^{34}\text{S}$ Values

The formation of diagenetic sulfides results from a set of reactions between dissolved sulfate and organic molecules that allow sulfate to be reduced. This set of reactions is commonly represented in its simplified form:



The hydrogen sulfide (H_2S) that is produced is then free to combine with reactive iron or other ions to produce pyrite or other sulfide minerals.

The reduction of sulfate to sulfide shows a strong preference for the light isotope (^{32}S), particularly when the process is driven by sulfate-reducing microbes, which have been shown in laboratory cultures to produce $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$ offsets of as large as 66‰ (Sim et al., 2011a). Because dissolved sulfate diffuses readily through porewater but mineralized sulfide does not, the effects of sulfate reduction on $\delta^{34}\text{S}$ in sediments are often discussed in terms of closed-system Rayleigh distillation (Rayleigh, 1896). In simple closed-system Rayleigh distillation, where additional reactants are not allowed to enter the system and products do not leave the system, the separation in $\delta^{34}\text{S}$ values between the reactant (sulfate) and the product (pyrite) is determined by the fractionation factor, α . As sulfate is converted to pyrite and the proportion of sulfur that remains in sulfate form drops, the $\delta^{34}\text{S}$ of remaining sulfate and newly precipitated pyrite both drift towards higher values. While the amount of pyrite precipitated grows, the aggregate “bulk” value of pyrite will approach the initial sulfate $\delta^{34}\text{S}$ value until all of the sulfate has been consumed (Figure 2.1).

Variability in early sulfide $\delta^{34}\text{S}$ values of sediment is often described in terms of Rayleigh distillation, as the ocean pool of seawater sulfate can be considered effectively infinite with constant $\delta^{34}\text{S}$, and during early diagenesis sulfate is distilled towards higher $\delta^{34}\text{S}$ values as it diffuses downwards into the sediment. However, it is important to note that this is not truly a closed system, is not strictly a Rayleigh distillation process, therefore cannot be assumed to behave reliably according to Rayleigh’s model. As pyrite precipitates the remaining sulfate becomes enriched in ^{34}S , resulting in a profile of increasing $\delta^{34}\text{S}$ sulfate with depth in young sediments (Claypool, 2004), and pyrites precipitated from the enriched sulfate pool will

themselves have elevated $\delta^{34}\text{S}$ values. Under the right conditions, this process can produce measurable $\delta^{34}\text{S}_{\text{pyrite}}$ variability in excess of 150‰ within sediments (Lin et al., 2016).

Diagenetic sulfate reduction is typically classified as occurring in two separate thermal regimes. Bacterial Sulfate Reduction (BSR) is biologically mediated and generally occurs below 60°C, with organic matter or methane serving as the electron acceptor. By contrast, Thermochemical Sulfate Reduction (TSR) is abiotic, typically occurs at 100-140°C in the presence of hydrocarbons (Machel, 2001). Both of these processes, and the $\delta^{34}\text{S}$ fractionations they produce, will be discussed in further detail in the following sections.

1.1.1 Bacterial Sulfate Reduction (BSR)

The reduction of sulfate to sulfide by microbial activity is a key process in sediments, particularly organic-rich ones, but the $\delta^{34}\text{S}$ fractionations involved are not yet well constrained enough to predict environment-specific $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$ associated with BSR. Various cell cultures have produced a wide range of fractionations from 66‰ to 2‰ (Detmers et al., 2001; Sim et al., 2011a). On top of this, experimental data yield larger fractionations in response to increasing sulfate concentration (Habicht et al., 2002) and decreasing cell-specific sulfate reduction rates (Harrison and Thode, 1958; Kaplan and Rittenberg, 1964; Chambers et al., 1975; Sim et al., 2011a; Sim et al., 2011b; Sim et al., 2012; Leavitt et al., 2013), so the fractionations induced by BSR are likely not constant during early burial.

A key factor in producing the early low- $\delta^{34}\text{S}$ pyrites observed in many sediments is that there are chemical pathways by which reduced phases of sulfur may be converted back into sulfate. The oxidation of sulfide and disproportionation of elemental sulfur, both of which

produce sulfate, are thought to play an active role in cycling sulfur in shallow sediments (Canfield and Thamdrup, 1994). More importantly to this discussion, the fractionations induced by these processes are substantially smaller than that produced during initial sulfate reduction (Fry et al., 1984; Fry et al., 1985; Fry et al., 1988; Canfield and Thamdrup, 1996; Habicht et al., 1998; Böttcher et al., 2001; Zerkle et al., 2009; Fike et al., 2015). In such systems, $\delta^{34}\text{S}$ values may be driven lower each time sulfur moves through the oxidation-reduction cycle. For these reasons, a general BSR $\delta^{34}\text{S}_{\text{sulfate-sulfide}}$ fractionation of about 40‰ is frequently reported in the literature (Rollinson, 1993; Fike et al., 2015), but the value may be higher or lower depending on environment and additional factors.

The formation of pyrite framboids (or polyframboids, if they form in a cluster) appears to be closely related to BSR in many settings, and framboidal pyrite is typically found to be an early phase petrographically. Why framboids are early remains uncertain, although it has been proposed that framboidal pyrite develops during rapid pyrite crystallization from H_2S supersaturation in euxinic waters and sediments (Rickard, 2012). Such supersaturation is most likely to occur prior to nucleation of the first sulfide minerals in the water column or the sediment.

1.1.2 Thermochemical Sulfate Reduction (TSR)

Thermochemical sulfate reduction (TSR) is an abiotic process by which sulfate reacts with hydrocarbons to produce H_2S , and the rate of reaction has been found to be highly temperature and pH dependent (Kiyosu, 1980; Ohmoto and Lasaga, 1982; Kiyosu and Krouse, 1990). As with BSR, TSR produces an H_2S product depleted in ^{34}S , but the fractionation remains relatively unconstrained. Ohmoto and Lasaga (1982) experimentally determined an equation

for the equilibrium dependence of $\Delta_{\text{sulfate-sulfide}}$ on temperature (Figure 2.2), but observed that the fractionations produced were significantly larger than what has been empirically calculated from many hydrothermal ore deposits. They postulated that the $\delta^{34}\text{S}$ values of many hydrothermal sulfides are kinetically influenced, as the rate of equilibration slows at lower temperatures and very high or low pH, such that coprecipitating sulfate and sulfide minerals at temperatures below 350°C tend to record nonequilibrium $\Delta_{\text{sulfate-sulfide}}$ values.

Kiyosu and Krouse (1990) experimentally determined an equation for the kinetic fractionation that produced $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$ of about 20‰ at 100°C and 10‰ at 200°C (Figure 2.2). Machel et al. (1995) observed that these values are similar to those observed in some natural systems in which TSR is believed to have occurred, and argued that the smaller $\Delta^{34}\text{S}_{\text{sulfate-pyrite}}$ observed in minerals in some sour gas fields was likely a result of near-total consumption of sulfate. Regardless of the true value of the fractionation produced during TSR, it is important to remember that the reactants and products may also be subject to closed and open-system distillation processes.

Experimental determination of $\Delta_{\text{pyrite-sulfide}}$ and $\Delta_{\text{sphalerite-sulfide}}$ has revealed relatively small (<5‰) equilibrium fractionations between hydrogen sulfide, pyrite, and sphalerite for the full range of diagenetic temperatures (Figure 2.2) (Ohmoto and Rye, 1979). It is for this reason that determining precise temperatures from the $\delta^{34}\text{S}$ values of pyrite-sphalerite mineral pairs is challenging.

1.2 Geological Setting

The Bakken Formation of the Williston Basin is Devonian-Mississippian in age, and is subdivided into upper and lower organic-rich shale members that bracket a middle mixed carbonate-siliciclastic member (Figures 2.3, 2.4). It formed in a shallow restricted basin, with the lower and upper members thought to reflect deeper and less-oxic conditions than the middle Bakken member. Total organic carbon in the shales averages 11% weight percent (LeFever et al., 2011; Sonnenberg, 2011), and the formation's large volume of maturing organic-rich shales make it a major U.S. target for hydrocarbon extraction. In 2013 the USGS estimated total unrecovered oil resources to be in excess of seven billion barrels (Gaswirth et al., 2013; Gaswirth and Marra, 2015). Burial temperatures in the basin center are estimated to have peaked at 165°C (Figure 2.3) (Kuhn et al., 2012).

The Bakken shales are rich in microfossils, predominantly radiolarians and palynomorphs (algal cysts, acritarchs, and spores); foraminifera are present, but less common (Egenhoff and Fishman, 2013; Fishman et al., 2015; Pocknall et al., 2015; Borcovsky et al., 2017). Lag deposits of macrofossil fragments and other grains are uncommon but present in both upper and lower members, indicating active mud transport through the system. Fecal strings, shells, burrows, and agglutinated foraminifera may also be found in the shales, indicating that anoxia was not continuous during deposition (Egenhoff and Fishman, 2013; Borcovsky et al., 2017).

Microfossils experienced extensive early silica diagenesis, which had a significant effect on porosity and permeability. Framboidal pyrite and massive pyrite and sphalerite grains may be found throughout both shale members, where in places the massive pyrite can replace dolomite rhombohedra. Clusters of framboids, known as polyframboids, are common. Locally

pyrite and sphalerite have been measured to reach concentrations of 22 and 16 rock wt. %, respectively (Fishman et al., 2015). As part of an early isotopic investigation of the Williston Basin, Thode (1981) performed bulk $\delta^{34}\text{S}$ analyses on oils, sulfate, organic sulfur, and sulfide are summarized in Figure 2.5.

2. Methods

2.1 Sample Collection and Preparation

Samples were collected from drill cores stored at the North Dakota Geological Survey (NDGS) Wilson M. Laird Core and Sample Library in Grand Forks, and the United States Geological Survey (USGS) Core Research Center in Denver. Samples were polished and imaged in backscattered electron (BSE) mode using a Hitachi S3400-N scanning electron microscope (SEM) in variable pressure mode; this was found to be the most efficient and effective way of quickly identifying and evaluating the quality of μm -scale diagenetic variability. Constituent mineralogies were confirmed by energy-dispersive X-ray spectrometry (EDS).

In total, six samples from five cores were selected for SIMS analysis (Table 2.1), as determined by which samples in each core show the greatest variability in the petrographic expression of sulfide minerals, and which had multiple generations of sulfide growth that could be identified from petrographic relationships. In preparation for SIMS analysis, 1-2 cm chips were cut from sample rock and embedded in Buehler epoxy in 2.54 cm-diameter round molds. In the center of each was mounted the UWPY-1 pyrite standard (Kozdon et al., 2010; Ushikubo et al., 2014).

2.2 SIMS Procedure

Values of $\delta^{34}\text{S}$ were measured on a CAMECA IMS 1280 large-radius, multi-collector secondary ion mass spectrometer (SIMS) at the University of Wisconsin-Madison WiscSIMS laboratory. Measurements were made during three separate sessions using established sample preparation and analysis procedures (Valley and Kita, 2009; Kita et al., 2009; Kozdon et al., 2010; Ushikubo et al. 2014); additional details for each session can be found in Table 2.2 and Appendices 2.1 and 2.2. Samples were analyzed using a focused $^{133}\text{Cs}^+$ primary beam with a 10 kV accelerating voltage and 20 keV impact energy; charge neutralization was performed with an electron flood gun and a conductive sample coat of either 60 nm of gold or 25 nm of carbon. The impact of the $^{133}\text{Cs}^+$ atoms sputters ions from the sample surface and excavates a pit. Sputtered ions are accelerated into a double-focusing mass spectrometer where they are sorted by mass/charge before reaching an array of 3 Faraday cup detectors (for $^{32}\text{S}^-$, $^{34}\text{S}^-$, and $^{32}\text{S}^{1}\text{H}^-$). In this study, all SIMS analyses of unknowns were made using UWPY-1 as a running standard, which has a $\delta^{34}\text{S}$ value of 16.04‰ by gas-source mass spectrometry (Kozdon et al., 2010; Ushikubo et al., 2014). Unknown analyses were standardized by bracketing groups of 8-16 analyses of unknowns with eight analyses on UWPY-1 (4 before the unknowns and 4 after). This bracketing was used to monitor and correct for small amounts of instrumental drift. Analytical precision for unknowns is reported as two standard deviations of the 8 bracketing standard analyses.

SIMS analyses were routinely monitored for internal precision (2SE) or SH^- count rates that were significantly above standard measurements, as well as ^{32}S count rates significantly above or below standard measurements; these analyses were excluded from later data interpretation. SEM imagery was routinely acquired of all SIMS pits to evaluate whether they

had intersected other mineral phases. All analyses are reported in permil notation relative to Vienna Canyon Diablo Troilite (VCDT), which has a $^{34}\text{S}/^{32}\text{S}$ ratio of 1/22.6436 (Ding et al., 2001).

Analyses on framboidal pyrite may be subject to a different instrumental bias than massive pyrites—particularly for analyses with significant interstitial material between microcrystal—and possibly resulting from different excavation rates between massive and framboidal pyrite. Authigenic framboidal pyrites commonly contain interstitial organic matter (MacLean et al., 2008; Vietti et al., 2015), and measurements made by SIMS and SEM-EDS confirm the presence of carbon in between the microcrystals of many study framboids. Analyses made by SIMS on mixed pyrite/epoxy reference materials (Appendix 3.4) produces $\delta^{34}\text{S}$ values on the SIMS that are lower than true by less than 5‰ under the instrumental conditions employed in this paper. However, we do not know for certain whether analyses on framboids themselves produces an instrumental bias different from that expected from massive pyrite, and cannot demonstrate with the data in hand that the epoxy/pyrite mixture behaves in an identical manner to analyses on framboids in organic matter. If the mixed pyrite/epoxy reference materials do behave analogously to framboids in organic matter, then the offset in instrumental bias will not exceed ~5‰. As the underlying process by which this offset occurs is not yet fully understood, this paper has not made an attempt to correct the framboid data further. This is discussed further in Appendix 3.4 of this thesis.

Sphalerite analyses in Sessions 1 and 3 were corrected by bracketing analyses of the BT-4 sphalerite standard (Kozdon et al., 2010) with UWPY-1 pyrite. One sphalerite standard analysis was made per standard grain with good reproducibility in both Session 1 (4 sphalerite grains, 2SD = $\pm 0.8\text{‰}$) and Session 3 (5 sphalerite grains, 2SD = ± 0.3). Kozdon et al. (2010)

reported an orientation effect ($n=20$, $2SD = \pm 1.7\%$) in sphalerite under 20 keV, 10 μm beam conditions, as was used in Session 3. Orientation effects on sphalerite are not reflected in the precision normally reported from the UWPY-1 standard bracket 2SD, but it is worth noting that evidence for them was not observed in the standard analyses made in this study. As the range of sample $\delta^{34}\text{S}$ values reported in this study is over an order of magnitude larger the range expected from previously reported orientation effects, any orientation effects on sphalerite analytical precision that were unresolved by the small number of BT-4 analyses made in Sessions 1 and 3 are considered to have no effect on the interpretations presented later in this paper.

3. Results

This section will present sample-specific petrographic and geochemical observations for each SIMS mount. Mounts are labeled with a “Core number-depth in feet” nomenclature for accurate comparison with other NDGS and USGS core records (that are measured in feet); equivalent depths below the surface in meters are provided with each sample name and in Table 2.1. Core depths measured to the nearest 0.1 feet are given in Table 1; sample names are rounded off to the nearest foot.

Samples E701-9923A and E701-9923B were prepared from the same billet and are separated in section by about 1 cm from each other; despite this proximity, very different petrographic expressions of sulfide are observed (Figures 2.6, 2.7a, 2.7b). Large-scale BSE maps of representative features and key petrographic relations for each sample are shown in Figures 2.7-2.13. SEM imagery and SIMS data from all analyzed areas may be found in Appendix 2.3.

The full sample maps used to create Appendix 2.3 were created in QGIS, an open-source cross-platform GIS mapping software (Linzmeier et al., 2018).

3.1 Sulfur Isotope Ratios

There is a bimodal distribution in $\delta^{34}\text{S}$ in all samples; the lower mode falls between -45 and -25‰ and the higher mode falls above -20‰ (Figure 2.14a-f). Petrographically the lower mode consists almost exclusively of data from framboidal pyrite (the only exceptions being closely associated with the polyframboids of E701-9923B and a single large octahedra in 17015-10423, e.g. Figures 2.9a and 2.12c). The upper mode consists almost exclusively of data from analysis of subhedral to massive pyrites and sphalerites that replace microfossils, dolomite, and other minerals to a lesser extent (the only exceptions are framboids showing very little discernable structure, possibly indicative of infilling or recrystallization, e.g. Figure 2.12d, Appendix 2.3).

3.2 Sample E701-9923A (3025 m)

This sample was collected from the lower Bakken Formation within 1 cm of E701-9923B (Figure 2.6), and targeted laminae rich in microfossils and sulfide mineralization (Figure 2.7a). Framboidal pyrites (Figure 2.8a, 2.8e, 2.8f) are mostly isolated and polyframboids are rare and small (<25 μm). Pyrites with rhombohedral forms are dispersed through the sediment and have fully or partially replaced dolomite rhombs (Figure 2.8b). The most volumetrically significant sulfides, though, are the large pyrites and sphalerites infilling, or possibly replacing, silicified microfossils (Figures 2.8c, 2.8d, 2.8e, 2.8f, 2.8g). Concentric bands of silica inclusions are sometimes preserved in microfossil pyrites (Figures 2.8c, 2.8d, 2.8e). Where pyrite and

sphalerite are found together, pyrite is sometimes surrounded by sphalerite (Figures 2.8e, 2.8g).

3.3 Sample E701-9923B (3025 m)

This sample was collected from the lower Bakken Formation within 1 cm of E701-9923A (Figure 2.6), and targeted two lag deposits (Figure 2.7b) consisting of apatite grains (including conodonts), fragments of organic matter, and other grains. Isolated framboidal pyrites are present throughout the SIMS mount, but most striking are the large (~100 μm) polyframboids present throughout the lag deposits. These polyframboids may be round (Figures 2.9a, 2.9c) or not (Figures 2.9b, 2.9d), but all show soft sediment deformation around them. Some contain only framboids (Figures 2.9a, 2.9b, 2.9c) and some contain a mixture of framboids and single euhedral to subhedral pyrite grains of similar diameter (Figures 2.9a, 2.9e). The interstitial material between polyframboid grains is a variable mixture of pyrite, sphalerite, silica, and organic matter.

Pyrites with rhombohedral forms are dispersed through the sediment and have fully or partially replaced dolomite rhombs (Figure 2.9d, 2.9f). Massive replacive pyrite may also be found in silicates or apatites (Figure 2.9e), but is not a dominant phase in this mount. Sphalerite is not a major constituent, but is sometimes found as the interstitial fill of polyframboids (Figures 2.9b, 2.9c) or in minor amounts near other pyrite (Figure 2.9e).

3.4 Sample 21706-11087.5 (3380 m)

This sample was taken at the middle-upper Bakken transition, with the lower third of the mount consisting primarily of carbonate minerals and the upper part consisting of black

shale (Figure 2.7c). Large massive to subhedral pyrites seem to only replace carbonates in this sample, such that they replace dolomite and skeletal calcites indiscriminately in the carbonate-rich lower portion of the mount (Figure 2.10c, 2.10f) but appear limited only to the skeletal calcite in the shaley upper portion (Figure 2.10e). Framboidal pyrite is also present, and individual framboids can grow to diameters in excess of 40 μm (Figure 2.10a). Where framboidal pyrite and massive pyrite are juxtaposed, the difference in their $\delta^{34}\text{S}$ values is stark (Figures 2.10b, 2.10d). No sphalerite was found.

3.5 Sample 12785-11351.25 (3460 m)

This sample was collected from the lower Bakken and targeted laminae rich in microfossils and sulfides (Figure 2.7d). Framboidal pyrites may be found as isolated individuals (Figures 2.11a, 2.11c, 2.11d) or in clusters (Figure 2.11d). Both massive sphalerite and massive to subhedral pyrite are present. Concentric bands of silica inclusions are sometimes preserved in microfossil pyrites (Figures 2.11a, 2.11e); $\delta^{34}\text{S}$ values of these pyrites increase from core to rim.

3.6 Sample 17015-10422.7 (3177 m)

This sample was collected from the lower Bakken and was chosen primarily for its varied framboid populations and large ~ 1 mm massive to subhedral pyrite (Figure 2.7e). Microcrystalline pyrite appears either as framboids or as dispersed masses closely associated with framboids (Figures 2.12a, 2.12b, 2.12c, 2.12d). This sample contains the only case outside of E701 of a massive pyrite with $\delta^{34}\text{S}$ values similar to framboidal pyrite (Figure 2.12c). All other massive and replacive sulfides have heavy $\delta^{34}\text{S}$ values (e.g., 2.12a, 2.12e). The bright white relict

inclusions in the pyrite in Figure 2.12e are composed of barite, which was almost certainly the source of sulfate for the ~1 mm pyrite growth.

3.7 Sample 16586-9791.3 (2984 m)

This sample (Figure 2.7f) was collected from the upper Bakken and was chosen primarily for banded pyrites in silicified microfossils. As with sample E701-9923A (discussed above), the replacive sulfides take up most of the sulfide population by volume. Laminae rich in replacive pyrite are dominant in the lower third of the mount, while laminae rich in replacive sphalerite are dominant in the upper two thirds of the mount. There are relatively few instances of pyrite and sphalerite making contact with each other, and the reason for this separation of sulfide phases vertically within the sample is not known. Framboids are present and for the most part isolated as individuals (Figures 2.13a, 2.13b). Replacive pyrites have concentric bands of silica inclusions and are zoned in $\delta^{34}\text{S}$ (Figures 2.13a, 2.13b, 2.13c). Sphalerite shows no inclusion banding and little evidence for $\delta^{34}\text{S}$ zonation (Figure 2.13d).

4. Discussion

4.1 Framboidal and Polyframboidal Pyrites

Framboidal pyrites are surrounded by later generations of sulfide, indicating that framboidal pyrites were the first sulfide phase to grow in the sediment. Polyframboids and even the larger single framboids commonly show visible soft-sediment deformation around them, necessitating that either they form during early diagenesis or replace/displace something else that maintained its shape through early diagenesis. Framboid clusters have been known to preferentially form in the localized environments of microfossils during BSR in shallow

sediments, and partially replaced features such as that seen in Figure 2.8a have been described in radiolarian tests from Jurassic sediments (Reolid, 2014). However, if the features documented here formed inside radiolarian tests, there is no relic of the original microfossil remaining.

Values of $\delta^{34}\text{S}$ for framboids generally fall in the -40 to -30‰ range (Figure 2.14) which gives them a $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$ of around 50 to 60‰ relative to contemporaneous sulfate in seawater (Thode, 1981). This is consistent with fractionations expected for BSR, and in line with observations from modern anoxic basins (Sweeney and Kaplan, 1980; Fry et al., 1991; Muramoto et al., 1991). The data in Figure 2.14 show no evidence of Rayleigh distillation processes being active during early pyrite formation, as such a process would be expected to produce much broader distributions of data (Figure 2.14g, also 2.1). The interstitial sulfides in the polyframboids of sample E701-9923B may be an exception due to their intermediate values, but it's not clear based on the data in hand whether they are geochemically distinct from later massive sulfide phases. The likely explanation for the presence of the low- $\delta^{34}\text{S}$ values in framboidal pyrites is that the system was open to SO_4 and H_2S for most of early sulfide precipitation, allowing for the generation of large fractionations.

As previously mentioned, high framboidal $\delta^{34}\text{S}$ values are always associated with less discernable structure—that is to say, within the framboid there is less space between microcrystals and individual microcrystals are more difficult to make out (e.g., Figure 2.12d). However, the reverse is not true—round pyrite mineralizations with poor microcrystal structure do not necessarily have significantly lower $\delta^{34}\text{S}$ values than other framboids (e.g., Figure 2.12d again, 2.9d, 2.10d). Observational evidence has led to the belief that framboidal pyrites will

recrystallize over time towards more massive or euhedral forms (Sawlowicz, 1993), but there is no reason to believe that this might occur at the same rate in every framboid, given the wide variability in size and microcrystal ordering already present in framboidal populations.

Therefore, it seems likely that framboidal pyrite $\delta^{34}\text{S}$ values can be overprinted by later stages of sulfide growth, but evidence in this case would indicate that the timing of this overprinting is independent of degree of overprinting.

All framboids with $\delta^{34}\text{S}$ analyses classified as framboidal or mixed (Figure 2.14) still had some degree of visible framboidal microcrystalline structure visible across all or part of the SIMS analysis pit. Small subhedral pyrite crystals of similar diameter and $\delta^{34}\text{S}$ value to neighboring framboids are present in contact with but not growing around framboids within some of the polyframboids of E701-9923B (e.g., Figure 2.9a), suggesting that both pyrite features formed coincident with each other. No internal structure was visible in these polyframboidal subhedral pyrites by SEM; the subhedral pyrite crystals may represent framboids that have fully recrystallized but not in a way that affects $\delta^{34}\text{S}$ value.

A more extensive discussion of the framboid $\delta^{34}\text{S}$ SIMS data, and its potential usefulness for environmental interpretation, can be found in Chapter 3 of this thesis.

4.2 Massive/Subhedral Pyrites and Sphalerites

Pyrites and sphalerites in this category have values greater than -20‰, although the range of $\delta^{34}\text{S}$ values shifts dramatically from sample to sample, such that the lowest $\delta^{34}\text{S}$ values in the population can vary by more than 20‰ between samples. Not all massive and subhedral sulfides show clear $\delta^{34}\text{S}$ zonation, but those that do have higher values towards the rim (e.g.,

Figures 2.8d, 2.11a, 2.13a), consistent with distillation processes and a pool of dissolved sulfate growing heavier with time. There are some instances where massive pyrite is observed to be surrounded by sphalerite, indicating that sphalerite precipitation postdates massive pyrite, at least partially. As with the polyframboids, many of the massive sulfides studied here show soft-sediment deformation around them. However, this observation could easily originate with the silicified microfossils and rhombohedral dolomites that they are replacing rather than any structural support the sulfides themselves provided during burial.

Bands of silica inclusions are sometimes present in microfossil pyrite (but never in sphalerite) are interpreted to correspond to bands of coincident growth, and where present provide useful guides by which to interpret $\delta^{34}\text{S}$ zonation. Why these inclusion bands were preserved is unclear, but likely indicates that pyrite growth rates were pulsed, rather than constant. Replacive pyrites in sample 12785 (Figure 2.11) appear to have broad bands where $\delta^{34}\text{S}$ values are relatively constant for periods of growth, which also supports the notion that H_2S fluxes may have been pulsed through the formation at the time.

4.3 Bimodal $\delta^{34}\text{S}$ Distribution

As has been previously mentioned, framboidal pyrites have much lower $\delta^{34}\text{S}$ values than the massive and replacive sulfides. This strong bimodal distribution is present in all samples (Figure 2.14) in spite of active effort during analysis to find intermediate values. Interestingly, the mean of the low- $\delta^{34}\text{S}$ population does not vary much between samples, but the mean of the high- $\delta^{34}\text{S}$ population does, and the separation between the two populations varies significantly from sample to sample.

Curiously, framboids commonly are not surrounded by sulfide overgrowths, though they may be immediately adjacent to large massive or subhedral sulfides (e.g., Figures 2.8a, 2.8f, 2.9d, 2.11a, 2.11c, 2.11d, 2.12a, 2.13a, 2.13b). This suggests that most framboidal pyrites did not act as nucleation points for further pyrite or sphalerite precipitation. We hypothesize that as burial progresses framboidal pyrites may become fortified by the organic matter that surrounds them; that is to say, there comes a point at which H_2S cannot diffuse quickly enough into the framboid and precipitation shifts elsewhere. This interpretation does not preclude the possibility of a hiatus or a rapid shift in mode of sulfide precipitation in between the precipitation of framboidal and massive sulfides.

The steep gradients in $\delta^{34}\text{S}$ between framboidal and massive pyrite (e.g., 42‰ within 10 μm ; Figure 2.10c, 2.10d) also indicates that there was no gradual transition from the processes that created the pyrite framboids and the massive sulfides. The bimodal distribution likely originated one of two ways: 1) All sulfides formed from BSR during early diagenesis, and a brief hiatus in microbial activity or change in vital effects during sediment burial generated a change in H_2S $\delta^{34}\text{S}$ prior to massive sulfide precipitation (Figure 2.15a), or 2) Framboids and framboid-associated pyrite phases formed during BSR, and later massive sulfides formed during TSR (Figure 2.15b).

These two models will be discussed in the following section.

4.3.1 Model 1: All BSR – Fractionation Factor Change or Hiatus Mid-Precipitation

The bimodal distribution of sulfide $\delta^{34}\text{S}$ values cannot be produced through simple Rayleigh distillation processes, as this would produce observable volumes of sulfide minerals in

the -25 to -20‰ range. So, while open-system BSR is the likely explanation for most of the framboidal pyrite, explaining the high- $\delta^{34}\text{S}$ massive pyrites requires an additional process. There are two ways by which this might occur if BSR is the mechanism for all sulfate reduction: 1) via a biologically driven fractionation factor change, or 2) via a hiatus in precipitation between framboidal and massive sulfides (Figure 2.15a).

As euxinic sediment is buried, cell activity and sulfate concentrations might both be expected to decrease. Both can affect the contemporaneous $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$ produced during BSR, but in opposite directions. Explaining the Bakken data would necessitate that low sulfate concentrations produced the larger effect. Framboidal pyrite is thought to form as a result of rapid precipitation processes, and if later massive sulfides formed more slowly, the change in sulfide's petrographic expression is not incompatible with this hypothesis.

Alternatively, one could argue that there is a temporal cessation in BSR activity (and corresponding increase in burial depth in sediment) between the formation of framboidal and massive sulfides, which would allow distillation to occur without requiring the precipitation of intermediate- $\delta^{34}\text{S}$ sulfides. However, while sufficient to explain the observed distributions, this hypothesis lacks a clear mechanism and is thereby ultimately unlikely.

4.3.2 Model 2: Open System BSR With Later TSR Overprint

The bimodal distribution of $\delta^{34}\text{S}$ values might be explained if BSR formed the framboidal populations and a later TSR overprint caused added growth of the massive sulfides (Figure 2.15b). However, a complicating factor in this model is that low- $\delta^{34}\text{S}$ framboidal pyrites almost certainly formed via BSR under open-system conditions. If this is the case, then why did pyrite

stop precipitating before distillation processes produced appreciable volumes of intermediate (-25 to -20‰) pyrite $\delta^{34}\text{S}$? One possibility is that the system never became closed or depleted in H_2S during burial, and it was the limitation of available Fe that stopped precipitation.

Alternatively, it may be that BSR simply slowed or stopped once a temperature or depth threshold was reached, or was limited to the water column. Finally, it may simply be that the volume of sulfide produced by open-system processes far outweighs the volume produced in distillation processes, and so distillation behavior is difficult to measure in early sulfides.

Perhaps the strongest argument for TSR overprints in these rocks is simply that all of the conditions required for the reaction have already been met. Temperatures are known to have exceeded 100°C and may have exceeded 160°C (Kuhn et al., 2012), the proximity of organic-rich shales means that there was certainly sufficient hydrocarbons to drive the reaction, and the continued presence of unreacted sulfate minerals within the Bakken itself (e.g., Figure 2.12e) indicates that sulfate would be available in solution. Even the presence of reactive iron in the system is likely, given the growth of late-burial ankeritic carbonates in the middle Bakken (Denny et al., 2019).

4.3.3 Comparing Models 1 and 2

The authors conclude that Model 2 is likely correct, due to the following lines of evidence: 1) early sulfides formed framboids in soft sediment where T was amenable to BSR; 2) later T's exceeded 100°C , above the limit for biological processes; 3) $\delta^{34}\text{S}_{\text{sulfide}}$ values are consistent with expected fractionations during TSR; 4) sulfate minerals (barite) are observed being actively replaced by massive pyrite (Figure 2.12e); 5) volumes of replacive pyrite are very large and $\delta^{34}\text{S}$ values have a very narrow range for an early diagenetic distillation process,

better reflecting a partially closed system with small fractionation where sulfate is derived locally; 6) the lack of massive pyrite nucleating on framboidal pyrite is better explained by a time hiatus than a shift in fractionation factor or chemical flux.

5. Conclusions

A bimodal distribution in $\delta^{34}\text{S}_{\text{sulfide}}$ values is present in Devonian to Mississippian-aged organic-rich Bakken shales, and sulfide $\delta^{34}\text{S}$ values are closely linked to petrographic expression. Framboidal sulfides fall in the -45 to -25‰ range for $\delta^{34}\text{S}$, forming by BSR processes in a dysoxic environment with open-system H_2S behavior. Large massive pyrites and sphalerites have higher $\delta^{34}\text{S}$ values above -20‰ and replace skeletal carbonates, silicified microfossils, and individual dolomite crystals. These replacive pyrites and sphalerites probably formed by TSR during hydrocarbon maturation, which indicates that they might be a useful indicator of shale maturity in the future.

An unsettling conclusion of this study relevant to the measurement of $\delta^{34}\text{S}$ analyses elsewhere—and thereby the interpretation of the sedimentary $\delta^{34}\text{S}$ record—is that there is a strong preference for later sulfides to precipitate and grow in microfossils and specific mineral phases. This means that there are strong depositional influences on where diffusing H_2S will ultimately precipitate as sulfide minerals, which has ramifications for any system that shows evidence of TSR overprinting or prolonged Rayleigh distillation during early diagenesis.

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Appendices

Appendix 2.1 – Condensed SIMS dataset (.xlsx)

Appendix 2.2 – Full SIMS datasets w/ standards and IMF corrections (.xlsx)

Appendix 2.3 – Mount maps of SIMS data

2.3.1 – SIMS mount E701-9922.8A (.pdf)

2.3.2 – SIMS mount E701-9922.8B (.pdf)

2.3.3 – SIMS mount 21706-11087.5 (.pdf)

2.3.4 – SIMS mount 12785-11351.25 (.pdf)

2.3.5 – SIMS mount 17015-10422.7 (.pdf)

2.3.6 – SIMS mount 16586-9791.3 (.pdf)

References

- Borcovsky D., Egenhoff S., Fishman N., Maletz J., Boelhke A. and Lowers H. (2017) Sedimentology, facies architecture, and sequence stratigraphy of a Mississippian black mudstone succession—The upper member of the Bakken Formation, North Dakota, United States. *American Association of Petroleum Geologists Bulletin* **101**, 1625–1673.
- Böttcher M. E., Thamdrup B. and Vennemann T. W. (2001) Oxygen and sulfur isotope fractionation during anaerobic bacterial disproportionation of elemental sulfur. *Geochimica et Cosmochimica Acta* **65**, 1601–1609.
- Bottrell S. H. and Newton R. J. (2006) Reconstruction of changes in global sulfur cycling from marine sulfate isotopes. *Earth-Science Reviews* **75**, 59–83.
- Canfield D. E. and Thamdrup B. (1996) Fate of elemental sulfur in an intertidal sediment. *FEMS Microbiol Ecology* **19**, 95–103.

- Canfield D. E. and Thamdrup B. (1994) The production of ^{34}S -depleted sulfide during bacterial disproportionation of elemental sulfur. *Science* **266**, 1973–1975.
- Chambers L. A., Trudinger P. A., Smith J. W. and Burns M. S. (1975) Fractionation of sulfur isotopes by continuous cultures of *Desulfovibrio desulfuricans*. *Canadian Journal of Microbiology* **21**, 1602–1607.
- Claypool G. E. (2004) Ventilation of marine sediments indicated by depth profiles of pore water sulfate and $\delta^{34}\text{S}$. In *The Geochemical Society Special Publications* (eds. R. J. Hill, J. Leventhal, Z. Aizenshtat, M. J. Baedeker, G. Claypool, R. Eganhouse, M. Goldhaber, and K. Peters). Geochemical Investigations in Earth and Space Science: A Tribute to Isaac R. Kaplan. Elsevier. pp. 59–65. Available at: <http://www.sciencedirect.com/science/article/pii/S1873988104800075>.
- Cui H., Kitajima K., Spicuzza M. J., Fournelle J. H., Denny A., Ishida A., Zhang F. and Valley J. W. (2018) Questioning the biogenicity of Neoproterozoic superheavy pyrite by SIMS. *American Mineralogist* **103**, 1362–1400.
- Detmers J., Brüchert V., Habicht K. S. and Kuever J. (2001) Diversity of Sulfur Isotope Fractionations by Sulfate-Reducing Prokaryotes. *Applied and Environmental Microbiology* **67**, 888–894.
- Ding T., Valkiers S., Kipphardt H., De Bièvre P., Taylor P. D. P., Gonfiantini R. and Krouse R. (2001) Calibrated sulfur isotope abundance ratios of three IAEA sulfur isotope reference materials and V-CDT with a reassessment of the atomic weight of sulfur. *Geochimica et Cosmochimica Acta* **65**, 2433–2437.
- Egenhoff S. O. and Fishman N. S. (2013) Traces in the dark—Sedimentary processes and facies gradients in the upper shale member of the Upper Devonian–Lower Mississippian Bakken Formation, Williston Basin, North Dakota, USA. *Journal of Sedimentary Research* **83**, 803–824.
- Farquhar J. and Wing B. A. (2003) Multiple sulfur isotopes and the evolution of the atmosphere. *Earth and Planetary Science Letters* **213**, 1–13.
- Fike D. A., Bradley A. S. and Rose C. V. (2015) Rethinking the Ancient Sulfur Cycle. *Annual Review of Earth and Planetary Sciences* **43**, 593–622.
- Fishman N. S., Egenhoff S. O., Boehlke A. R. and Lowers H. A. (2015) Petrology and diagenetic history of the upper shale member of the Late Devonian–Early Mississippian Bakken Formation, Williston Basin, North Dakota. *Geological Society of America Special Papers* **515**, SPE515–07.
- Fry B., Gest H. and Hayes J. M. (1984) Isotope effects associated with the anaerobic oxidation of sulfide by the purple photosynthetic bacterium, *Chromatium vinosum*. *FEMS Microbiology Letters* **22**, 283–287.

- Fry B., Gest H. and Hayes J. M. (1985) Isotope effects associated with the anaerobic oxidation of sulfite and thiosulfate by the photosynthetic bacterium, *Chromatium vinosum*. *FEMS Microbiology Letters* **27**, 227–232.
- Fry B., Jannasch H. W., Molyneux S. J., Wirsén C. O., Muramoto J. A. and King S. (1991) Stable isotope studies of the carbon, nitrogen and sulfur cycles in the Black Sea and the Cariaco Trench. *Deep Sea Research Part A. Oceanographic Research Papers* **38**, S1003–S1019.
- Fry B., Ruf W., Gest H. and Hayes J. M. (1988) Sulfur isotope effects associated with oxidation of sulfide by O₂ in aqueous solution. *Chemical Geology: Isotope Geoscience section* **73**, 205–210.
- Gaswirth S. B. and Marra K. R. (2015) U.S. Geological Survey 2013 assessment of undiscovered resources in the Bakken and Three Forks Formations of the U.S. Williston Basin Province. *AAPG Bulletin* **99**, 639–660.
- Gaswirth S. B., Marra K. R., Cook T. A., Charpentier R. R., Gautier D. L., Higley D. K., Klett T. R., Lewan M. D., Lillis P. G. and Schenk C. J. (2013) *Assessment of undiscovered oil resources in the Bakken and Three Forks formations, Williston Basin Province, Montana, North Dakota, and South Dakota*, 4 p.
- Habicht K. S., Canfield D. E. and Rethmeier J. (1998) Sulfur isotope fractionation during bacterial reduction and disproportionation of thiosulfate and sulfite. *Geochimica et Cosmochimica Acta* **62**, 2585–2595.
- Habicht K. S., Gade M., Thamdrup B., Berg P. and Canfield D. E. (2002) Calibration of Sulfate Levels in the Archean Ocean. *Science* **298**, 2372–2374.
- Harrison A. G. and Thode H. G. (1958) Mechanism of the bacterial reduction of sulphate from isotope fractionation studies. *Transactions of the Faraday Society* **54**, 84–92.
- Johnston D. T. (2011) Multiple sulfur isotopes and the evolution of Earth's surface sulfur cycle. *Earth-Science Reviews* **106**, 161–183.
- Kaplan I. R. and Rittenberg S. C. (1964) Microbiological Fractionation of Sulphur Isotopes. *Microbiology* **34**, 195–212.
- Kita N. T., Ushikubo T., Fu B. and Valley J. W. (2009) High precision SIMS oxygen isotope analysis and the effect of sample topography. *Chemical Geology* **264**, 43–57.
- Kiyosu Y. (1980) Chemical reduction and sulfur-isotope effects of sulfate by organic matter under hydrothermal conditions. *Chemical Geology* **30**, 47–56.
- Kiyosu Y. and Krouse H. R. (1990) The role of organic acid in the abiogenic reduction of sulfate and the sulfur isotope effect. *Geochemical Journal* **24**, 21–27.

- Kozdon R., Kita N. T., Huberty J. M., Fournelle J. H., Johnson C. A. and Valley J. W. (2010) In situ sulfur isotope analysis of sulfide minerals by SIMS: Precision and accuracy, with application to thermometry of ~ 3.5 Ga Pilbara cherts. *Chemical Geology* **275**, 243–253.
- Kuhn P. P., di Primio R., Hill R., Lawrence J. R. and Horsfield B. (2012) Three-dimensional modeling study of the low-permeability petroleum system of the Bakken Formation. *American Association of Petroleum Geologists Bulletin* **96**, 1867–1897.
- Leavitt W. D., Halevy I., Bradley A. S. and Johnston D. T. (2013) Influence of sulfate reduction rates on the Phanerozoic sulfur isotope record. *Proceedings of the National Academy of Sciences* **110**, 11244–11249.
- LeFever J. A., Fever R. D. L. and Nordeng S. H. (2011) Chapter 1: Revised Nomenclature for the Bakken Formation (Mississippian-Devonian), North Dakota. In *The Bakken–Three Forks Petroleum System in the Williston Basin* (eds. J. W. Robinson, J. A. Lefever, and S. B. Gaswirth). Rocky Mountain Association of Geologists, Denver, Colorado. pp. 11–26. Available at: http://archives.datapages.com/data/rocky-mtn-geologist-pubs/data/002/002001/11_rmag-bk0020011.htm [Accessed August 29, 2016].
- Lin Z., Sun X., Peckmann J., Lu Y., Xu L., Strauss H., Zhou H., Gong J., Lu H. and Teichert B. M. A. (2016) How sulfate-driven anaerobic oxidation of methane affects the sulfur isotopic composition of pyrite: A SIMS study from the South China Sea. *Chemical Geology* **440**, 26–41.
- Linzmeier B. J., Kitajima K., Denny A. C. and Cammack J. N. (2018) Making maps on a micrometer scale. *EOS* **99**, 24–28.
- Machel H. G. (2001) Bacterial and thermochemical sulfate reduction in diagenetic settings — old and new insights. *Sedimentary Geology* **140**, 143–175.
- MacLean L. C. W., Tyliszczak T., Gilbert P., Zhou D., Pray T. J., Onstott T. C. and Southam G. (2008) A high-resolution chemical and structural study of framboidal pyrite formed within a low-temperature bacterial biofilm. *Geobiology* **6**, 471–480.
- Muramoto J. A., Honjo S., Fry B., Hay B. J., Howarth R. W. and Cisne J. L. (1991) Sulfur, iron and organic carbon fluxes in the Black Sea: sulfur isotopic evidence for origin of sulfur fluxes. *Deep Sea Research Part A. Oceanographic Research Papers* **38**, S1151–S1187.
- Ohmoto H. and Lasaga A. C. (1982) Kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems. *Geochimica et Cosmochimica Acta* **46**, 1727–1745.
- Ohmoto H. and Rye R. O. (1979) Isotopes of sulfur and carbon. In *Geochemistry of hydrothermal ore deposits* (ed. H. L. Barnes). Wiley, New York, NY. pp. 509–567.

- Pasquier V., Sansjofre P., Rabineau M., Revillon S., Houghton J. and Fike D. A. (2017) Pyrite sulfur isotopes reveal glacial- interglacial environmental changes. *Proceedings of the National Academy of Sciences* **114**, 5941–5945.
- Pocknall D. T., Hohman J. and Anonymous (2015) Palynology and sedimentology/stratigraphy of the Bakken Formation, North Dakota. *Abstracts with Programs - Geological Society of America* **47**, 654.
- Reolid M. (2014) Pyritized radiolarians and siliceous sponges from oxygen-restricted deposits (Lower Toarcian, Jurassic). *Facies* **60**, 789–799.
- Rickard D. (2012) *Sulfidic Sediments and Sedimentary Rocks*, Newnes.
- Rollinson H. R. (1993) *Using geochemical data: evaluation, presentation, interpretation*, Pearson Education.
- Sawlowicz Z. (1993) Pyrite framboids and their development: a new conceptual mechanism. *Geologische Rundschau* **82**, 148–156.
- Sim M. S., Bosak T. and Ono S. (2011a) Large Sulfur Isotope Fractionation Does Not Require Disproportionation. *Science* **333**, 74–77.
- Sim M. S., Ono S. and Bosak T. (2012) Effects of Iron and Nitrogen Limitation on Sulfur Isotope Fractionation during Microbial Sulfate Reduction. *Applied and Environmental Microbiology* **78**, 8368–8376.
- Sim M. S., Ono S., Donovan K., Templer S. P. and Bosak T. (2011b) Effect of electron donors on the fractionation of sulfur isotopes by a marine *Desulfovibrio* sp. *Geochimica et Cosmochimica Acta* **75**, 4244–4259.
- Sonnenberg S. A. (2011) Chapter 11: TOC and Pyrolysis Data for the Bakken Shales, Williston Basin, North Dakota and Montana. In *The Bakken–Three Forks Petroleum System in the Williston Basin* (eds. J. W. Robinson, J. A. LeFever, and S. B. Gaswirth). Denver, Colorado. pp. 308–331. Available at: http://archives.datapages.com/data/rocky-mtn-geologist-pubs/data/002/002001/308_rmag-bk0020308.htm [Accessed August 29, 2016].
- Sweeney R. E. and Kaplan I. R. (1980) Stable isotope composition of dissolved sulfate and hydrogen sulfide in the Black Sea. *Marine Chemistry* **9**, 145–152.
- Thode H. G. (1981) Sulfur Isotope Ratios in Petroleum Research and Exploration: Williston Basin. *American Association of Petroleum Geologists Bulletin* **65**, 1527–1535.
- Thode H. G. and Monster J. (1965) Sulfur-Isotope Geochemistry of Petroleum, Evaporites, and Ancient Seas. In *American Association of Petroleum Geologists Memoirs*: 4. pp. 367–377.

- Ushikubo T., Williford K. H., Farquhar J., Johnston D. T., Van Kranendonk M. J. and Valley J. W. (2014) Development of in situ sulfur four-isotope analysis with multiple Faraday cup detectors by SIMS and application to pyrite grains in a Paleoproterozoic glaciogenic sandstone. *Chemical Geology* **383**, 86–99.
- Valley J. W. and Kita N. T. (2009) *In situ* oxygen isotope geochemistry by ion microprobe. *Mineralogical Association of Canada Short Course* **41**, 19–63.
- Zerkle A. L., Farquhar J., Johnston D. T., Cox R. P. and Canfield D. E. (2009) Fractionation of multiple sulfur isotopes during phototrophic oxidation of sulfide and elemental sulfur by a green sulfur bacterium. *Geochimica et Cosmochimica Acta* **73**, 291–306.

Figures

Table 2.1. Name, depth, and location information for the 5 cores sampled from the Bakken Formation, North Dakota, USA.

Core Name, Source	Latitude, Longitude	Member	# of SIMS mounts	Depth of SIMS sample (ft from surface)	Depth of SIMS sample (~m from surface)	Modeled Max Temperature (°C, Kuhn et al., 2012)
E701, USGS	48.379442, -104.135898	lower	2	9922.8	3024.5	135
21706, NDGS	47.8179408, -103.1718619	upper/middle	1	11087.5	3379.5	160-165
12785, NDGS	47.542727, -102.963685	lower	1	11351.25	3459.9	150-155
17015, NDGS	48.2913654, -102.828463	lower	1	10422.7	3176.8	145-150
16586, NDGS	48.3405436, -102.545948	upper	1	9791.3	2984.4	130-135

Table 2.2. Analytical conditions for three SIMS sessions of sulfur isotope analysis.

Session	Date	Pit Dimensions	Beam Intensity	Mean Analytical Precision (2SD)
1	October 17, 2016	~ 3x2 μm	~ 30 pA	$\pm 0.7\text{‰}$
2	June 7, 2017	~ 3x3 μm	~ 29 pA	$\pm 1.3\text{‰}$
3	August 20, 2018	~ 10x8 μm	~ 1.4 nA	$\pm 0.1\text{‰}$

Figure 2.1. Closed-system $\delta^{34}\text{S}$ Rayleigh fractionation for pyrite precipitating from a sulfate pool with $\alpha_{\text{sulfate-sulfide}} = 1.05$. Initial sulfate composition has been set to $\delta^{34}\text{S} = 17\text{‰}$, which is a reasonable estimate for contemporaneous seawater during Bakken deposition (Thode and Monster, 1965; Thode, 1981).

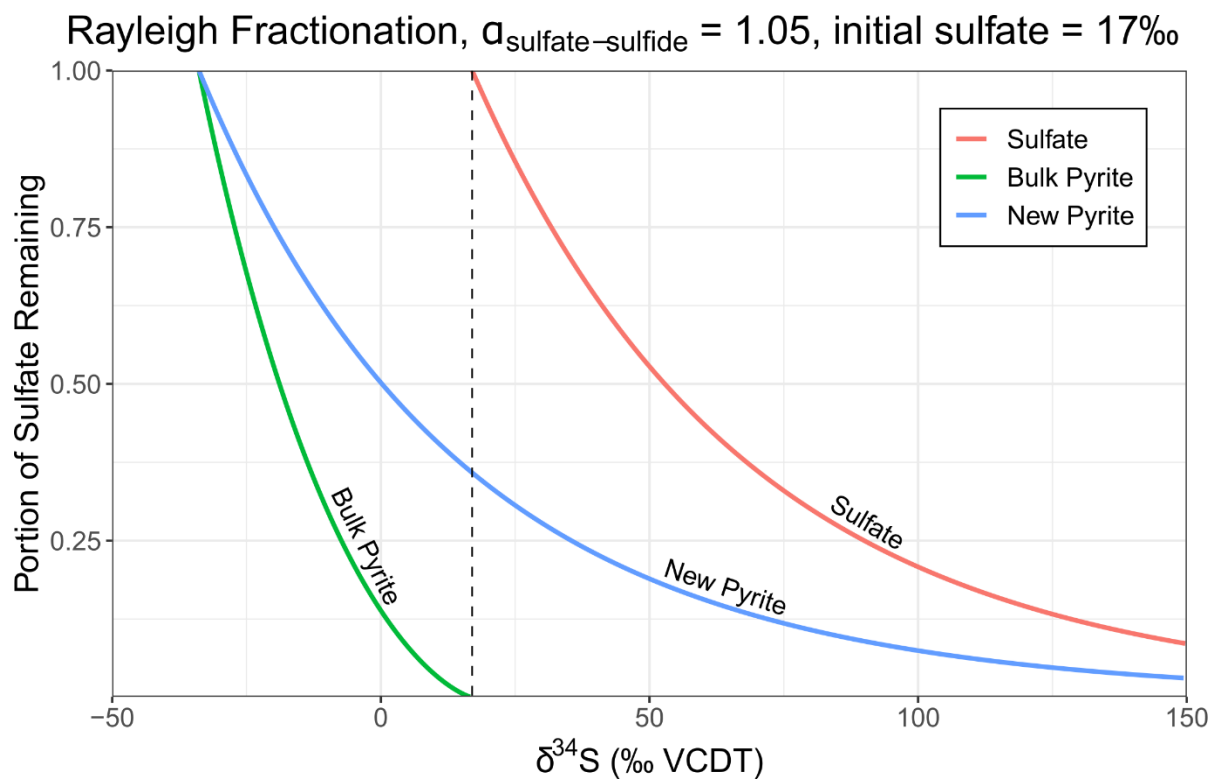


Figure 2.2. Temperature-dependent $\delta^{34}\text{S}$ fractionations between chemical phases of interest and H_2S .

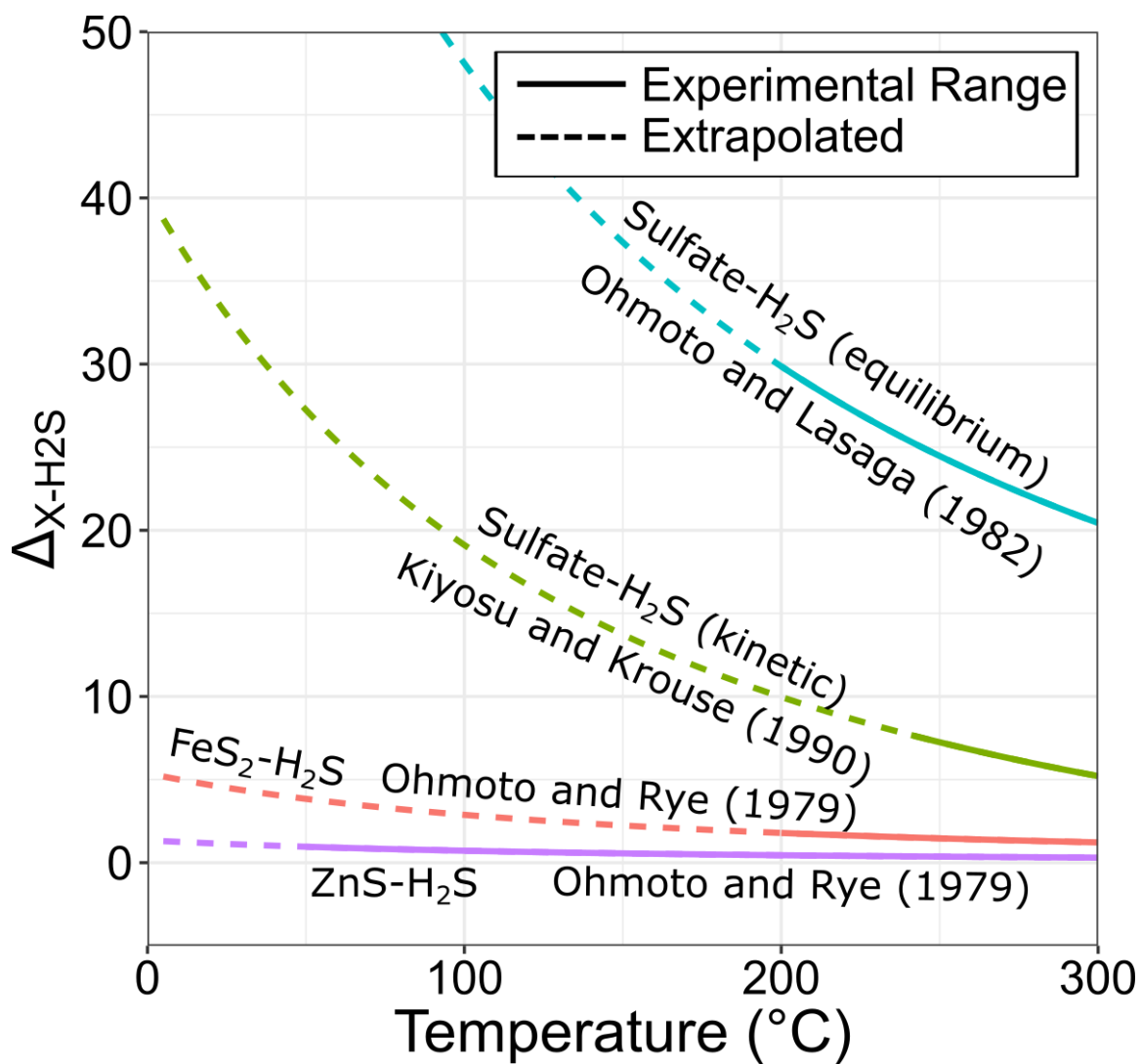


Figure 2.3. Map of structure-depth contours (solid lines) for the Bakken Formation in western North Dakota, with maximum burial temperature isotherms (dashed lines) and the locations of drill core samples analyzed (stars). Note that contours displayed here are measured relative to sea level so as to best convey the basin's structure; all other depths reported in this paper are relative to the local surface elevation. Figure modified from Sonnenberg et al. (2011) and Kuhn et al. (2012).

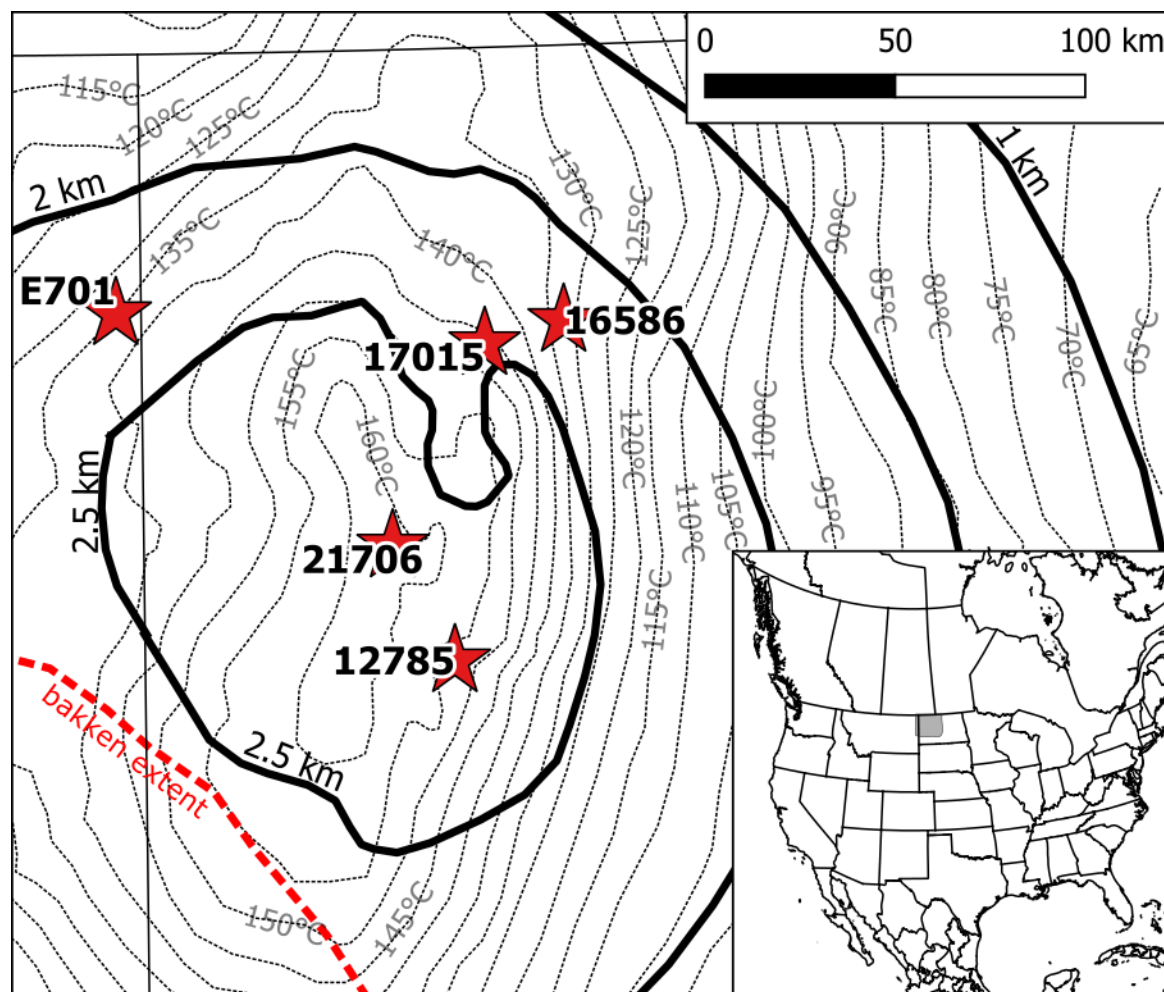


Figure 2.4. Sample locations from studied drill core are marked by stars, with major units and subunits labeled. L = Lodgepole, UB = Upper Bakken, MB = Middle Bakken, LB = Lower Bakken, TF = Three Forks.

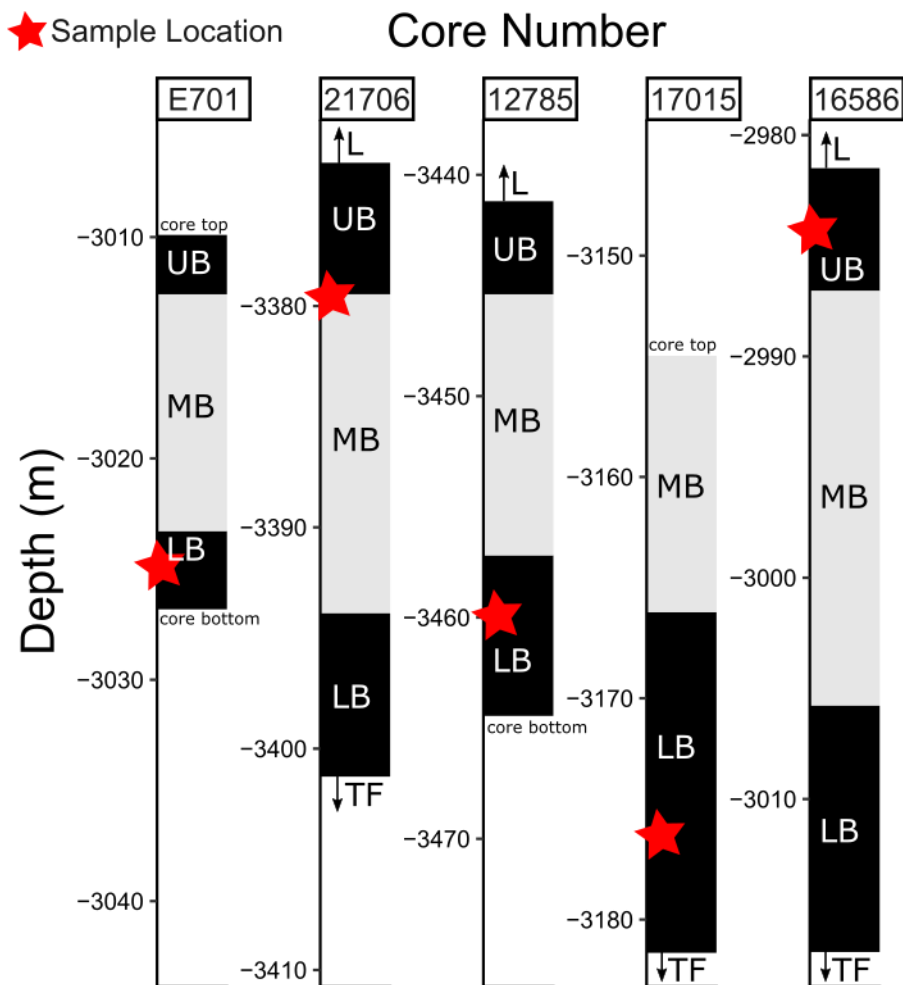


Figure 2.5. Previously reported bulk $\delta^{34}\text{S}$ values for contemporaneous seawater, Bakken oils, sulfates, organic sulfur and pyrite from the upper, middle, and lower Bakken members. Values are from Thode (1981).

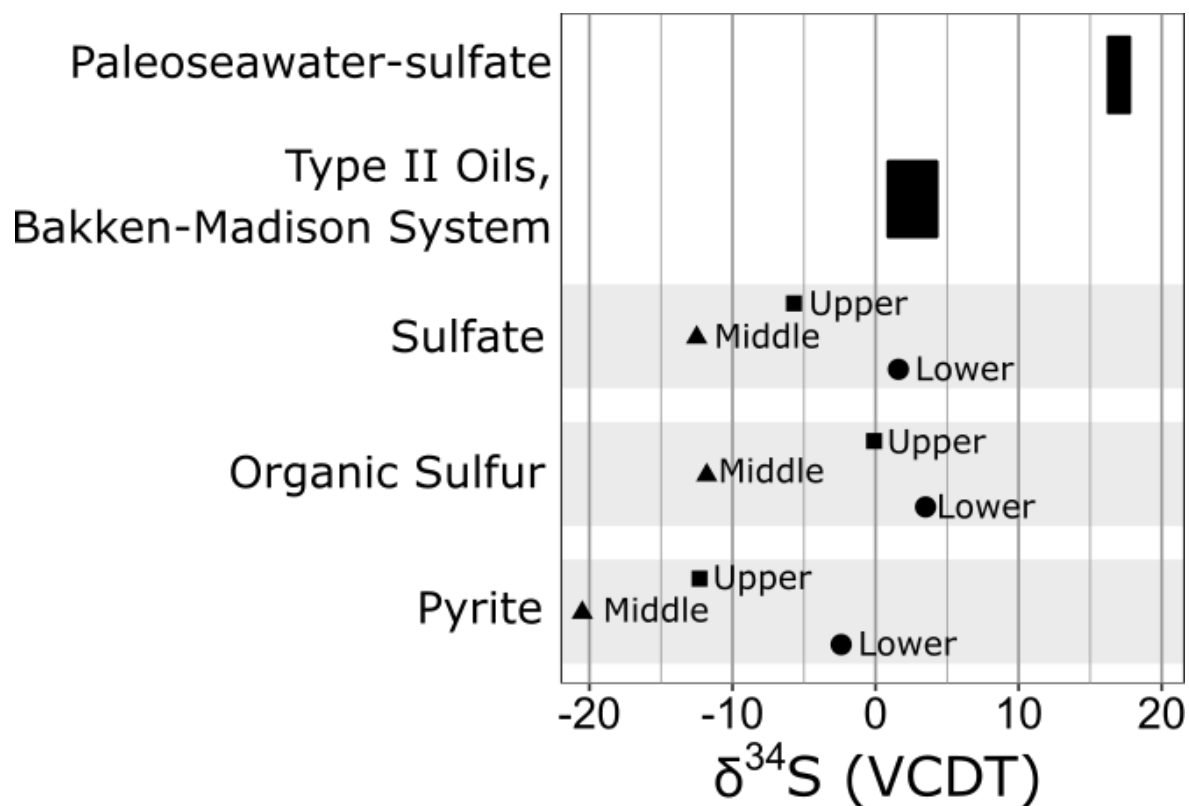


Figure 2.6. Visible light photograph of a polished billet from drillcore E701. Laminae rich in golden-colored specks are particularly rich in framboidal or massive pyrite; dark grains visible in the lag deposits are apatite. Two SIMS mounts separated by ~1 vertical cm were created from this billet; both mounts are shown by BSE-SEM imagery in Figures 2.7a and 2.7b and with finer-scale diagnostic petrographic features in Figures 2.8 and 2.9, respectively.

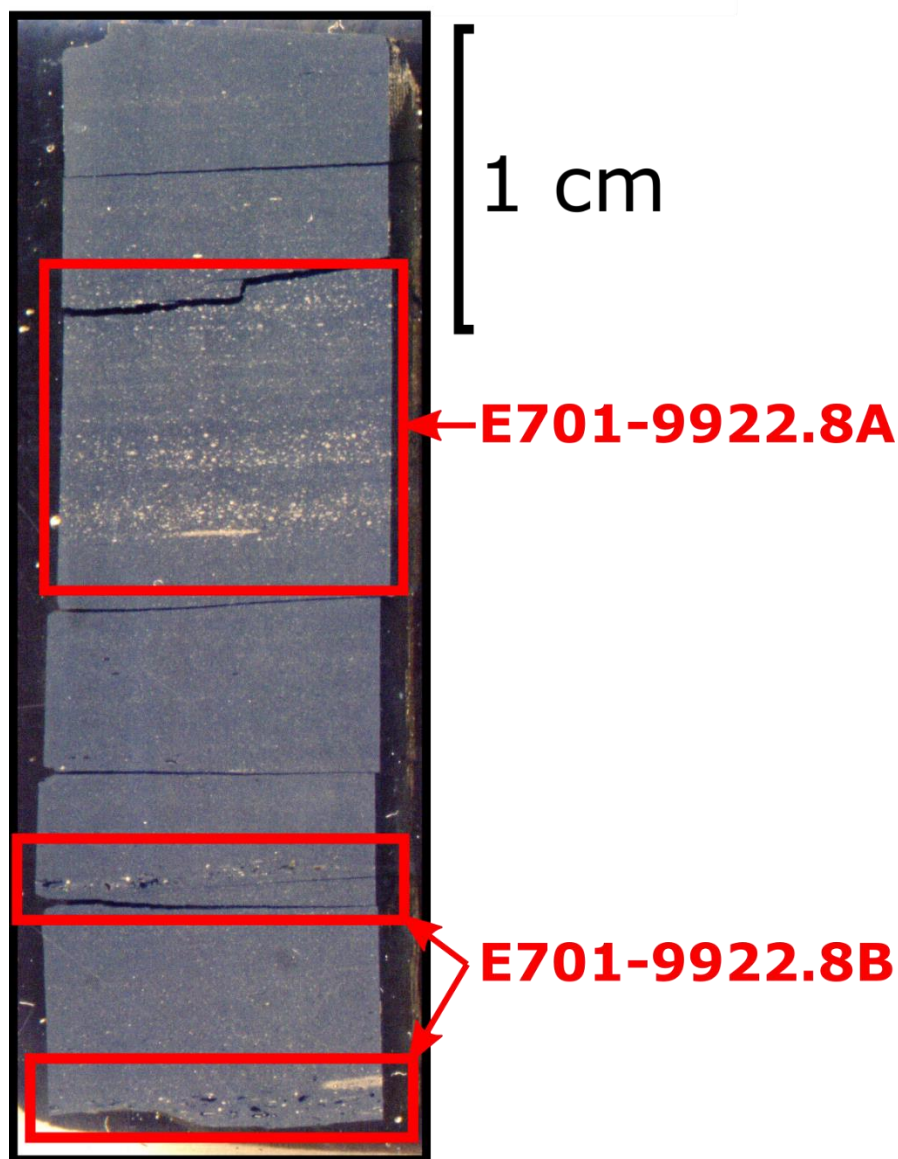


Figure 2.7. SEM-BSE maps of each SIMS mount studied; bright areas correspond to the locations of sulfide mineralization. Several areas analyzed by SIMS on each mount are magnified in the following figures, and the location of each area in the mount is marked here. Images of additional analytical areas may be found in Appendix 2.3. Round areas in the centers of (a), (c), (d), (e), and (f) contain embedded standards.

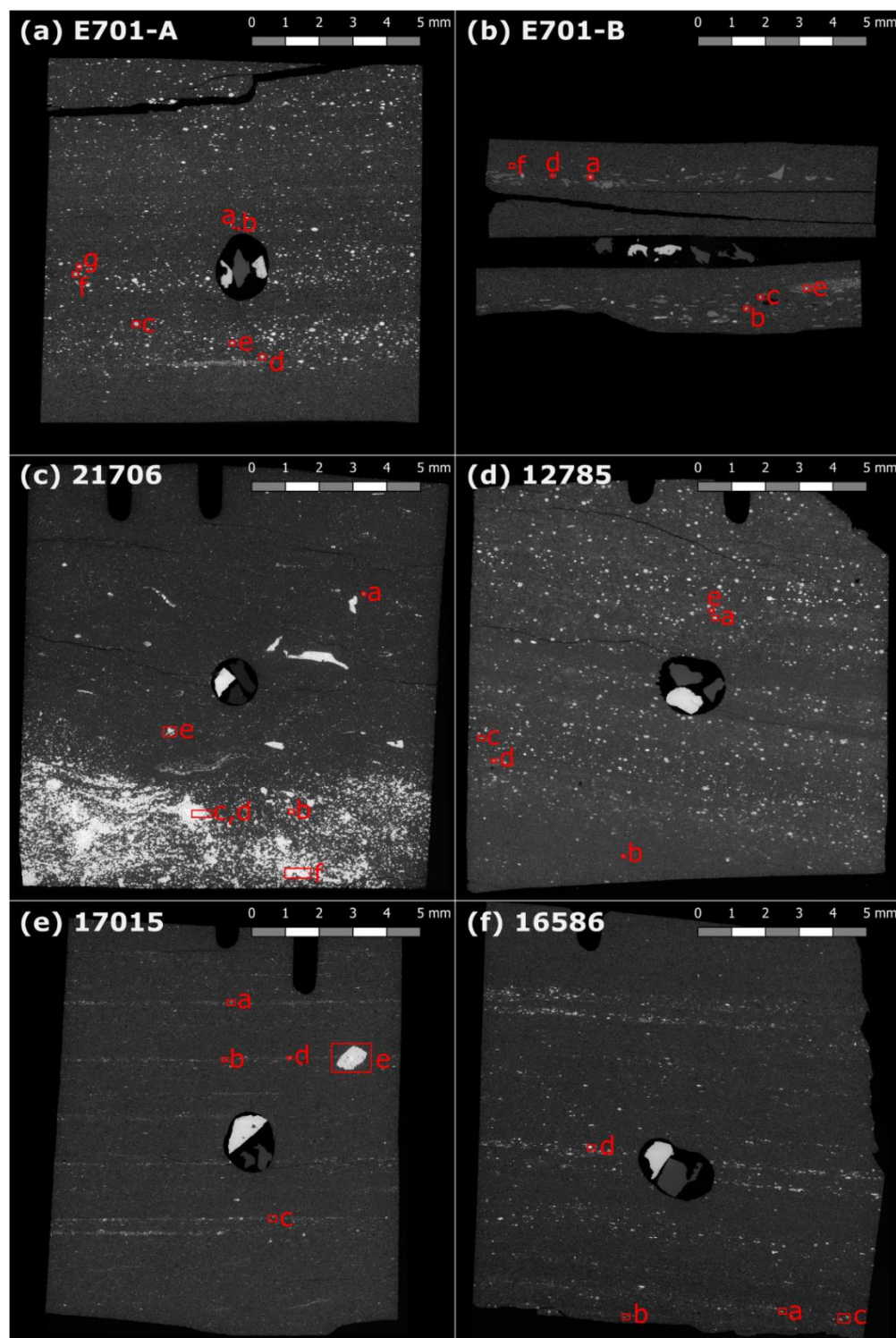


Figure 2.8. Sample E701-9922.8A: SEM-BSE imagery of representative sample sulfide features. SIMS analysis pits are marked by open circles and labeled with values of $\delta^{34}\text{S}$ (‰ VCDT). Key minerals are marked: Py = Pyrite, Sp = Sphalerite, Qz = Quartz, OM = Organic Matter.

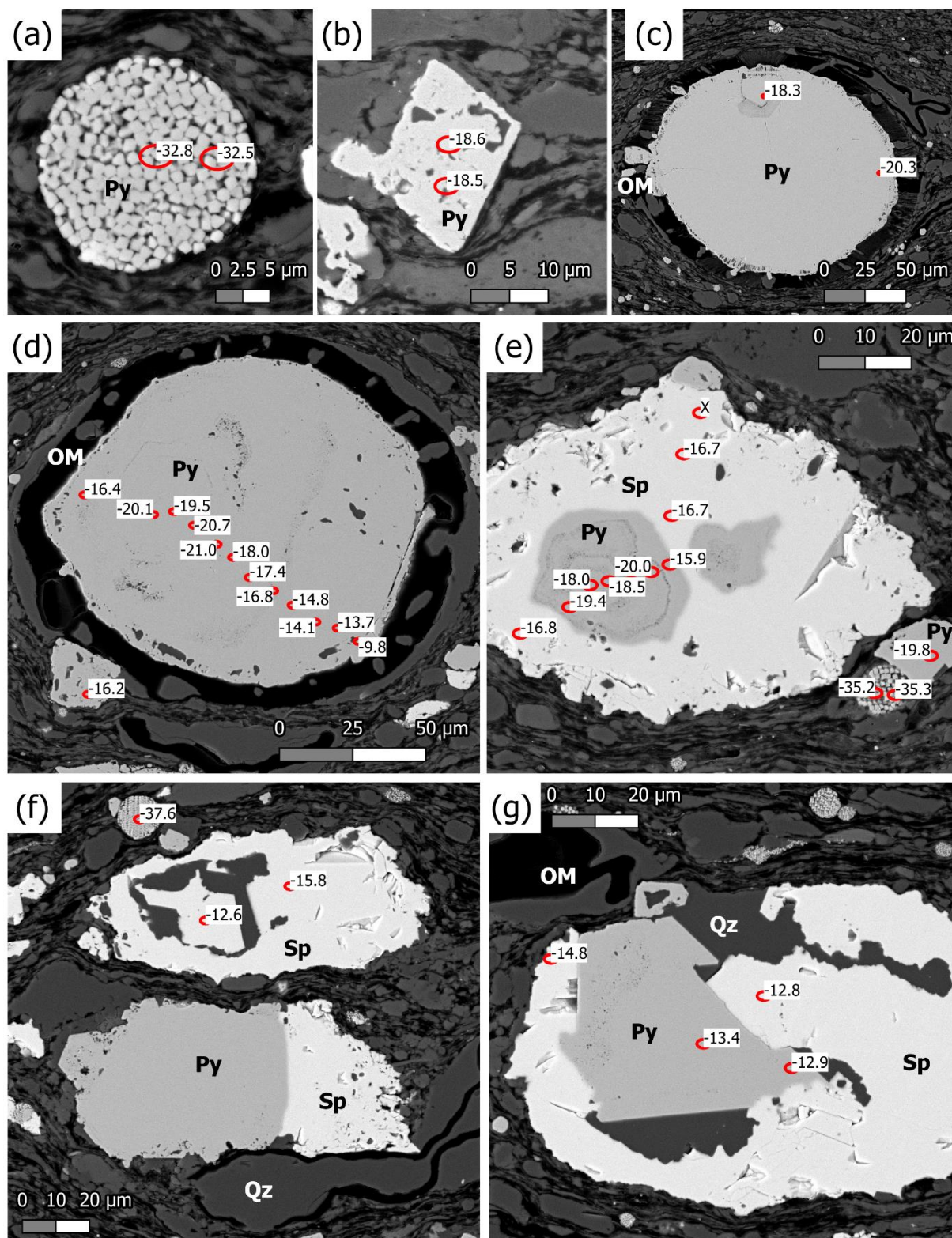


Figure 2.9. Sample E701-9922.8B: SEM-BSE imagery of representative sample sulfide features. SIMS analysis pits are marked by open circles and labeled with values of $\delta^{34}\text{S}$ (‰ VCDT). Key minerals are marked: Py = Pyrite, Sp = Sphalerite, Ap = Apatite.

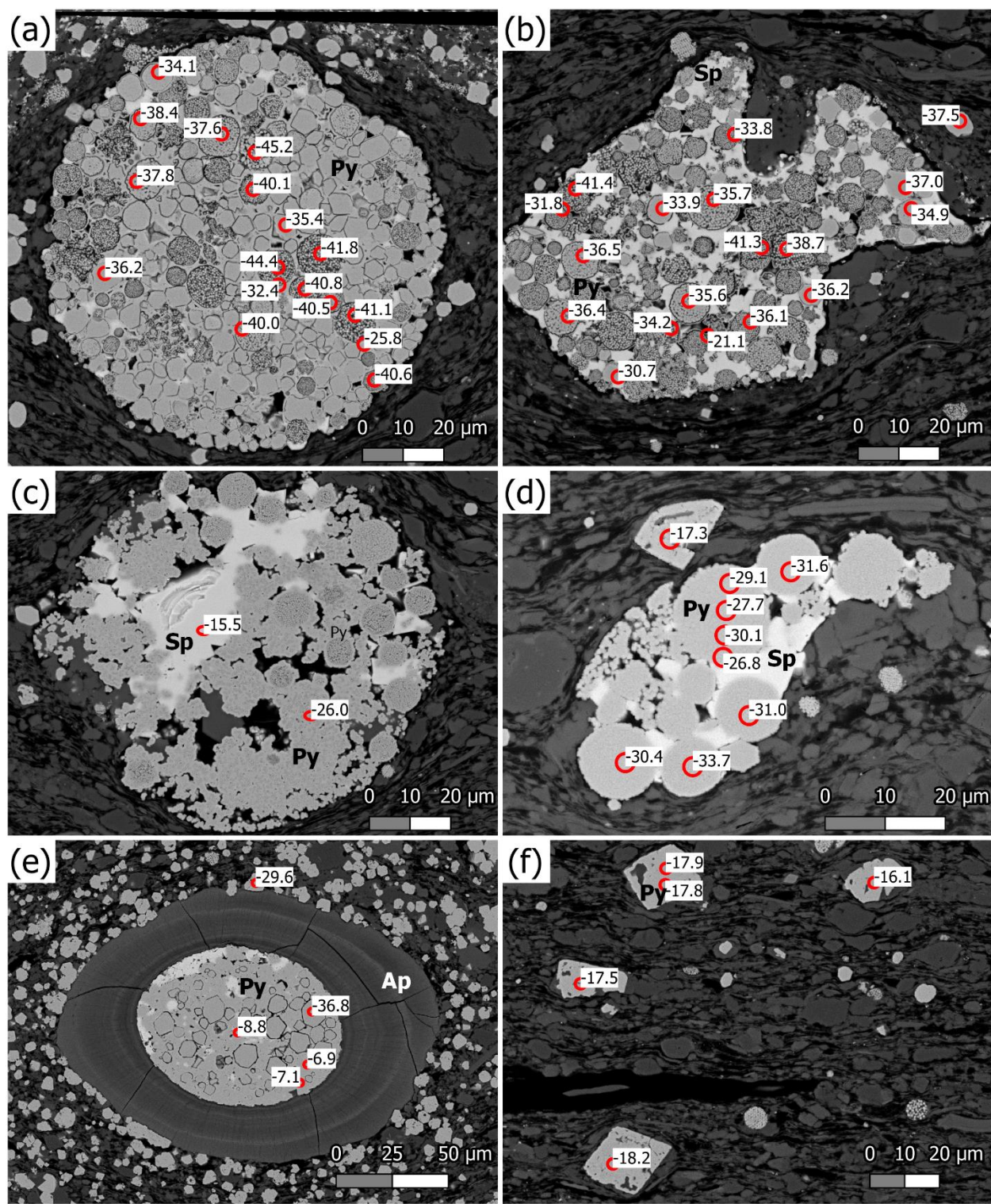


Figure 2.10. Sample 21706-11087.5: SEM-BSE imagery of representative sample sulfide features. SIMS analysis pits are marked by open circles and labeled with values of $\delta^{34}\text{S}$ (‰ VCDT). Key minerals are marked: Py = Pyrite, Sp = Sphalerite, Qz = Quartz, Cal = Calcite. (d) is an SEM-SE image of two SIMS pits in the area marked in (c).

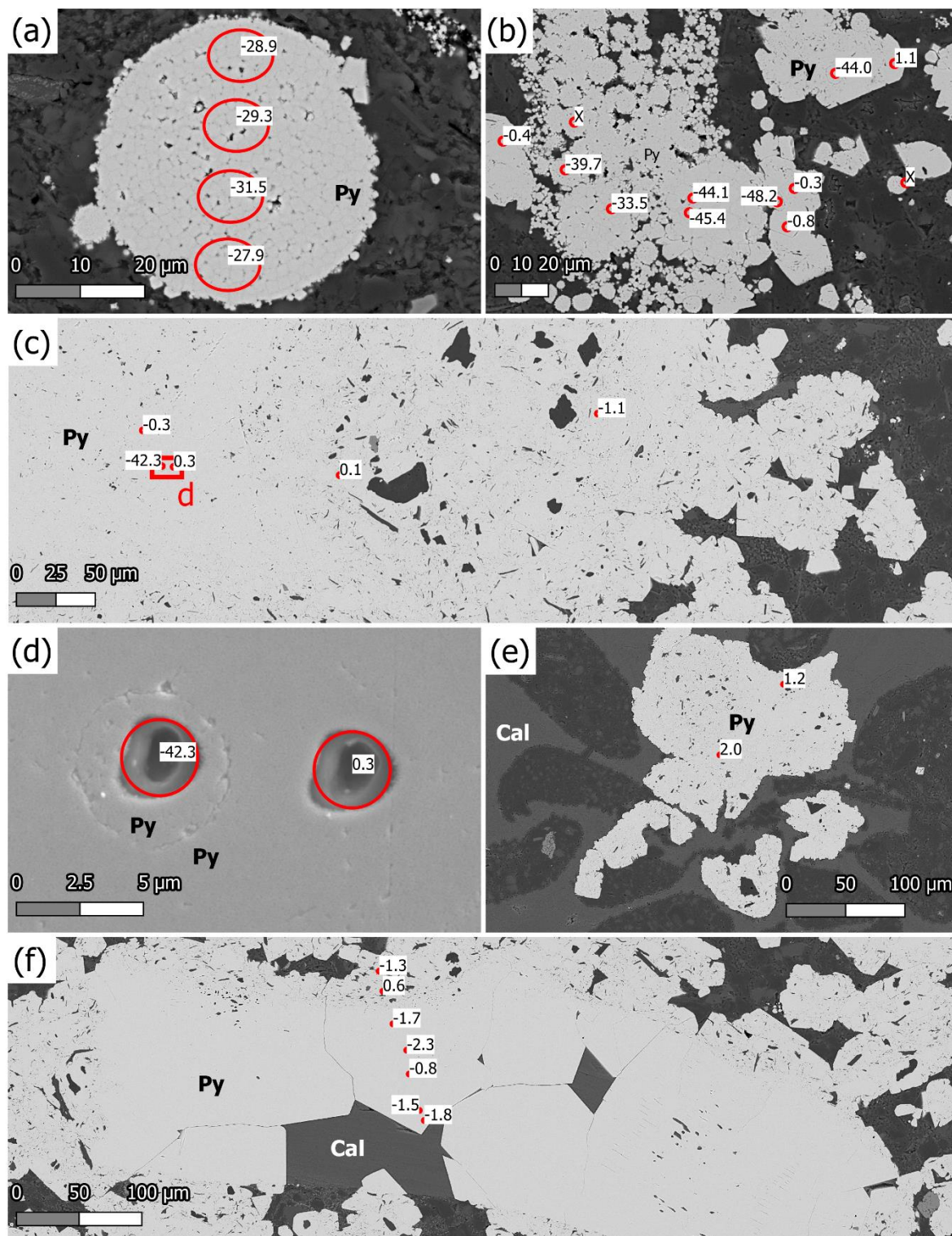


Figure 2.11. Sample 12785-11351.25: SEM-BSE imagery of representative sample sulfide features. SIMS analysis pits are marked by open circles and labeled with values of $\delta^{34}\text{S}$ (‰ VCDT). Key minerals are marked: Py = Pyrite, Sp = Sphalerite, Qz = Quartz, Cal = Calcite.

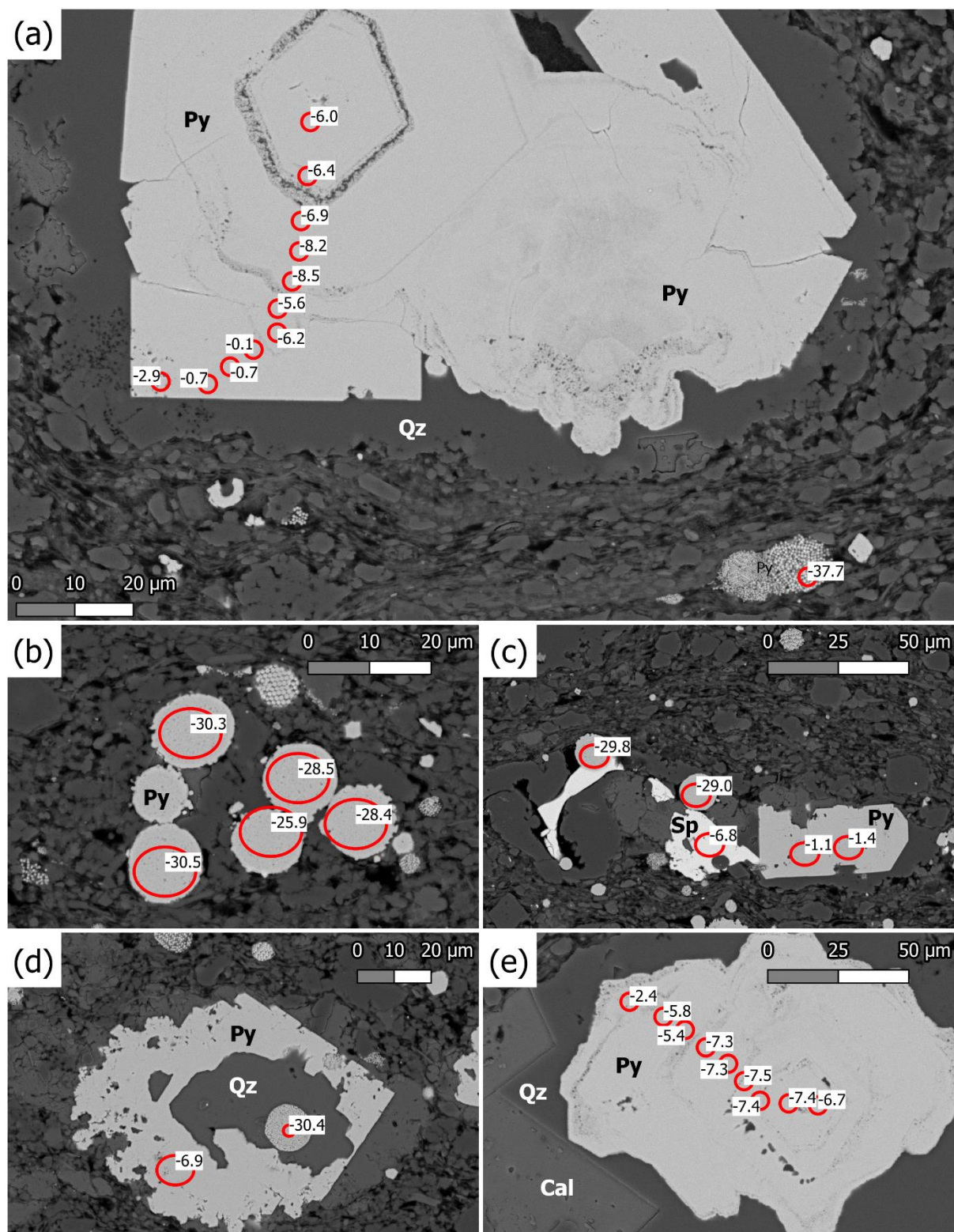


Figure 2.12. Sample 17015-10422.7: SEM-BSE imagery of representative sample sulfide features. SIMS analysis pits are marked by open and labeled with values of $\delta^{34}\text{S}$ (‰ VCDT). Key minerals are marked: Py = Pyrite, Sp = Sphalerite, Qz = Quartz, Ap = Apatite, Brt = Barite.

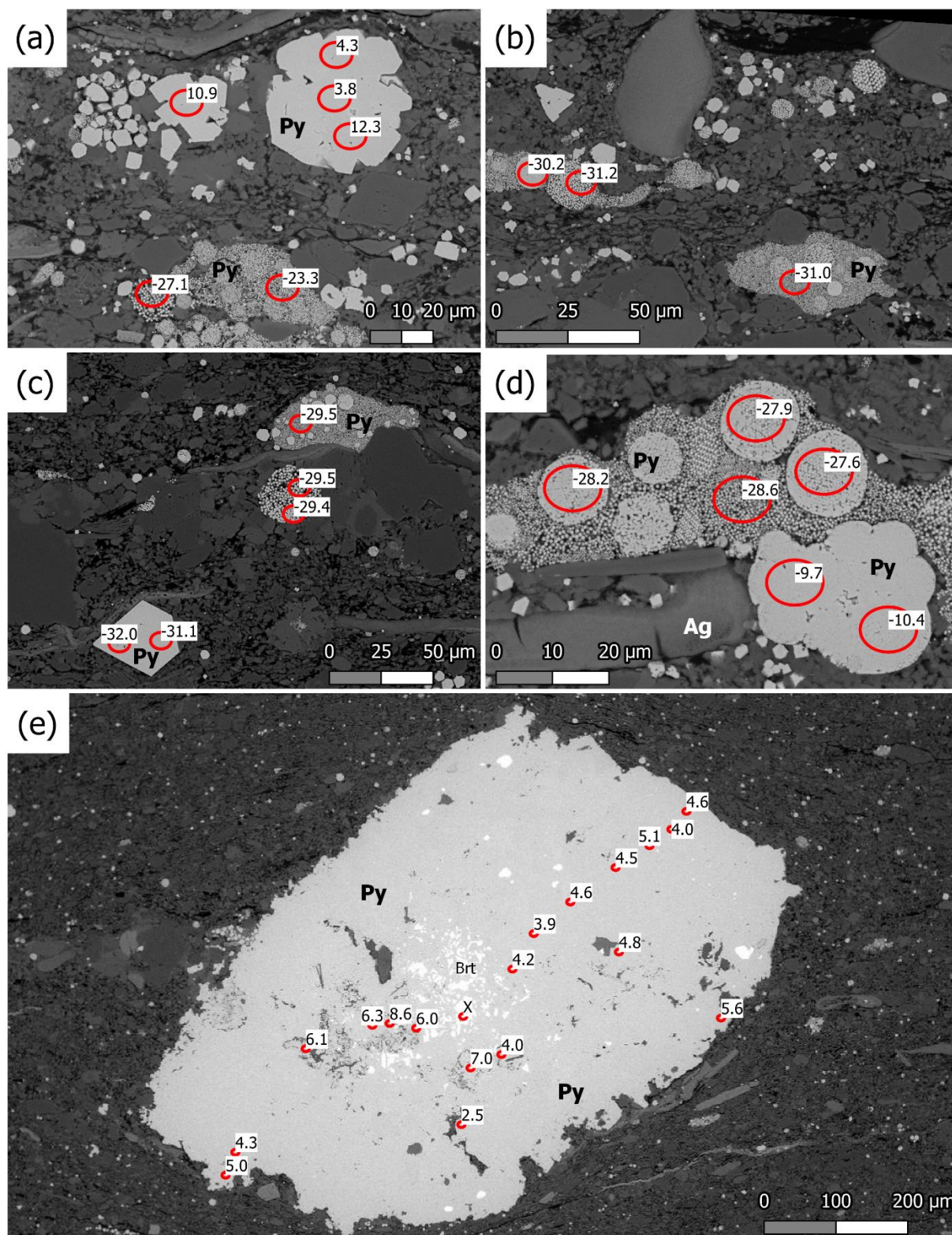


Figure 2.13. Sample 16586-9791.3: SEM-BSE imagery of representative sample sulfide features. SIMS analysis pits are marked by open circles and values of $\delta^{34}\text{S}$ are reported in ‰ relative to VCDT. Key minerals are marked: Py = Pyrite, Sp = Sphalerite, Qz = Quartz.

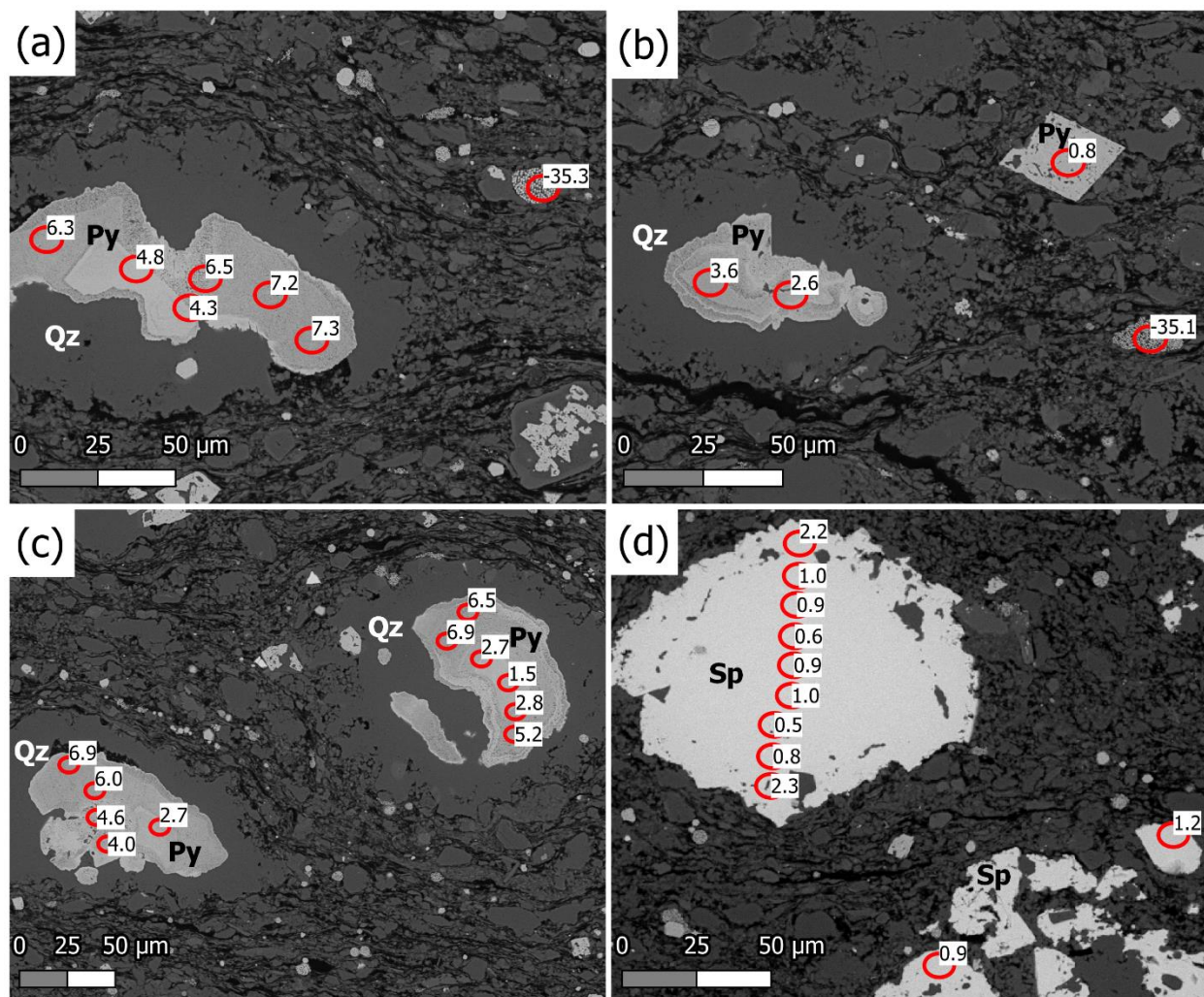


Figure 2.14. (a-f) Histograms for each sample showing the distribution of $\delta^{34}\text{S}$ values amongst different petrographic phases of pyrite and sphalerite. **(g)** Expected distributions of SIMS data assuming closed system Raleigh distillation with sulfate $\delta^{34}\text{S} = 17\text{‰}$ and $\alpha = 1.05, 1.03, \text{ and } 1.01$.

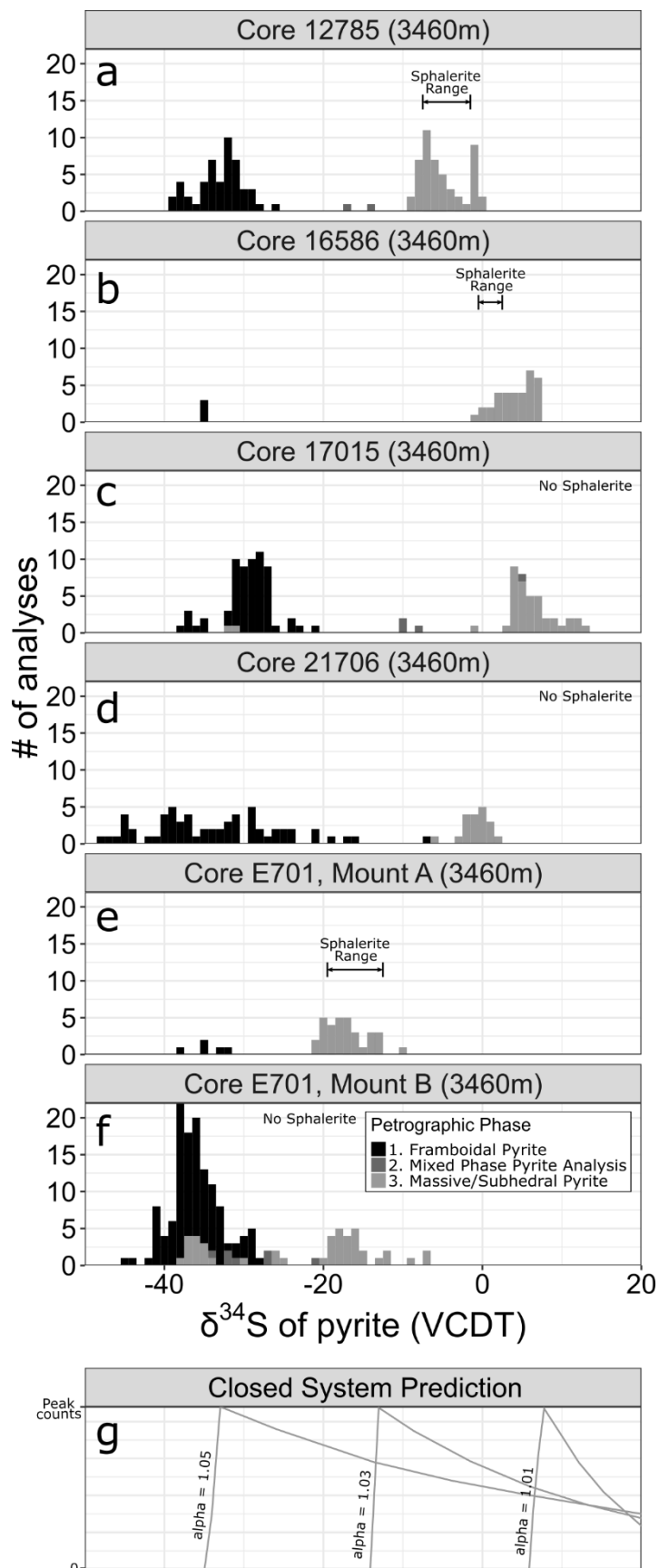
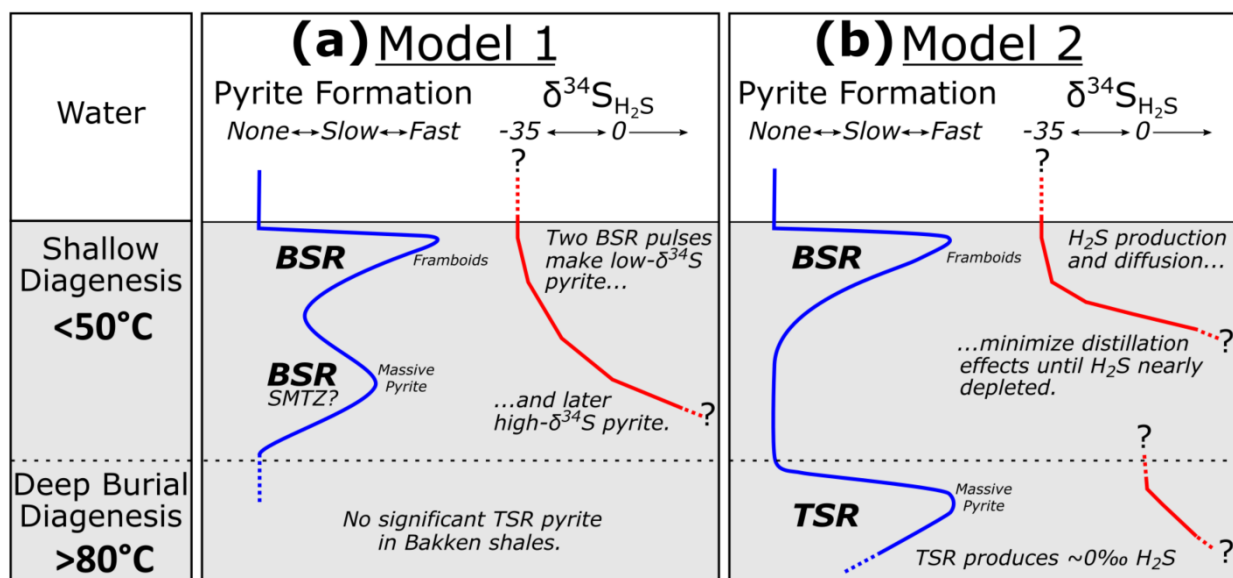


Figure 2.15. Two diagenetic models for explaining the observed bimodal $\delta^{34}\text{S}$ distribution in the Bakken. BSR = Bacterial Sulfate Reduction, TSR = Thermochemical Sulfate Reduction, SMTZ = Sulfate Methane Transition Zone. **(a)** In Model 1, all pyrite forms during shallow burial. The bimodal $\delta^{34}\text{S}_{\text{pyrite}}$ distribution results from two pulses of pyrite formation that sample a shared sulfate reservoir that is increasingly depleted and distilled towards higher $\delta^{34}\text{S}$ values with depth. A likely mechanism for two BSR pulses involves an initial pulse of BSR when sulfate concentrations (and H_2S production rates) are very high, and a second pulse where biogenic methane diffuses upwards and is consumed in the SMTZ. **(b)** In Model 2, all framboidal pyrite and framboid-associated pyrites form during shallow diagenesis, and later massive sulfides form much later via TSR.



CHAPTER 3: Black Shale Framboid Sulfur Isotope Population Analyses: Observations and Insight from the Bakken Formation

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CONTRIBUTIONS: Samples were acquired from the North Dakota Geologic Survey and the United States Geological Survey core repositories in collaboration with staff there. Benjamin Barnes and Maciej Śliwiński provided additional assistance with sample collection. Bil Schneider provided instrument support on the SEM. Instrumental support in the WiscSIMS lab was provided Kouki Kitajima, Aki Ishida, and Noriko Kita. Chapter contents were reviewed and edited by John Valley, Clay Kelly, Alan Carroll, Stephen Meyers, and Matthew Ginder-Vogel.

Abstract

Pyrite framboids are widespread and easily recognizable features in sedimentary rocks worldwide, though the processes controlling their development remain enigmatic. Their formation in sediments is tied to microbial metabolism and the $\delta^{34}\text{S}$ value of seawater sulfate, making them powerful indicators of past environmental conditions. This paper reports in situ analysis of $\delta^{34}\text{S}$ by SIMS (3 and 10 μm spots) that establishes constraints on how framboidal pyrite grows and what it indicates about diagenetic processes. SIMS $\delta^{34}\text{S}$ analyses made on framboid populations from the Devonian to Mississippian-aged Bakken Formation indicate the following. 1) There is no systematic isotope zonation from the core to rim of pyrite in framboids, showing that these features do not grow by progressive precipitation along the framboid's rim, as is typical with single crystals. 2) Variability in $\delta^{34}\text{S}$ within framboids indicates isotope zonation within microcrystalline pyrite, indicating that framboids grow primarily through synchronized microcrystal growth. 3) Framboids show greater variability in $\delta^{34}\text{S}$ than can be explained by changes in instrumental offset, and suggest different rates or durations of formation. 4) Recrystallization or later $\delta^{34}\text{S}$ overprinting can compromise original framboid isotope values. 5) Different generations of pyrite can be resolved with careful SEM imaging and SIMS analysis (SEM-SIMS).

1. Introduction

Pyrite framboids can form extremely quickly (weeks to months) in sea water and in soft sediment (Wilkin and Barnes, 1997; Vietti et al., 2015; Rickard, 2019), and thus they exhibit one of the highest temporal resolutions of any mineral found in sediment. The close association of framboids with seawater and bacterial processes gives them enormous potential for

paleoenvironmental interpretation. Despite this, current understanding is limited by uncertainties in the factors controlling framboid aggregation and growth.

In the following manuscript we investigate the potential that $\delta^{34}\text{S}$ measurements of pyrite framboids have for understanding paleoenvironment and framboid formation processes, and discuss the analytical challenges associated with this approach. Previous SIMS studies have reported μm -scale $\delta^{34}\text{S}$ of framboidal pyrite (Lin et al., 2016; Cui et al., 2018; Bryant et al., 2019), but to our knowledge this is the first study to use $\delta^{34}\text{S}$ to investigate the relations between textures and $\delta^{34}\text{S}$ to constrain various models of framboid population formation from detailed in situ SEM-SIMS analysis of non-disaggregated sedimentary rock.

2. Background

2.1 Geologic Setting

The Bakken Formation of the Williston Basin is Devonian-Mississippian in age, and is subdivided into upper and lower organic-rich shale members that bracket a middle mixed carbonate-siliciclastic member (LeFever et al., 2011). The shales contain 11 weight percent organic carbon (Sonnenberg, 2011), and are a world-class source rock and major target for hydrocarbon exploration and production (Gaswirth et al., 2013; Gaswirth and Marra, 2015). Lag deposits of micro- and macrofossil fragments and other grains within the Bakken shales indicate active mud transport through the sedimentary system. Bakken shales were likely deposited in a dysoxic environment, or one that alternated between oxic and anoxic conditions, as evidenced by rare burrows, shell fragments, agglutinated foraminifera, and fecal strings (Egenhoff and Fishman, 2013; Borcovsky et al., 2017). Open-system $\delta^{34}\text{S}$ behavior and large (diagenetic) low-

$\delta^{34}\text{S}$ framboidal pyrites both also argue for a water column that was at least periodically oxic (Chapter 2).

Framboidal pyrites are found in close association with coarser massive to subhedral pyrite and sphalerite are present throughout both Bakken shale members. In places in the rock, pyrite and sphalerite can reach measurable concentrations of 22 and 16 wt. %, respectively (Fishman et al., 2015). Sulfide $\delta^{34}\text{S}$ values show a bimodal distribution that is interpreted to record temporally separated events, with framboidal pyrites forming in soft sediment and a later period of replacive pyrite and sphalerite growth associated with thermochemical sulfate reduction (Chapter 2).

2.2 Framboidal Pyrite: Features and Formation

Framboids are spheroidal to subspherical masses of equant, equidimensional microcrystals (Rickard, 2012). They are most commonly composed of pyrite (Rickard, 2012), but primary framboids composed of greigite, magnetite, magnesioferrite, and marcasite have all been observed (Wilkin and Barnes, 1997; Bryant et al., 2019). In addition, hematite, limonite, chalcocite, chalcopyrite, bornite, sphalerite, and galena have all been reported to have framboidal morphologies, though these may only arise from metamorphic processes or oxidative replacement of primary framboids (Wilkin and Barnes, 1997; Hu et al., 2018). It is estimated that as many as 10^{30} framboids may be distributed globally amongst sediments, sedimentary rocks, and hydrothermal environments (Rickard, 2015). Despite the importance of framboids in sediments, there remains uncertainty around the mechanisms driving their

creation and how they might thereby be interpreted. Key features of framboids, and theories concerning how they form, are discussed in the following sections.

2.1.1 Framboid Morphology and Size

Framboids may form either authigenically (in sediment) or in the water column under euxinic conditions. If the water column is euxinic, then the framboids that form in the water column will settle to the bottom once they reach a size at which they can no longer be supported by hydrodynamic processes. Authigenic framboids, by contrast, are not size-limited and may grow to much larger sizes. By studying the distribution of framboid sizes within a sedimentary rock, one can determine if framboids grew in the sediment or in the water column, and thereby infer if bottom waters were euxinic or not. This technique was first successfully tested in the Black Sea (Wilkin et al., 1996; Wilkin et al., 1997), and has since seen use as a test of euxinia in sedimentary rocks (Wignall and Newton, 1998; Wignall et al., 2005; Raiswell et al., 2008; Bond and Wignall, 2010; Guan et al., 2014; Gallego-Torres et al., 2015).

Framboids may be found in sediment as either isolated individuals or in clusters. The term polyframboid was first used to describe a spherical or laminar cluster of framboids by Love (1971). Petrographic evidence suggests that polyframboids can form either aggradationally through sedimentary processes (Love, 1971) or authigenically under favorable conditions (Reolid, 2014; Lin et al., 2016; Liu et al., 2019).

2.1.2 Microcrystal Morphology and Size

Framboid microcrystals are commonly euhedral with octahedral forms, although cubic, pyritohedral or spheroidal microcrystals have also been observed (Wilkin and Barnes, 1997).

While not necessary, it is common for groups of microcrystals to share common orientations, with the most highly-ordered and densely packed microcrystals approaching cubic closest packing (Ohfuji et al., 2005; Ohfuji et al., 2006). Different subdomains within a framboid can have differently oriented cubic closest packing networks of microcrystals, and in some framboids these domains may be icosahedral, creating internal trigonal or pentagonal structures (Skrupchenko and Berber'yan, 1976; Ohfuji and Akai, 2002).

A correlation has been reported between microcrystal size and framboid diameter, with larger framboids exhibiting larger microcrystals. (Skrupchenko and Berber'yan, 1976; Wilkin et al., 1996; Ohfuji and Akai, 2002).

2.1.3 Models of Formation

Studies into framboid growth rates indicate that rates of formation are extremely rapid. Authigenic framboids have been constrained by sedimentation rates to formation within years, while settling rates constrain framboid formation in euxinic water columns to the order of months or less (Wilkin et al., 1996). In a simulated bone decay experiment at a simulated seawater-sediment interface, framboids up to 5 μm in diameter with octahedral microcrystals were observed to form within 3 weeks (Vietti et al., 2015).

Many hypotheses have been advanced over the years to explain both the spherical nature of framboids and the complex internal structure of their microcrystals, including replacement or infilling of organic globules and gaseous vacuoles (Rickard, 1970), and aggregation by magnetism of a greigite intermediary (Wilkin and Barnes, 1997). The morphological similarity between framboids and bacterial consortia has led to the proposal that

there is a direct formational link between the two. However, framboids have also been found in locations considered inhospitable to microbial life, and the size of microcrystals found in closely packed framboids can be $<0.25\text{ }\mu\text{m}$, well below the size of individual cells. In addition, creation of framboid structures in abiotic lab conditions demonstrates that no microbial activity is required, and the framboidal structure therefore can arise from another process (Ohfuji and Rickard, 2005). Spontaneous pyrite nucleation can require extremely high supersaturations ($>10^{11}$ times greater than equilibrium values), allowing for dense and rapid growth once the nucleation threshold is reached (Rickard, 2012). The association of framboidal pyrite with localities that experience bacterial sulfate reduction is therefore due to the rapid production of H_2S in such environments, rather than any direct requirements from microbial activity on morphology.

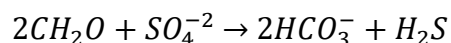
More recently, a model of framboid aggregation involving coupled rapid nucleation followed by free surface energy minimization has been advanced that appears to be the best explanation for a wide variety of observations. Biological surfaces act to lower the limiting supersaturation by several orders of magnitude (Rickard et al., 2007), which provides a compelling explanation for the closely spaced non-framboidal pyrite octahedra that are commonly seen closely associated with organic matter in organic-rich shales. The discovery that each microcrystal in a framboid is often misoriented relative to its neighbors is strong evidence that framboid microcrystal growth is not crystallographically controlled and that framboids are rather aggregates of microcrystals (Ohfuji et al., 2005; Ohfuji et al., 2006). Additionally, framboidal (and icosahedral) structures have now been shown to be capable of aggregating

naturally from colloids through minimization of surface free energy, given the right conditions (Meng et al., 2010; Wang et al., 2018).

2.3 Factors Controlling $\delta^{34}\text{S}$ of Sedimentary Sulfides

The full set of processes that influence the formation of sedimentary sulfides and their $\delta^{34}\text{S}$ values are complex and have been discussed elsewhere (Chapter 2; Machel et al., 1995; Machel, 2001; Rickard, 2012; Fike et al., 2015). For the purposes of later discussion, the key mechanisms that might influence the $\delta^{34}\text{S}$ values of sedimentary framboids will be outlined here.

The formation of diagenetic sulfides results from a set of reactions between dissolved sulfate and organic molecules that allow sulfate to be reduced. This set of reactions is commonly represented in its simplified form:



The hydrogen sulfide (H_2S) produced combines with reactive iron or other ions to produce pyrite or other sulfide minerals.

The reduction of sulfate to sulfide shows a strong preference for the light isotope (^{32}S), particularly when the process is driven by sulfate-reducing microbes, which have been shown in laboratory cultures to produce $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$ values as large as 66‰ (Sim et al., 2011a). Because dissolved sulfate diffuses readily through porewater but mineralized sulfide does not, it is useful to begin thinking of the effects of sulfate reduction on $\delta^{34}\text{S}$ in sediments by first putting it in terms of Rayleigh fractionation. In simple closed-system Rayleigh fractionation, no

sulfur species enter or leave the rock and there is no exchange between pyrite and sulfate. The separation in $\delta^{34}\text{S}$ values between the reactant (sulfate) and the product (pyrite) is determined by the fractionation factor, α , and the reaction progress. As sulfate is converted to pyrite and the proportion of sulfur that remains in sulfate drops, the $\delta^{34}\text{S}$ values of remaining sulfate and newly precipitated pyrite both shift towards higher values. While the last pyrite to precipitate can have very high $\delta^{34}\text{S}$ values, the aggregate “bulk” $\delta^{34}\text{S}$ value of pyrite will approach the initial sulfate value as all of the sulfate is consumed (Figure 3.1).

During early diagenesis sulfate diffuses downwards into sediment from a pool of seawater sulfate that is assumed to have constant $\delta^{34}\text{S}$. As pyrite precipitates the remaining sulfate is enriched in ^{34}S resulting in a profile of increasing $\delta^{34}\text{S}$ sulfate with depth in young sediments (Claypool, 2004), and pyrites precipitated from the enriched sulfate pool will themselves have elevated $\delta^{34}\text{S}$ values. Under the right conditions, this process can produce measurable $\delta^{34}\text{S}_{\text{pyrite}}$ variability in excess of 150‰ within sediments (Lin et al., 2016).

The reduction of sulfate to sulfide by microbial activity is a key process in sediments, particularly organic-rich ones, but the $\delta^{34}\text{S}$ fractionations involved are not yet well constrained enough to predict environment-specific $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$ associated with bacterial sulfate reduction. Various cell cultures have produced a wide range of fractionations from 66‰ to 2‰ (Detmers et al., 2001; Sim et al., 2011a). On top of this, experimental data yield larger fractionations in response to increasing sulfate concentration (Habicht et al., 2002) and decreasing cell-specific sulfate reduction rates (Harrison and Thode, 1958; Kaplan and Rittenberg, 1964; Chambers et al., 1975; Sim et al., 2011a; Sim et al., 2011b; Sim et al., 2012; Leavitt et al., 2013), so the fractionations induced by bacterial sulfate reduction are likely not

constant during early burial. The close association of pyrite framboids with bacterial sulfate reduction may arise from H_2S supersaturation in euxinic waters and sediments, driving rapid nucleation and crystal growth (Rickard, 2012).

2.4 Framboid $\delta^{34}\text{S}$ Hypothesis Testing

Because of the rapid precipitation rates of framboidal pyrite in environments where distillation processes occur, it is reasonable to consider $\delta^{34}\text{S}_{\text{sulfide}}$ as likely to change over the duration of framboid crystallization. If individual framboids can be analyzed for $\delta^{34}\text{S}_{\text{pyrite}}$ at sufficient spatial resolution, intra-framboid and interior-rim $\delta^{34}\text{S}_{\text{pyrite}}$ value comparisons will constrain mechanistic models for framboid growth (Figure 3.2). In addition, if many framboids within a single sample are measured for $\delta^{34}\text{S}$, the distribution of values within the population should be an effective measure of environment, rates, and timing of framboid formation (Figure 3.3). The endmember models depicted in Figures 3.2 and 3.3 will be respectively referred to as Growth Models 1-4 and Population Models 1-3 in the following sections, and will be tested against analytical data.

Growth Models 1 through 4 (Figure 3.2) show the expected distributions of $\delta^{34}\text{S}_{\text{pyrite}}$ values under different models of growth for individual framboids. These models are testable by SIMS, provided $\delta^{34}\text{S}_{\text{pyrite}}$ has become heavier over the course of framboid growth. If the size of a SIMS spot is much larger than the microcrystal diameter (homogenizing microcrystal $\delta^{34}\text{S}$ values), one should still be able to distinguish Growth Models 1 and 2 (3.2a, 3.2b) from Growth Models 3 and 4 (3.2c, 3.2d) on the basis of whether values change systematically from framboid core to rim. If, however, the SIMS spot is of similar size to or smaller than the microcrystals,

then detectable non-concentric intraframoid variability should be detectable under Growth Models 1 and 2, and not present in Growth Models 3 and 4.

Similarly, if $\delta^{34}\text{S}_{\text{pyrite}}$ changed during the growth of a population of framboids, the data obtained by SIMS for that population will provide additional information about how the population developed. For example, in the idealized situation where $\alpha_{\text{sulfate-sulfide}}$ is large and relatively constant, then homogenous $\delta^{34}\text{S}$ distributions in framoid populations can only be produced by different growth rates that are proportional to each other (Population Model 2, Figure 3.3) or open-system behavior. If the different growth rates of Population Model 2 are related to H_2S production rates, and if those rates are sufficiently variable to kinetically affect fractionations, then variable $\delta^{34}\text{S}$ population distributions would be expected. The $\delta^{34}\text{S}$ population size distribution may also provide information on whether the framboids began growing at different times (Population Model 1, Figure 3.3) and stopped growing at different times (Population Model 3, Figure 3.3).

3. Methods

3.1 Sample Collection and Preparation

Samples were collected from drill cores stored at the North Dakota Geological Survey (NDGS) Wilson M. Laird Core and Sample Library in Grand Forks, North Dakota, and the United States Geological Survey (USGS) Core Research Center in Denver, Colorado. Samples were polished and surveyed by imaging in backscattered electron (BSE) mode using a Hitachi S3400-N scanning electron microscope (SEM) in variable pressure mode; this was found to be the most efficient and effective way of quickly identifying and evaluating the quality of μm -scale

diagenetic variability. Constituent mineralogy was confirmed by energy-dispersive X-ray spectrometry (EDS).

In total, six samples from five cores were selected for SIMS analysis (Table 3.1), as determined by which samples in each core captured the greatest variability in the petrographic expression of sulfide minerals, and which had multiple generations of sulfide growth that could be identified from petrographic relationships. In preparation for SIMS analysis, 1-2 cm chips were cut from sample rock and cast in Buehler epoxy in 2.54 cm-diameter round molds. In the center of each was mounted the UWPpy-1 pyrite standard (Kozdon et al., 2010; Ushikubo et al., 2014).

3.2 SIMS Procedure

Values of $\delta^{34}\text{S}$ were measured on a CAMECA IMS 1280 large-radius, multi-collector secondary ion mass spectrometer (SIMS) at the University of Wisconsin-Madison WiscSIMS laboratory. Measurements were made during three separate sessions (Table 3.2) using established sample preparation and analysis procedures (Valley and Kita, 2009; Kita et al., 2009; Kozdon et al., 2010); additional details for each session are provided in subsequent sections. Samples were analyzed using a focused $^{133}\text{Cs}^+$ primary beam with a 10 kV accelerating voltage and 20 keV impact energy; charge neutralization is performed with an electron flood gun and a conductive sample coat of either 60 nm of gold or 25 nm of carbon. The impact of the $^{133}\text{Cs}^+$ atoms sputters ions off of the sample surface and excavates a pit. Sputtered ions are accelerated into a double-focusing mass spectrometer where they are sorted by energy and by mass/charge before reaching an array of 3 Faraday cup detectors (for $^{32}\text{S}^-$, $^{34}\text{S}^-$, and $^{32}\text{S}^1\text{H}^-$). In

this study, all SIMS analyses of unknowns were made using Balmat pyrite UWPY-1 as a running standard; UWPY-1 has a $\delta^{34}\text{S}$ value of 16.04‰ (VCDT) determined by gas-source mass spectrometry (Kozdon et al., 2010; Ushikubo et al., 2014). Unknown analyses are standardized by bracketing groups of 8-16 analyses of unknowns with eight analyses on the UWPY-1 standard (4 before the unknowns and 4 after). This bracketing allows users to monitor and correct for small amounts of instrumental drift. Analytical precision for unknowns is reported as two standard deviations of the 8 bracketing standard analyses.

SIMS analyses were routinely monitored for internal errors (2SE) or SH^- count rates that were significantly above standard measurements, as well as ^{32}S count rates significantly above or below standard measurements; these analyses were excluded from later data interpretation. SEM imagery was routinely acquired of all SIMS pits to evaluate whether they had intersected other phases. The depths of a representative subset of SIMS pits were determined using a Zygo New View 6300 Interferometer. All analyses are reported in permil notation relative to Vienna Canyon Diablo Troilite (VCDT), which has a $^{34}\text{S}/^{32}\text{S}$ ratio of 1/22.6436 (Ding et al., 2001).

The SIMS data discussed here may be found in Appendices 2.1 and 2.2. The locations of SIMS $\delta^{34}\text{S}$ analyses overlain on SEM-BSE imagery may be found in Appendix 2.3. The full sample maps used to create Appendix 2.3 were created in QGIS, an open-source cross-platform GIS mapping software (Linzmeier et al., 2018).

4. Results

4.1 Framboid Petrography and $\delta^{34}\text{S}$ Results

The diameters and microcrystal sizes of 515 pyrite framboids from across all six samples were measured by SEM imagery. These measurements may underestimate framboid diameter for a portion of framboids, as sample surfaces can only provide 2D slices of 3D objects. Despite this, there is a strong linear relationship between microcrystal size and framboid diameter (Figures 3.4, 3.5), as has been observed elsewhere by previous authors (Skripchenko and Berber'yan, 1976; Wilkin et al., 1996; Ohfuji and Akai, 2002).

Representative BSE-SEM imagery and locations of SIMS pits in framboidal pyrite of the 4 most heavily analyzed samples (12785, 17015, 21706, and E701B) can be seen in Figures 3.6, 3.7, 3.8, and 3.9, respectively. All SIMS data are reported in Appendices 2.1 and 2.2. Additional imagery of analysis locations may be found in Appendix 2.3.

Framboid microcrystals in all samples exhibit primarily octahedral forms; alternate hybrid forms are also present, for example, larger octahedral microcrystals commonly show truncated points indicative of faces on the (100) plane, particularly when approaching higher degrees of ordering in tightly packed configurations (e.g. Figures 3.6b, 3.6g). Framboids exhibit varying degrees and manifestations of microcrystal ordering, from near-perfect packing (e.g., Figures 3.6a, 3.6e, 3.7e, 3.9e) to near-total disorder (e.g., Figures 3.7c, 3.8a, 3.9b). Some framboids contain microcrystals arranged radially into concentric layers or shells (e.g., Figures 3.7d, 3.9d). Some framboids, generally those larger in size or associated with low amounts of intracrystal organic matter, possess an additional odd feature: they appear to have a truncated rim that does not conform to microcrystal dimensions, but rather smoothly crosscuts microcrystals in a curve all the way around the framboid (e.g., Figures 3.6b, 3.6g, 3.7e, 3.7g, 3.8d, 3.8e, 3.9b, 3.9c, 3.9e). Not all large framboids show this smooth boundary, and some

framboids that show smooth boundaries are found immediately adjacent to framboids order bounded by pure microcrystal forms (e.g., the adjacent framboids in Figure 3.8a).

5. Discussion

5.1 Framboid Petrographic Observations

Framboids larger than 10 μm are rare in samples 16586 and E701A (Figures 3.5b, 3.5e), which when compared with observations by Wilkins (1996) and others is consistent with truncated or absent framboid growth in sediment, and thereby implies that the water column was significantly more anoxic during deposition of those samples.

The degree to which microcrystals exist as discrete entities within framboids, separate from one another, also varies from framboid to framboid. Petrographic observations of microcrystals losing their separate identities (Figures 3.6a, 3.6c, 3.7b, 3.7f, 3.7g), indistinguishable microcrystal structures (Figures 3.7f, 3.7g, 3.8c, 3.8e), and intra-microcrystal pyrite fills (Figures 3.8b, 3.8f) all indicate evidence that framboid recrystallization or infilling of intra-microcrystal space by later generations of pyrite has occurred in some, but not all, framboids.

5.2 Framboid $\delta^{34}\text{S}$ Analysis Considerations

Authigenic framboidal pyrites commonly contain interstitial organic matter (MacLean et al., 2008; Vietti et al., 2015), and measurements made by SIMS and SEM-EDS confirm the presence of carbon in between the microcrystals of many framboids in this study. Therefore, analyses on framboidal pyrite may be subject to a different instrumental bias than massive pyrites—particularly for analyses with significant interstitial material between microcrystals.

Mixtures of finely crushed UWPpy-1 and epoxy were made to evaluate if differences in IMF exist vs. larger grains of pure UWPpy-1. Epoxy differs from organic matter in samples, but provides a starting material to evaluate IMF's. Analyses made by SIMS on mixed pyrite/epoxy reference materials produce $\delta^{34}\text{S}$ values on the SIMS that are systematically lower than the true value by less than 5‰ under the instrumental conditions employed in this paper (see Appendix 3.4 for more details). The cause of these differences is not known. They may result from a mixture of matrix effects and different excavation rates between massive and framboidal pyrite. These preliminary results suggest the need for caution in interpreting small differences in $\delta^{34}\text{S}$ for framboids, but it is not known whether analyses on framboids produce similar variability of instrumental bias. If the synthetic pyrite/epoxy mixtures do behave analogously to framboids containing organic matter, then the offset in instrumental bias will not exceed ~5‰. We know of no samples or data appropriate to test matrix effects in mixtures of organic matter and pyrite, and thus data in this paper are standardized with UWPpy-1.

5.3 Framboid $\delta^{34}\text{S}$ Observations

As values of $\delta^{34}\text{S}$ were measured in framboidal pyrites in three different sessions with three different pit sizes, additional care must be taken in comparing data acquired between samples. Analysis size itself has an impact on interpretation; larger spot sizes homogenize more of the framboid, and $\delta^{34}\text{S}$ values acquired in this way are more likely to lie close to the true framboid $\delta^{34}\text{S}$ value than smaller spots. By contrast, small spots are better able to capture potential $\delta^{34}\text{S}$ heterogeneity, whether it be present through microcrystal zonation or through later recrystallization.

In five out of six samples, framboid $\delta^{34}\text{S}$ variability exceeds the range in instrumental biases induced from measurements of mixtures of pyrite and epoxy (Figures 3.10, 3.11). The exception to this is 16586-9791.3, which has an analysis on each of three separate framboids. While most framboids were analyzed with only one spot, some framboids were analyzed multiple times, sometimes across multiple sessions. Some of those repeatedly measured framboids are shown here (Figures 3.6a, 3.6b, 3.6g, 3.7e, 3.8a-f, 3.9a, 3.9b, 3.9f) and others are available in Appendix 2.3. While significant $\delta^{34}\text{S}$ variability is observed within framboids, there is no evidence to suggest that framboids are concentrically zoned in $\delta^{34}\text{S}$, which eliminates Growth Models 3 and 4 (Figure 3.2) as methods of framboid formation. Intra-framboid variability must therefore arise either from individual microcrystals that are isotopically zoned, or from later intra-crystal sulfide cements not associated with early diagenesis.

Curiously, this large degree ($> 5\%$) of $\delta^{34}\text{S}$ variability is sometimes observed within individual polyframboids, at a scale at which one might expect that the H_2S $\delta^{34}\text{S}$ pool from which framboids form was homogenized. For analyses with an analysis:microcrystal size ratio that should be sufficiently large to homogenize intra-microcrystal isotope zonation, and with similar microcrystal sizes and microcrystal ordering, significant interframboid variability may still be observed (Figures 3.6d, 3.7b, 3.8b). The most striking example of this is the two adjacent framboids in Figure 3.8b, which show similar degrees of infilling and similar microcrystal sizes, but a $\sim 20\%$ difference in $\delta^{34}\text{S}$. If these framboids formed in place, observations can only be explained by large variations in $\delta^{34}\text{S}$ of H_2S across very short distances (10s of μm) at the time of framboid formation. The alternative is that these clusters of framboids do not necessarily form adjacent to one another, and may aggregate as they are pushed around by currents on the sea

floor. If true, then different frambooids within a polyframbooid do not require to be formed in adjacent environments, and steep $\delta^{34}\text{S}$ gradients for H_2S are not required at the μm scale.

If different growth processes or growth rates control frambooid size, and if $\delta^{34}\text{S}_{\text{pyrite}}$ values are changed during frambooid growth, then there should be a discernable relationship between bulk frambooid $\delta^{34}\text{S}$ and microcrystal size. This is explored in Figures 3.10 and 3.11, and relevant plots are provided for reference in Figures 3.6h, 3.7h, 3.8g, and 3.9g. Strong positive trends appear in the small spot Session 1 datasets (Figure 3.11a, 3.11b). Taking all three sessions in aggregate there is little discernable correlation between microcrystal size and frambooid $\delta^{34}\text{S}$ analysis value, but this may reflect the greater uncertainties present for the session 2 and 3 analytical conditions. The wide range in microcrystal size with little impact on $\delta^{34}\text{S}$ implies that frambooid populations formed under one of two possible conditions: 1) Frambooids all formed under strong open system behavior with respect to H_2S , or 2) Frambooids grew to different sizes at proportional rates, thereby hiding any distillation effects that may have occurred (Figure 3.3, Population Model 2). In both cases, large differences in $\delta^{34}\text{S}$ values within polyframbooids indicate that the $>10\%$ variability in $\delta^{34}\text{S}$ measured in most of these samples likely reflects local differences in H_2S flux that do not scale with size.

Frambooid rims sometimes crosscut microcrystals (e.g. Figures 3.6b, 3.6g, 3.7e, 3.8e, 3.9c) rather than being bounded by them. These features appear to be more frequent in larger frambooids. If frambooids grow radially and preserve microcrystal form and size during growth (as in Growth Model 4, Figure 3.2), then this boundary is the most recent front along which the frambooid grew. However, this hypothesis is incompatible with other published models for frambooid growth and the $\delta^{34}\text{S}$ values measured in this study, as concentric core to rim frambooid

zonation would be expected if this process were occurring. This smooth framboid rim is therefore most likely a result of concentric degradation of some of the rimwards portion of the framboid, which could be caused by either dissolution or erosive processes. If this crosscutting is due to mechanical abrasion, it is notable that this texture is more common in larger framboids suggesting that large framboids may travel significant distances and experience multiple periods of growth and mobilization along the sea floor before final deposition. If this crosscutting is due instead to pyrite dissolution or oxidation during diagenesis in sediments, then the close proximity of partially dissolved framboids to nondissolved framboids indicates that an additional factor, possibly variable amounts of chemical or diffusive shielding by variable amounts of organic matter, acts as a powerful control on dissolution rates.

Of key relevance to how these framboidal values may be interpreted are the questions of the extent to which later diagenetic $\delta^{34}\text{S}$ phases may be capable of overprinting framboid analyses, and how such overprints might be identified. There is petrographic evidence in non-framboidal pyrite phases for later post-framboidal phases of sulfide mineral growth with high $\delta^{34}\text{S}$ values in all of these samples (see Chapter 2), which raises the question of whether framboidal analyses might be affected by late diagenetic overprints. Clearly such overprints do exist, and a subset of these framboids show obvious evidence of this overprint through pyrite infilling. Microcrystals in one particularly large framboid show cubic overgrowths on original octahedral crystals (Figure 3.8f, boundaries drawn to aid the reader); this is consistent with the interpretation that octahedra represent faster crystallization rates than do cubic pyrite forms, as the (100) face has the lowest surface energy in pyrite (Murowchick and Barnes, 1987). Large

pyrites in other parts of the sample show elevated $\delta^{34}\text{S}$ values ($\sim 0\%$), reflecting late diagenetic overprinting.

Careful BSE-SEM and SE-SEM imagery are key to distinguishing later overprints from early framboidal pyrite $\delta^{34}\text{S}$. For the purposes of interpretation in this study, framboids containing microcrystals clearly separated from neighboring microcrystals and exhibiting clearly-defined crystal forms are considered most likely to have unaltered $\delta^{34}\text{S}$ values since initial formation. SEM imagery sometimes provides additional evidence that higher $\delta^{34}\text{S}$ values from late diagenetic pyrite have cemented framboid octahedra (e.g., the crystallized core framboid core in Figure 3.6a, or the octahedra in Figure 3.8f), however, it is evident that SEM imagery showing cementation is not a good predictor of $\delta^{34}\text{S}$ values. Comparing dispersed and tightly bound microcrystals in examples such as those in Figures 3.7f and 3.7g show instances where cementation has not consistently resulted in a different $\delta^{34}\text{S}$ value. It may be that recrystallization or infilling textures develop in pyrite framboids under a whole range of conditions during sedimentary burial, making timing of pyrite growth events associated with framboids difficult to constrain based on imagery alone, and necessitating the additional geochemical constraints that microanalysis can provide.

6. Conclusions

This is the first SIMS study integrating μm -scale $\delta^{34}\text{S}$ analyses of framboids with careful petrographic observations concerning the framboids themselves. Small but significant differences in instrumental mass bias were found to occur during analysis of mixtures of pyrite and epoxy, suggesting caution in interpreting small differences in $\delta^{34}\text{S}$ measured for the

microcrystals of pyrite if they are surrounded by organic matter in natural framboids. This offset in bias may arise from matrix effects or depth profiling, and possible influences of organic matter on SIMS bias should be considered during analyses of framboids, which often contain both pyrite and organic matter. Several conclusions can be drawn about framboid formation in the Bakken black shales. First, variability within framboid populations and even within polyframboids exceeds potential variation of instrumental bias, as the observed variability can be >5‰ even between framboids displaying identical petrographic textures. Secondly, there is no consistent interior to rim $\delta^{34}\text{S}$ trend in framboids, demonstrating that they develop through the growth of their individual microcrystals rather than some sequential or radial aggradation process. Finally, while not concentric, variability in $\delta^{34}\text{S}$ within framboids themselves argues for framboid microcrystals themselves being isotopically zoned, perhaps arising if sufficient sulfur reservoir distillation occurred during framboid growth. These observations are consistent with Bakken framboids forming extremely rapidly in open system conditions, as evidenced by the short (10s of μm s) distance that $\delta^{34}\text{S}$ gradients must have operated under, and may indicate that framboids themselves were remobilized on the seafloor by currents before final deposition.

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Appendices

Appendix 2.1 – Condensed SIMS dataset (.xlsx)

Appendix 2.2 – Full SIMS datasets w/ standards and IMF corrections (.xlsx)

Appendix 2.3 – Mount maps of SIMS data

2.3.1 – SIMS mount E701-9922.8A (.pdf)

2.3.2 – SIMS mount E701-9922.8B (.pdf)

2.3.3 – SIMS mount 21706-11087.5 (.pdf)

2.3.4 – SIMS mount 12785-11351.25 (.pdf)

2.3.5 – SIMS mount 17015-10422.7 (.pdf)

2.3.6 – SIMS mount 16586-9791.3 (.pdf)

Appendix 3.4 – Discussion of SIMS analyses on pyrite/epoxy mixture (.doc)

References

- Bond D. P. G. and Wignall P. B. (2010) Pyrite framboid study of marine Permian–Triassic boundary sections: A complex anoxic event and its relationship to contemporaneous mass extinction. *Geological Society of America Bulletin* **122**, 1265–1279.
- Borcovsky D., Egenhoff S., Fishman N., Maletz J., Boelhke A. and Lowers H. (2017) Sedimentology, facies architecture, and sequence stratigraphy of a Mississippian black mudstone succession—The upper member of the Bakken Formation, North Dakota, United States. *American Association of Petroleum Geologists Bulletin* **101**, 1625–1673.
- Bryant R. N., Jones C., Raven M. R., Gomes M. L., Berelson W. M., Bradley A. S. and Fike D. A. (2019) Sulfur isotope analysis of microcrystalline iron sulfides using SIMS imaging: Extracting local paleo-environmental information from modern and ancient sediments. *Rapid Communications in Mass Spectrometry*, 491–502.
- Cui H., Kitajima K., Spicuzza M. J., Fournelle J. H., Denny A., Ishida A., Zhang F. and Valley J. W. (2018) Questioning the biogenicity of Neoproterozoic superheavy pyrite by SIMS. *American Mineralogist: Journal of Earth and Planetary Materials* **103**, 1362–1400.
- Ding T., Valkiers S., Kipphardt H., De Bièvre P., Taylor P. D. P., Gonfiantini R. and Krouse R. (2001) Calibrated sulfur isotope abundance ratios of three IAEA sulfur isotope reference materials and V-CDT with a reassessment of the atomic weight of sulfur. *Geochimica et Cosmochimica Acta* **65**, 2433–2437.
- Egenhoff S. O. and Fishman N. S. (2013) Traces in the dark—Sedimentary processes and facies gradients in the upper shale member of the Upper Devonian–Lower Mississippian Bakken Formation, Williston Basin, North Dakota, USA. *Journal of Sedimentary Research* **83**, 803–824.
- Fike D. A., Bradley A. S. and Rose C. V. (2015) Rethinking the Ancient Sulfur Cycle. *Annual Review of Earth and Planetary Sciences* **43**, 593–622.
- Fishman N. S., Egenhoff S. O., Boehlke A. R. and Lowers H. A. (2015) Petrology and diagenetic history of the upper shale member of the Late Devonian–Early Mississippian Bakken Formation, Williston Basin, North Dakota. *Geological Society of America Special Papers* **515**, SPE515–07.
- Gallego-Torres D., Reolid M., Nieto-Moreno V. and Martínez-Casado F. J. (2015) Pyrite framboid size distribution as a record for relative variations in sedimentation rate: An example on the Toarcian Oceanic Anoxic Event in South Iberian Palaeomargin. *Sedimentary Geology* **330**, 59–73.

- Gaswirth S. B. and Marra K. R. (2015) U.S. Geological Survey 2013 assessment of undiscovered resources in the Bakken and Three Forks Formations of the U.S. Williston Basin Province. *AAPG Bulletin* **99**, 639–660.
- Gaswirth S. B., Marra K. R., Cook T. A., Charpentier R. R., Gautier D. L., Higley D. K., Klett T. R., Lewan M. D., Lillis P. G. and Schenk C. J. (2013) *Assessment of undiscovered oil resources in the Bakken and Three Forks formations, Williston Basin Province, Montana, North Dakota, and South Dakota, 2013*.
- Guan C., Zhou C., Wang W., Wan B., Yuan X. and Chen Z. (2014) Fluctuation of shelf basin redox conditions in the early Ediacaran: Evidence from Lantian Formation black shales in South China. *Precambrian Research* **245**, 1–12.
- Hu S.-Y., Evans K., Rempel K., Guagliardo P., Kilburn M., Craw D., Grice K. and Dick J. (2018) Sequestration of Zn into mixed pyrite-zinc sulfide framboids: A key to Zn cycling in the ocean? *Geochimica et Cosmochimica Acta* **241**, 95–107.
- Kita N. T., Ushikubo T., Fu B. and Valley J. W. (2009) High precision SIMS oxygen isotope analysis and the effect of sample topography. *Chemical Geology* **264**, 43–57.
- Kozdon R., Kita N. T., Huberty J. M., Fournelle J. H., Johnson C. A. and Valley J. W. (2010) In situ sulfur isotope analysis of sulfide minerals by SIMS: Precision and accuracy, with application to thermometry of ~ 3.5 Ga Pilbara cherts. *Chemical Geology* **275**, 243–253.
- LeFever J. A., Fever R. D. L. and Nordeng S. H. (2011) Chapter 1: Revised Nomenclature for the Bakken Formation (Mississippian-Devonian), North Dakota. In *The Bakken–Three Forks Petroleum System in the Williston Basin* (eds. J. W. Robinson, J. A. Lefever, and S. B. Gaswirth). Rocky Mountain Association of Geologists, Denver, Colorado. pp. 11–26. Available at: http://archives.datapages.com/data/rocky-mtn-geologist-pubs/data/002/002001/11_rmag-bk0020011.htm [Accessed August 29, 2016].
- Lin Q., Wang J., Algeo T. J., Sun F. and Lin R. (2016) Enhanced framboidal pyrite formation related to anaerobic oxidation of methane in the sulfate-methane transition zone of the northern South China Sea. *Marine Geology* **379**, 100–108.
- Linzmeier B. J., Kitajima K., Denny A. C. and Cammack J. N. (2018) Making maps on a micrometer scale. *EOS* **99**, 24–28.
- Liu X., Fike D., Li A., Dong J., Xu F., Zhuang G., Rendle-Bühning R. and Wan S. (2019) Pyrite sulfur isotopes constrained by sedimentation rates: Evidence from sediments on the East China Sea inner shelf since the late Pleistocene. *Chemical Geology* **505**, 66–75.
- Love L. G. (1971) Early diagenetic polyframboidal pyrite, primary and redeposited, from the Wenlockian Denbigh Grit Group, Conway, North Wales, U.K. *Journal of Sedimentary Research* **41**, 1038–1044.

- Machel H. G. (2001) Bacterial and thermochemical sulfate reduction in diagenetic settings — old and new insights. *Sedimentary Geology* **140**, 143–175.
- Machel H. G., Krouse H. R. and Sassen R. (1995) Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. *Applied Geochemistry* **10**, 373–389.
- MacLean L. C. W., Tyliszczak T., Gilbert P., Zhou D., Pray T. J., Onstott T. C. and Southam G. (2008) A high-resolution chemical and structural study of framboidal pyrite formed within a low-temperature bacterial biofilm. *Geobiology* **6**, 471–480.
- Meng G., Arkus N., Brenner M. P. and Manoharan V. N. (2010) The Free-Energy Landscape of Clusters of Attractive Hard Spheres. *Science* **327**, 560–563.
- Murowchick J. B. and Barnes H. L. (1987) Effects of temperature and degree of supersaturation on pyrite morphology. *American Mineralogist* **72**, 1241–1250.
- Ohfuji H. and Akai J. (2002) Icosahedral domain structure of framboidal pyrite. *American Mineralogist* **87**, 176–180.
- Ohfuji H., Boyle A. P., Prior D. J. and Rickard D. (2005) Structure of framboidal pyrite: An electron backscatter diffraction study. *American Mineralogist* **90**, 1693–1704.
- Ohfuji H. and Rickard D. (2005) Experimental syntheses of framboids—a review. *Earth-Science Reviews* **71**, 147–170.
- Ohfuji H., Rickard D., Mark E. and Hursthouse M. B. (2006) Structure of framboidal pyrite: a single crystal X-ray diffraction study. *European journal of mineralogy* **18**, 93–98.
- Raiswell R., Newton R., Bottrell S. H., Coburn P. M., Briggs D. E. G., Bond D. P. G. and Poulton S. W. (2008) Turbidite depositional influences on the diagenesis of Beecher's Trilobite Bed and the Hunsrück Slate; sites of soft tissue pyritization. *American Journal of Science* **308**, 105–129.
- Reolid M. (2014) Pyritized radiolarians and siliceous sponges from oxygen-restricted deposits (Lower Toarcian, Jurassic). *Facies* **60**, 789–799.
- Rickard D. (2019) How long does it take a pyrite framboid to form? *Earth and Planetary Science Letters* **513**, 64–68.
- Rickard D. (2015) *Pyrite: A Natural History of Fool's Gold.*, Oxford University Press.
- Rickard D. (2012) *Sulfidic Sediments and Sedimentary Rocks.*, Newnes.
- Rickard D., Grimes S., Butler I., Oldroyd A. and Davies K. L. (2007) Botanical constraints on pyrite formation. *Chemical Geology* **236**, 228–246.
- Rickard D. T. (1970) The origin of framboids. *Lithos* **3**, 269–293.

- Skripchenko N. S. and Berber'yan T. K. (1976) The structure of framboidal pyrite. *International Geology Review* **18**, 1435–1439.
- Sonnenberg S. A. (2011) Chapter 11: TOC and Pyrolysis Data for the Bakken Shales, Williston Basin, North Dakota and Montana. In *The Bakken–Three Forks Petroleum System in the Williston Basin* (eds. J. W. Robinson, J. A. LeFever, and S. B. Gaswirth). Denver, Colorado. pp. 308–331. Available at: http://archives.datapages.com/data/rocky-mtn-geologist-pubs/data/002/002001/308_rmag-bk0020308.htm [Accessed August 29, 2016].
- Thode H. G. (1981) Sulfur Isotope Ratios in Petroleum Research and Exploration: Williston Basin. *AAPG Bulletin* **65**, 1527–1535.
- Thode H. G. and Monster J. (1965) Sulfur-Isotope Geochemistry of Petroleum, Evaporites, and Ancient Seas. In American Association of Petroleum Geologists Memoirs: 4. pp. 367–377.
- Ushikubo T., Williford K. H., Farquhar J., Johnston D. T., Van Kranendonk M. J. and Valley J. W. (2014) Development of in situ sulfur four-isotope analysis with multiple Faraday cup detectors by SIMS and application to pyrite grains in a Paleoproterozoic glaciogenic sandstone. *Chemical Geology* **383**, 86–99.
- Valley J. W. and Kita N. T. (2009) *In situ* oxygen isotope geochemistry by ion microprobe. *Mineralogical Association of Canada Short Course* **41**, 19–63.
- Vietti L. A., Bailey J. V., Fox D. L. and Rogers R. R. (2015) Rapid formation of framboidal sulfides on bone surfaces from a simulated marine carcass fall. *PALAIOS* **30**, 327–334.
- Wang J., Mbah C. F., Przybilla T., Zubiri B. A., Spiecker E., Engel M. and Vogel N. (2018) Magic number colloidal clusters as minimum free energy structures. *Nature Communications* **9**, 5259.
- Wignall P. B. and Newton R. (1998) Pyrite framboid diameter as a measure of oxygen deficiency in ancient mudrocks. *American Journal of Science* **298**, 537–552.
- Wignall P. B., Newton R. and Brookfield M. E. (2005) Pyrite framboid evidence for oxygen-poor deposition during the Permian–Triassic crisis in Kashmir. *Palaeogeography, Palaeoclimatology, Palaeoecology* **216**, 183–188.
- Wilkin R. T., Arthur M. A. and Dean W. E. (1997) History of water-column anoxia in the Black Sea indicated by pyrite framboid size distributions. *Earth and Planetary Science Letters* **148**, 517–525.
- Wilkin R. T. and Barnes H. L. (1997) Formation processes of framboidal pyrite. *Geochimica et Cosmochimica Acta* **61**, 323–339.

Wilkin R. T., Barnes H. L. and Brantley S. L. (1996) The size distribution of framboidal pyrite in modern sediments: An indicator of redox conditions. *Geochimica et Cosmochimica Acta* **60**, 3897–3912.

Figures

Table 3.1. Name, depth, and location information for the 5 cores sampled from the Bakken Formation, North Dakota, USA.

Core Name, Source	Latitude, Longitude	Member	# of SIMS mounts	Depth of SIMS sample (ft from surface)	Depth of SIMS sample (~m from surface)	Modeled Max Temperature (°C, Kuhn et al., 2012)
E701, USGS	48.379442, -104.135898	lower	2	9922.8	3025	135
21706, NDGS	47.8179408, -103.1718619	upper/middle	1	11087.5	3380	160-165
12785, NDGS	47.542727, -102.963685	lower	1	11351.25	3460	150-155
17015, NDGS	48.2913654, -102.828463	lower	1	10422.7	3177	145-150
16586, NDGS	48.3405436, -102.545948	upper	1	9791.3	2984	130-135

Table 3.2. Analytical conditions for three SIMS sessions for $\delta^{34}\text{S}_{(\text{pyrite})}$ from the upper and lower Bakken Formation, North Dakota, USA.

Session	Date	Pit Dimensions	Beam Intensity	Mean Analytical Precision (2SD)
1	October 17, 2016	~ 3x2 μm	~ 30 pA	$\pm 0.7\text{‰}$
2	June 7, 2017	~ 3x3 μm	~ 29 pA	$\pm 1.3\text{‰}$
3	August 20, 2018	~ 10x8 μm	~ 1.4 nA	$\pm 0.1\text{‰}$

Figure 3.1. Closed-system $\delta^{34}\text{S}$ Rayleigh fractionation for pyrite precipitating from a sulfate pool, with $\alpha_{\text{sulfate-sulfide}} = 1.05$ and an initial $\delta^{34}\text{S}(\text{sulfate})$ value of 17‰ based on estimates for contemporaneous seawater (Thode and Monster, 1965; Thode, 1981).

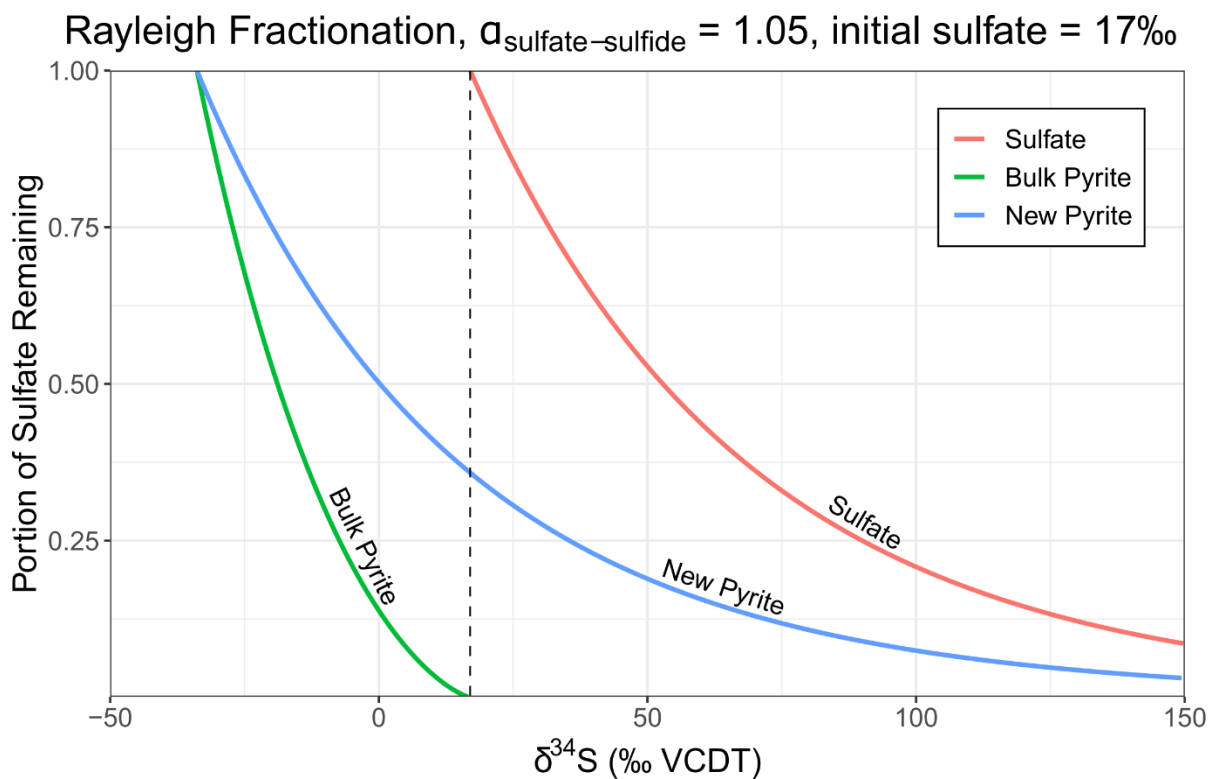


Figure 3.2. Growth endmember models by which framboids may form. These models can be tested with in situ $\delta^{34}\text{S}$ analyses. **(1)** Microcrystals are fully grown and may be zoned prior to framboid formation by aggradation. **(2)** Microcrystals grow in tandem with framboid growth, resulting in microcrystal $\delta^{34}\text{S}$ zonation. **(3)** Microcrystal size is set during initial framboid growth; later microcrystals grow continuously outside of framboids and are aggraded if they are a complimentary size. **(4)** Microcrystal size is set during initial framboid growth, and microcrystal structure is preserved as pyrite grows radially outwards. Models 1 and 2 will not show interior to rim $\delta^{34}\text{S}$ zonation, while Models 3 and 4 will. Models 1 and 2 will show $\delta^{34}\text{S}$ variability if the analysis: microcrystal size ratio is sufficiently small, whereas Models 3 and 4 will not. In addition to their respective growth processes, Models 1, 2, and 3 will require the addition chemical or erosional process to produce the rounded rims observed in many framboids; Model 4 does not require this.

Endmember Models of Framboid Growth

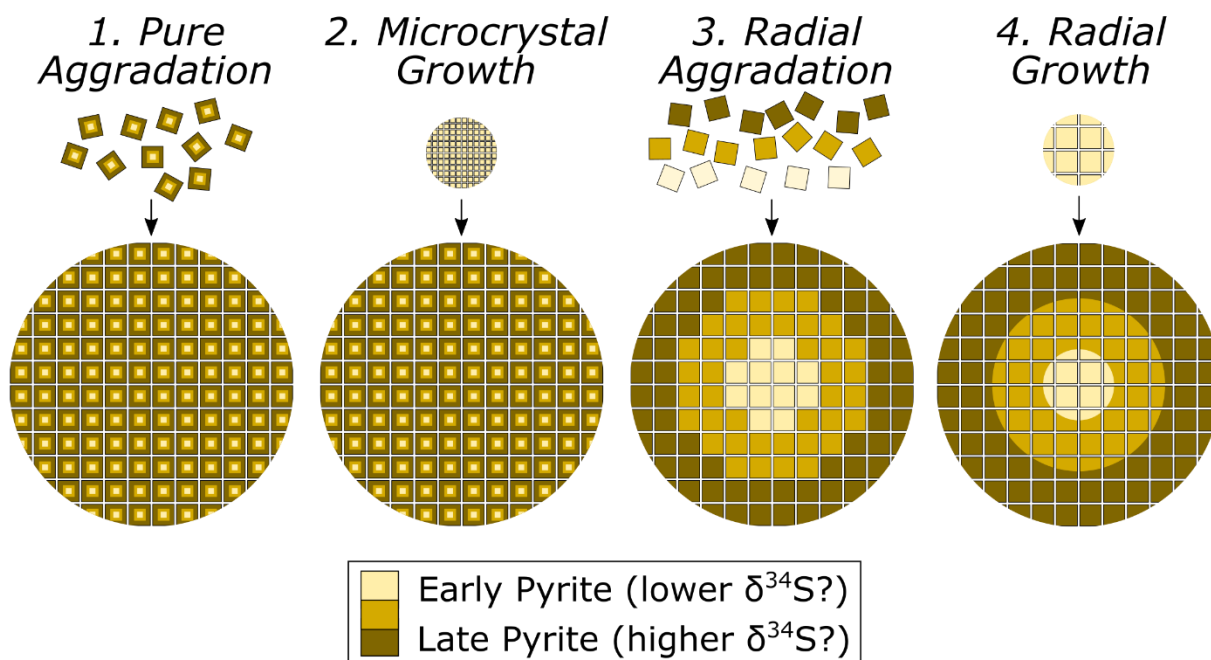
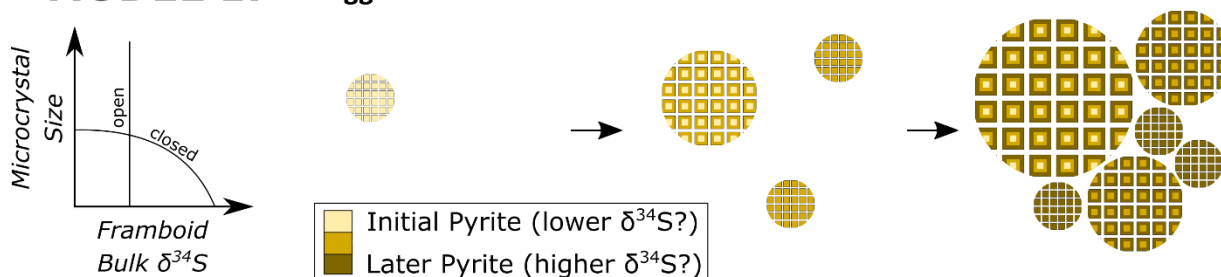


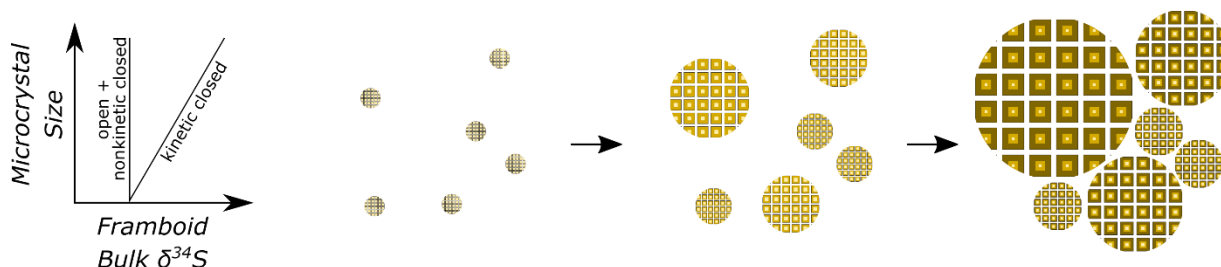
Figure 3.3. Population models for $\delta^{34}\text{S}$ distribution amongst different framboids, assuming different mechanisms for the variable size distributions observed in sedimentary rocks. If $\alpha_{\text{sulfate-sulfide}}$ is large and relatively constant, then homogenous $\delta^{34}\text{S}$ distributions in framboid populations can only be produced by different growth rates that are proportional to each other (Population Model 2) or open-system behavior. If the different growth rates of Population Model 2 are related to H_2S production rates, and if those rates are sufficiently variable to kinetically affect fractionations, then variable $\delta^{34}\text{S}$ population distributions would be expected.

Endmember Models for Framboid $\delta^{34}\text{S}$ Population Distributions

MODEL 1: Staggered Nucleation -> Similar Growth Rates -> Simultaneous Cessation



MODEL 2: Simultaneous Nucleation -> Different Growth Rates -> Simultaneous Cessation



MODEL 3: Simultaneous Nucleation -> Similar Growth Rates -> Staggered Cessation

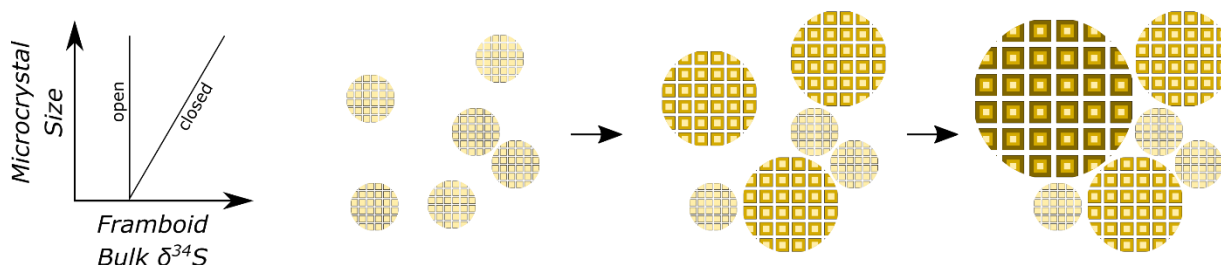


Figure 3.4. Relationship between framboïd diameter and microcrystal size for all samples.

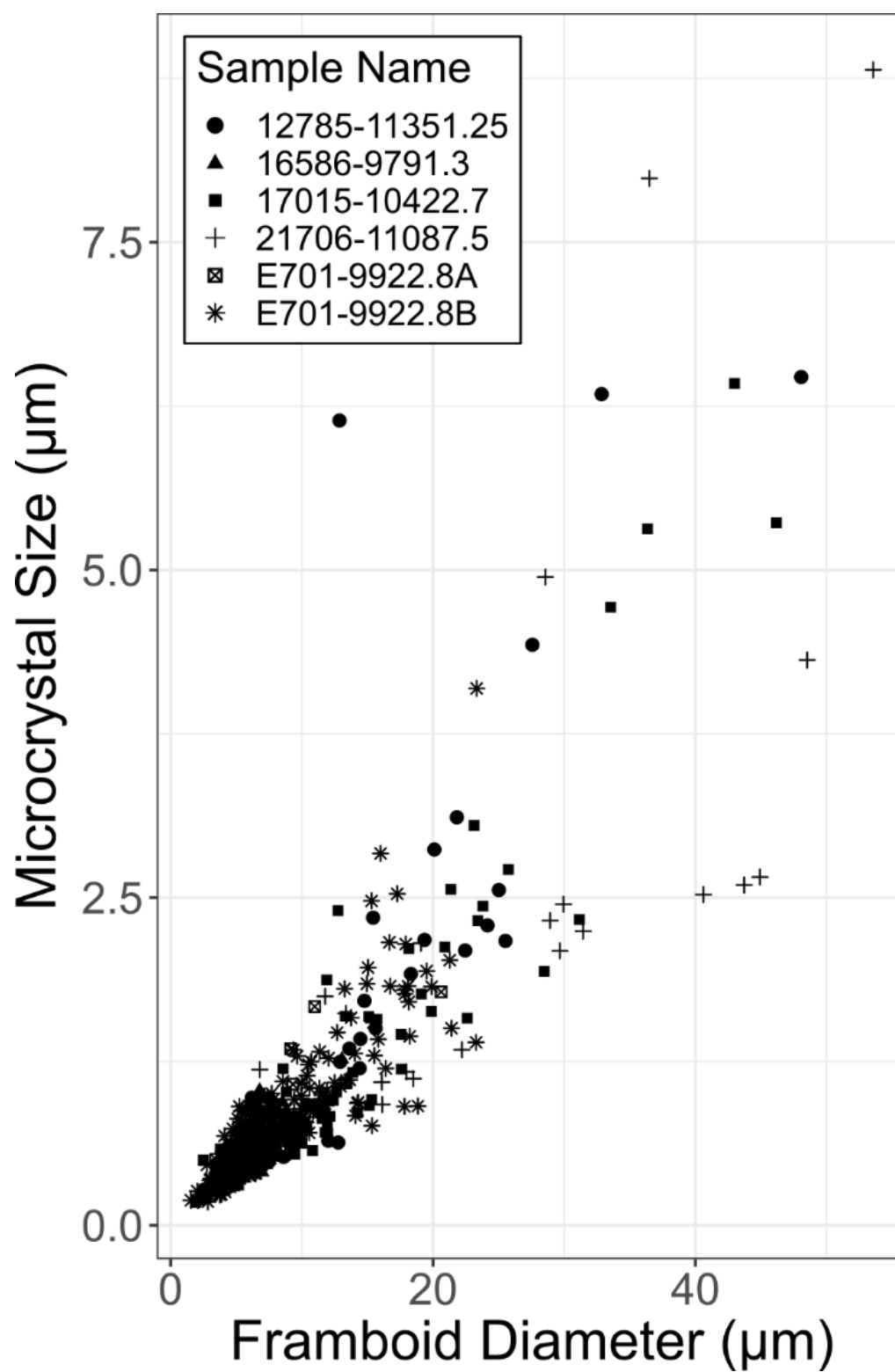


Figure 3.5. Relationship between framboïd diameter and microcrystal size for each sample.

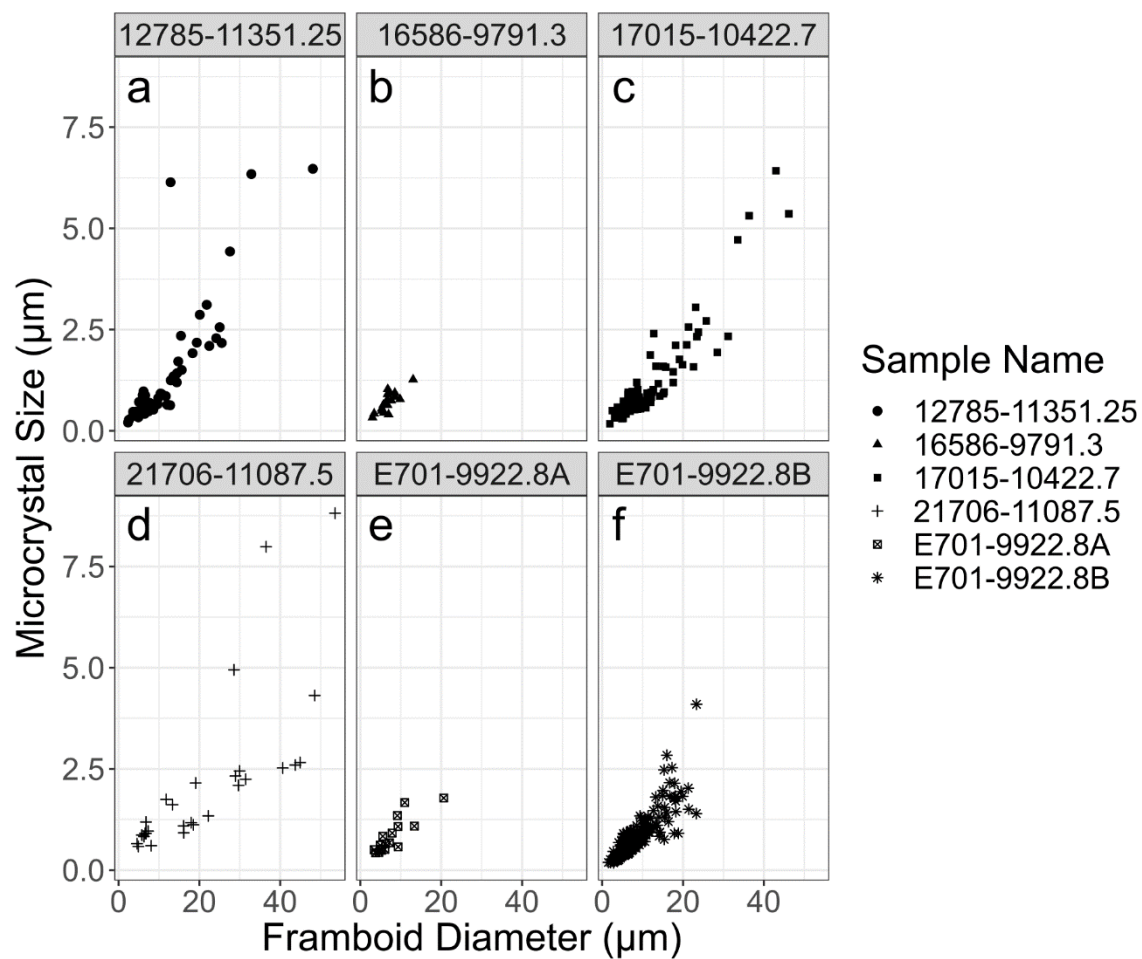


Figure 3.6. SEM-BSE imagery of a subset of framboids from sample 12785-11351.25. Red circles show area of SIMS analyses, with values reported in ‰ VPDB. Additional imagery and values are available in Appendix 2.3.

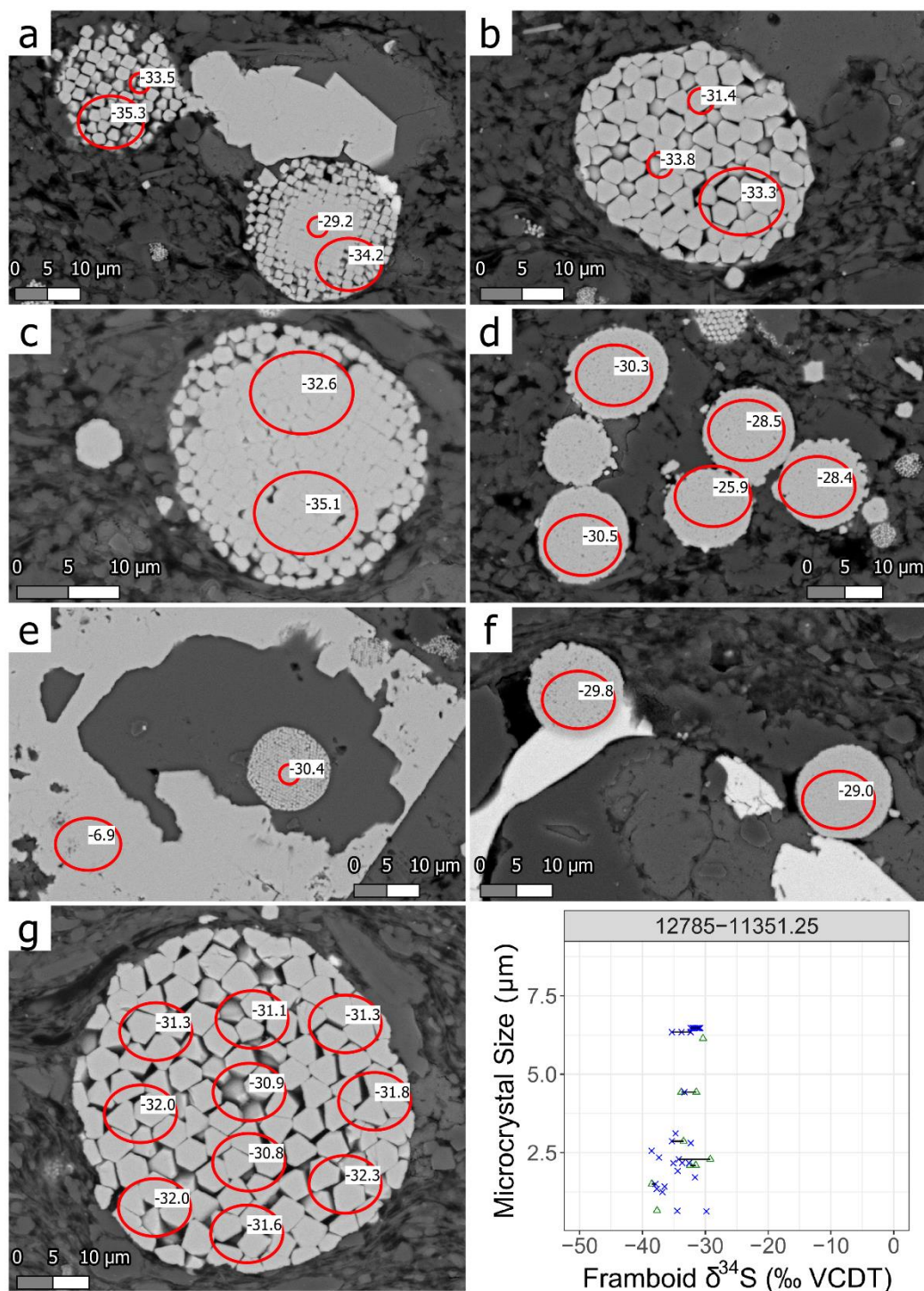


Figure 3.7. SEM-BSE imagery of a subset of framboids from sample 17015-10422.7. Red circles show area of SIMS analyses, with values reported in ‰ VPDB. Additional imagery and values are available in Appendix 2.3.

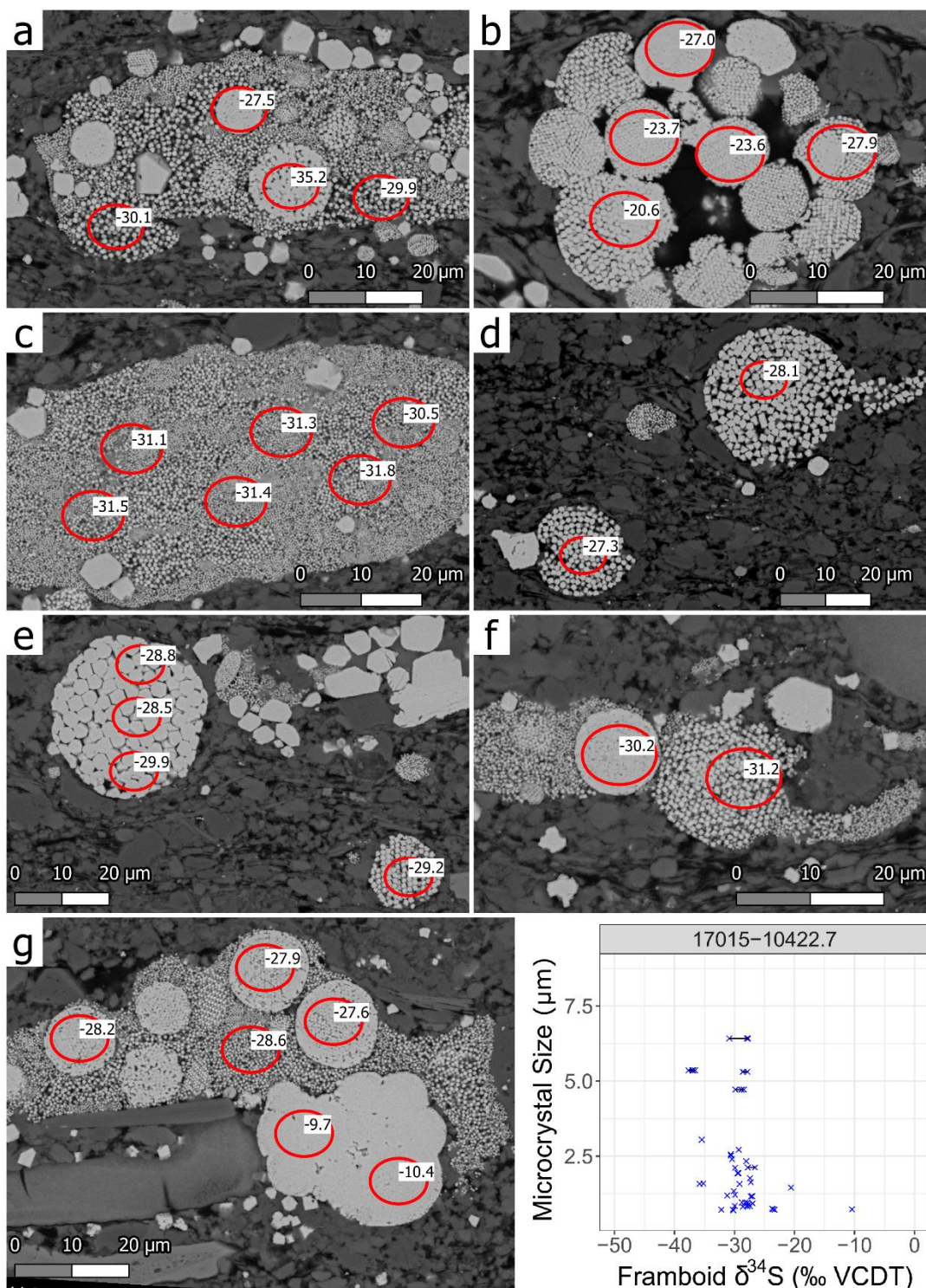


Figure 3.8. SEM-BSE imagery of a subset of framboids from sample 21706-11087.5. Red circles show area of SIMS analyses, with values reported in ‰ VPDB. Additional imagery and values are available in Appendix 2.3. (f) Black outlines have been drawn to accentuate visible boundaries between octahedral microcrystals and cubic overgrowths.

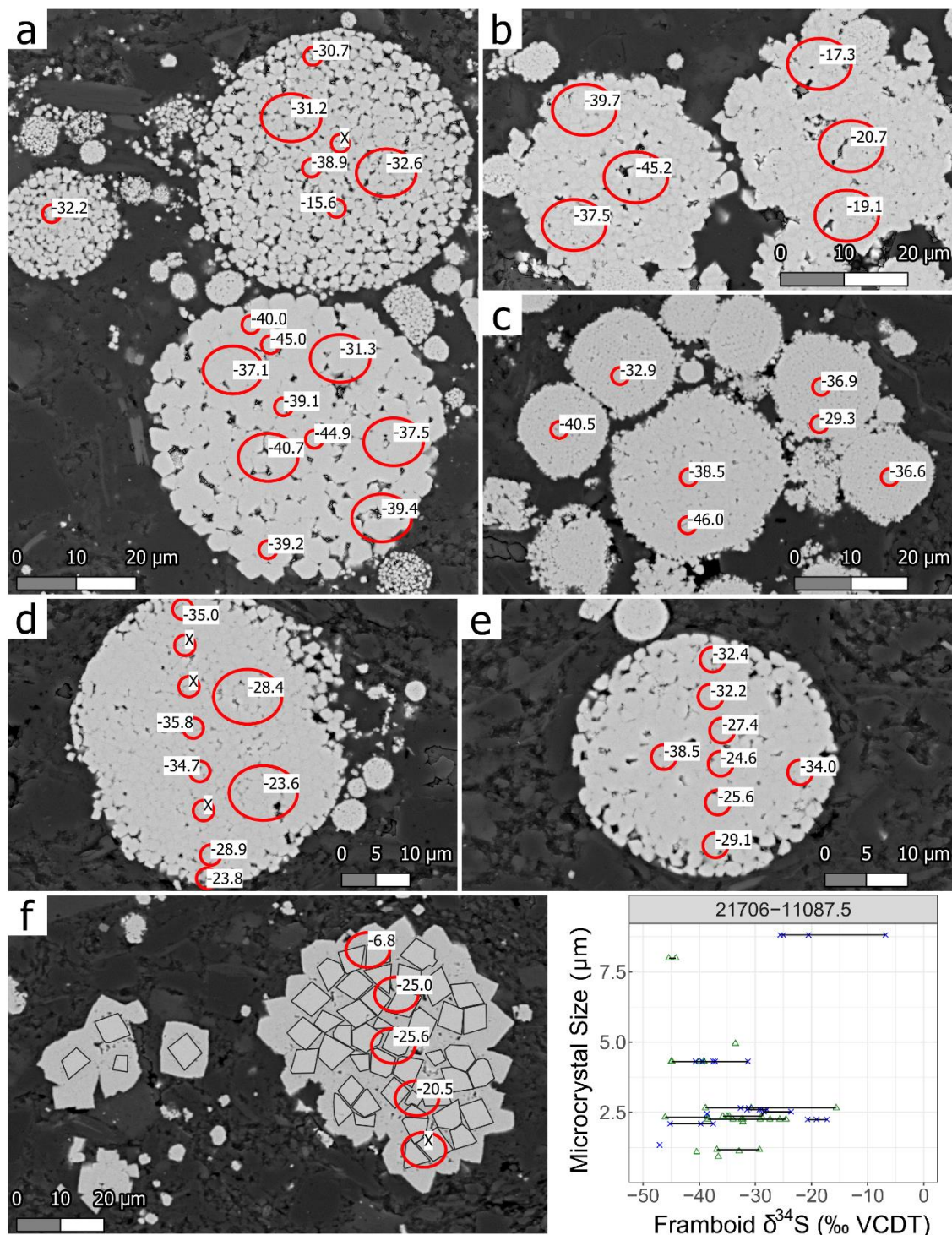


Figure 3.9. SEM-BSE imagery of a subset of framboids from sample E701-9922.8B. Red circles show area of SIMS analyses, with values reported in ‰ VPDB. Additional imagery and values are available in Appendix 2.3.

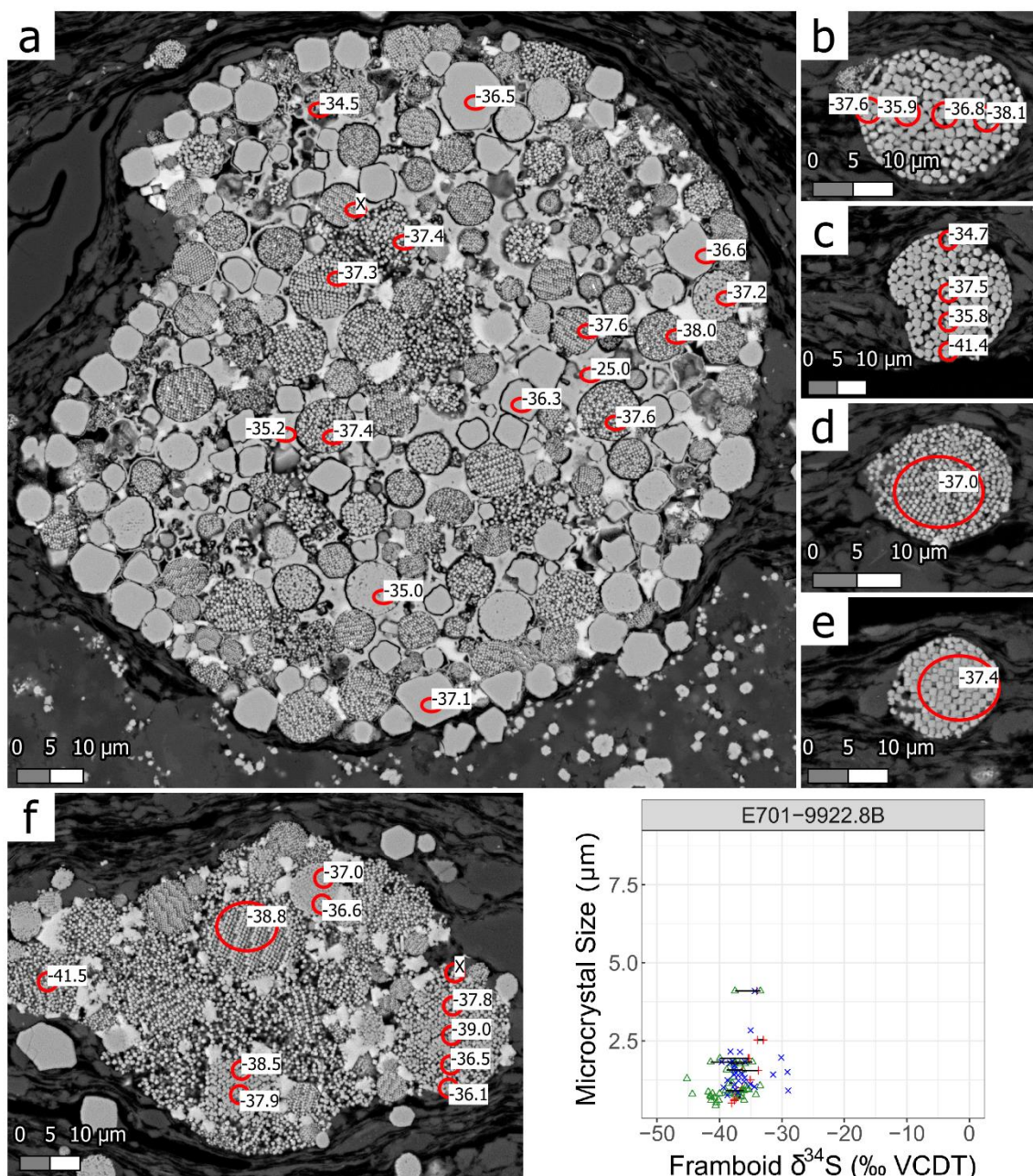


Figure 3.10. Sample-specific framboïd $\delta^{34}\text{S}$ and microcrystal size as measured across all three sessions. Solid lines connect multiple analyses made on the same framboïd.

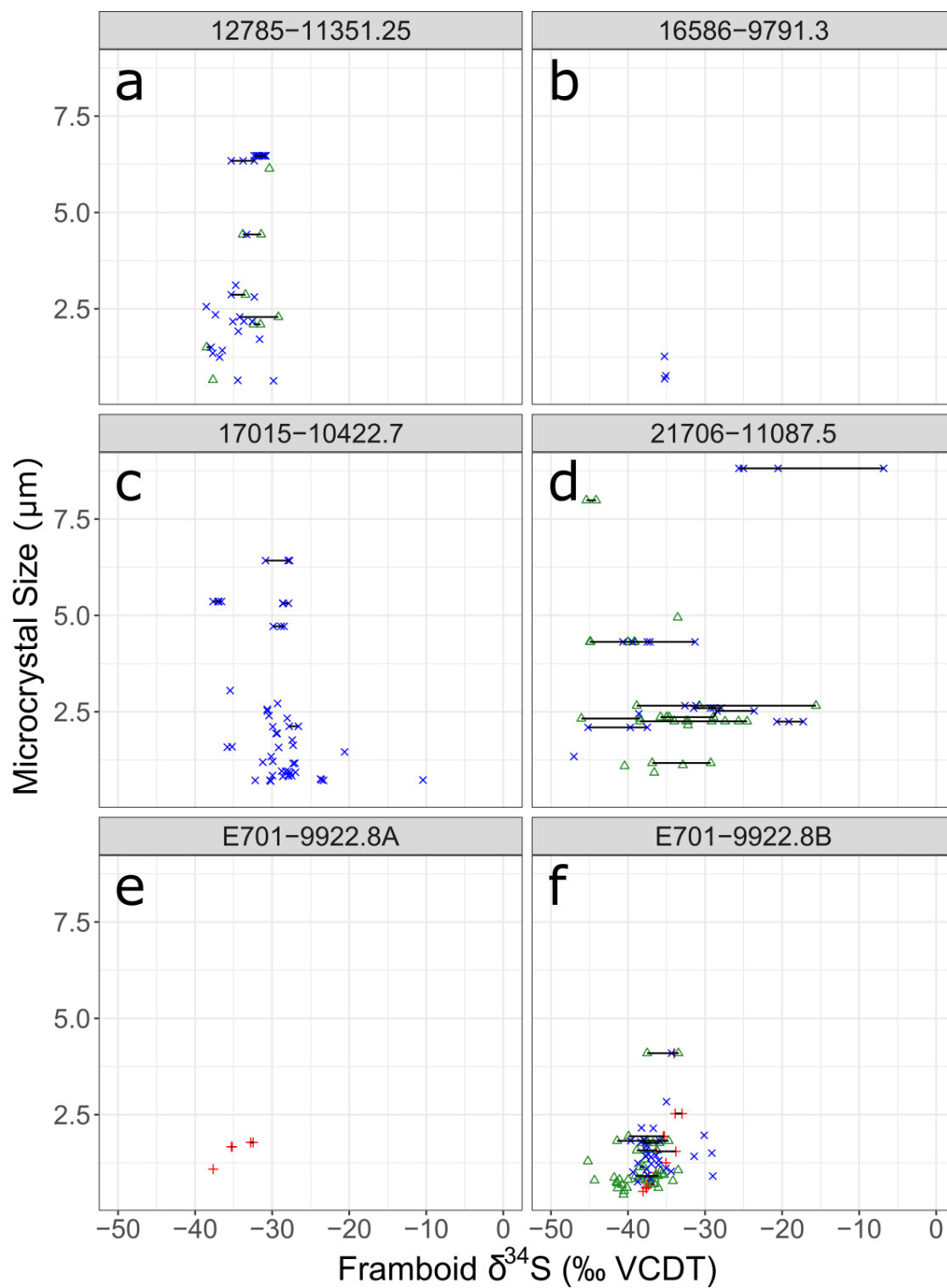
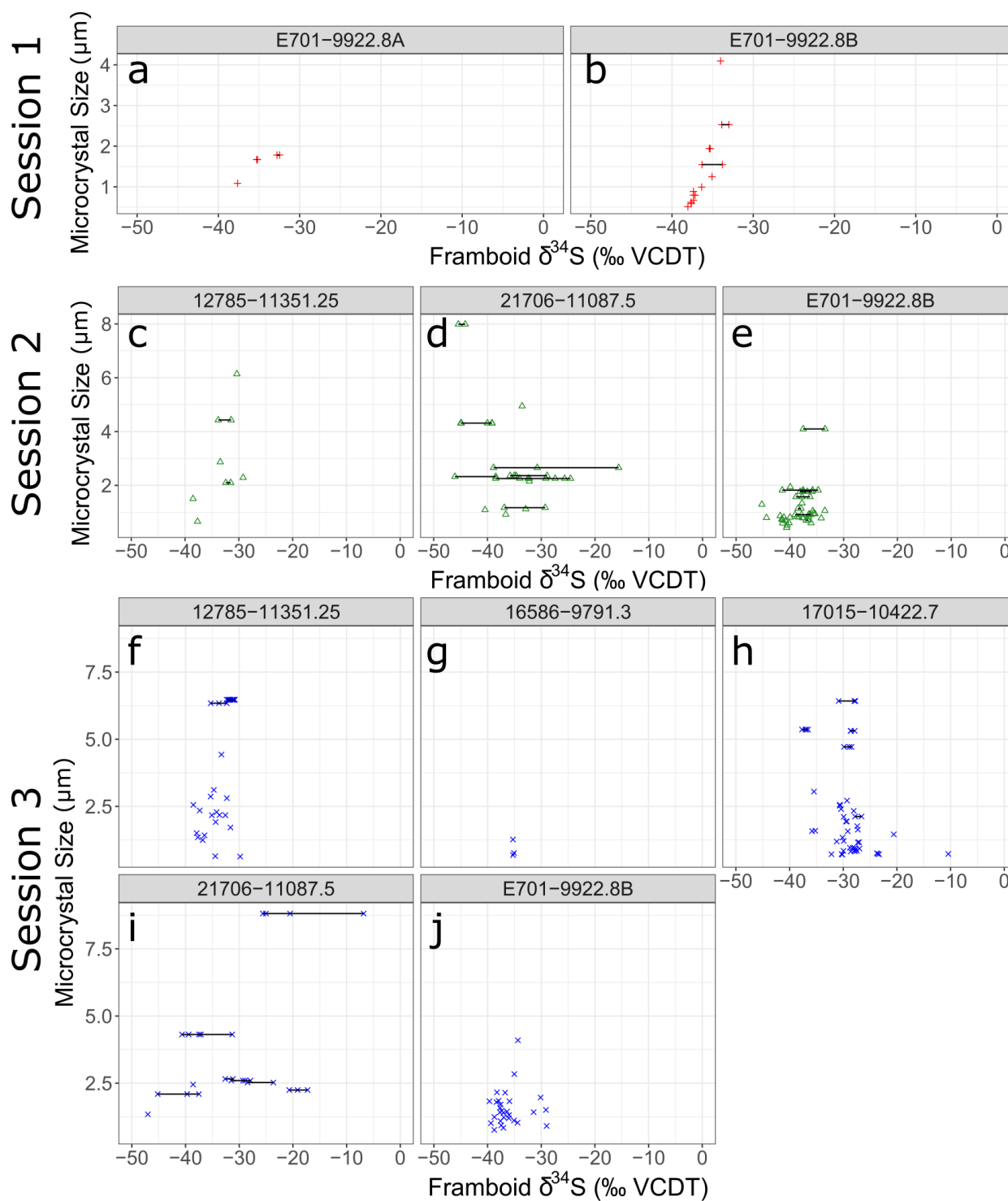


Figure 3.11. Session-specific framboïd $\delta^{34}\text{S}$ and microcrystal size as measured across all three sessions. Solid lines connect multiple analyses made on the same framboïd. (a,b) Session 1. (c-e) Session 2. (f-j) Session 3.



CHAPTER 4: A History of Pore Water Oxygen Isotope Evolution in the Cretaceous Travis Peak Formation in East Texas

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CONTRIBUTIONS: Fluid inclusion work was conducted by András Fall at the Jackson School of Geosciences, University of Texas at Austin. Bil Schneider provided instrument support on the SEM. Brian Hess prepared and polished the sample prior to SIMS analysis. Instrumental support in the WiscSIMS lab was provided by Ian Orland, Kouki Kitajima, and Noriko Kita. Benjamin Linzmeier provided feedback on the model. Chapter contents were reviewed and edited by András Fall, Ian Orland, Peter Eichhubl, Stephen Laubach, John Valley, Clay Kelly, Alan Carroll, Stephen Meyers, and Matthew Ginder-Vogel.

Denny, AC, Fall, A, Orland, IJ, Valley, JW, Eichhubl, P, and Laubach, SE. (2019) A History of Pore Water Oxygen Isotope Evolution in the Cretaceous Travis Peak Formation in East Texas. Bulletin of the Geological Society of America, in review July 2019.

Abstract

Oxygen isotope analyses of diagenetic cements can provide detailed evidence of sedimentary burial processes and conditions, as the $\delta^{18}\text{O}$ values of precipitating minerals reflect contemporaneous local $\delta^{18}\text{O}_{\text{water}}$ and temperature conditions. Uncertainties in the timing and rates of pore water $\delta^{18}\text{O}$ evolution in sedimentary basins can complicate interpretation of these records. Fracture-bridging (0.5-1 mm) quartz cements observed in sandstones of the Cretaceous Travis Peak Formation in the East Texas basin show clear growth-zoning by cathodoluminescence and contain detailed fluid inclusion records of temperature that make them excellent candidates for interrogating prolonged histories of basin temperature and the evolution of $\delta^{18}\text{O}$ in basin pore water. New SIMS $\delta^{18}\text{O}_{\text{quartz}}$ isotopic data from fluid inclusion-rich quartz bridges in Travis Peak sandstones record a steady increase of pore water $\delta^{18}\text{O}$ values from ~5 to 7‰ (VSMOW) as the sandstone warms from ~130 to 150°C. To help evaluate whether this trend could be generated solely from local water-rock interactions in response to burial compaction, a one-dimensional closed system isotopic burial model was created to simulate how $\delta^{18}\text{O}_{\text{water}}$ values change in a quartz-dominated sandstone during diagenesis. Using both directly measured and inferred rates of Travis Peak compaction, the magnitude of change in $\delta^{18}\text{O}_{\text{water}}$ that we calculate from quartz bridge geochemistry cannot be reasonably modeled solely by local quartz mechanical compaction, pressure solution, and cementation processes, necessitating significant fluxes of silica and high- $\delta^{18}\text{O}$ water from outside of the sandstones prior to maximum burial. This indicates that even units which appear surrounded by significant barriers to fluid flow (i.e., mudrock-bounded channel sandstones) may have been infiltrated and diagenetically modified by large fluxes of fluid on geologic time scales.

1. Introduction

Diagenetic cements are the manifestation of a host of chemical and physical processes that occur in sedimentary rocks shallower than 15 km deep and at temperatures below 250°C (Worden and Burley, 2003). As a result, cements preserve extensive chemical records of mineral reactions, temperature, ion fluxes, water composition, and basin-wide fluid flow. Constraints on temperature are particularly useful to studies of sedimentary basin histories, as temperature is a major control on reaction, dissolution and precipitation rates, and can be an indicator of economically important fluid flow events that move metalliferous brines or hydrocarbons around a basin (Bethke, 1986; Bethke et al., 1991).

Measuring the oxygen isotope ratios of diagenetic silicates and carbonates is a powerful tool for interrogating sedimentary basin evolution. The $\delta^{18}\text{O}$ of an equilibrated fluid can be predicted as a function of the $\delta^{18}\text{O}$ of a precipitated mineral phase and the ambient temperature (Figure 4.1). For quartz in an environment below 200°C and at a constant $\delta^{18}\text{O}_{\text{water}}$, an increase of 10°C will increase the precipitated $\delta^{18}\text{O}_{\text{quartz}}$ by 1-2‰ (Clayton et al., 1972; Friedman and O'Neil, 1977). Isotopic data from diagenetic carbonates and silicates have repeatedly aided in constraining basinal temperature and pore-fluid histories (Milliken et al., 1981; McBride et al., 1987; Ayalon and Longstaffe, 1988; Dutton and Land, 1988; Lee et al., 1989; Aplin and Warren, 1994; Marchand et al., 2000), but traditional analysis requires mineral separation or microdrilling procedures that are both susceptible to homogenization of finer scale isotopic zonation (Graham et al., 1996). The development of Secondary Ion Mass Spectrometry (SIMS) as a tool for geological samples has seen significant advancement in recent years, particularly for minerals of diagenetic importance (Valley et al., 1998; Valley and

Kita, 2009; Kita et al., 2009). SIMS is capable of acquiring precise isotopic measurements from regions < 10 μm in diameter, which has greatly expanded the possibilities for interrogating basin histories from mineral grains smaller than a few hundred microns in extent (Williams et al., 1997; Kelly et al., 2007; Pollington et al., 2011, 2016; Harwood et al., 2013; Hyodo et al., 2014; Śliwiński et al., 2016; Denny et al., 2017).

A continuing challenge in studies of basin fluids is that the $\delta^{18}\text{O}$ of a diagenetic mineral depends on both temperature and $\delta^{18}\text{O}$ of pore water at the time of precipitation. Thus, analysis will produce non-unique solutions if only one of these three variables is known (e.g., Figure 4.1). To improve interpretations of oxygen isotope analyses of diagenetic cements, it is necessary to obtain values of either $\delta^{18}\text{O}_{\text{water}}$ or temperature, so that the other variable might then be constrained. Unfortunately, pore water $\delta^{18}\text{O}$ values commonly change throughout basin evolution and analyses of modern pore water are not reliable for inferring conditions of cementation. In contrast with $\delta^{18}\text{O}$ evolution, thermal histories are currently easier to constrain for basins, as temperature can be estimated from fluid inclusions, organic maturation proxies, sedimentation rates, and estimated burial geotherms. The combination of oxygen isotope analysis with fluid inclusion microthermometry provides an independent estimate of fluid temperature, thus aiding in the interpretation of inorganic diagenetic mineral histories.

If independent temperature estimates are unavailable, then modeling the pore water $\delta^{18}\text{O}$ history of a basin becomes the next best approach to constraining the isotopic system. Some progress has been made in modeling the response of pore water $\delta^{18}\text{O}$ during water-rock interaction in carbonates and shales (Land, 1980; Land et al., 1983; Suchecky and Land, 1983; Wilkinson et al., 1992; Heydari, 1997), and in measuring this response in the rock record (e.g.,

Millán et al., 2016), but much work remains to be done towards understanding the effects of water-rock interactions in a mixed sedimentary sequence on pore water $\delta^{18}\text{O}$ history. To that end, in this study we coupled fluid inclusion temperature records to SIMS analyses to find pore water $\delta^{18}\text{O}$ trends through time, and then compared those results to a simple model predicting pore water $\delta^{18}\text{O}$ behavior for pure quartz sandstone burial.

2. Geologic Background

2.1 Travis Peak Formation in Eastern Texas

The Travis Peak Formation is a Lower Cretaceous sequence of fluvial, paralic, and deltaic terrigenous sandstones and mudstones underlying the coastal plain along the Gulf of Mexico. In eastern Texas the fluvial deposits comprise the bulk of the formation, interfingering with deltaic sediments at the formation's base and paralic sediments at the formation's top (Dutton et al., 1991). This middle interval of fluvial channel deposits may be further subdivided into a lower braided low-sinuosity system and an upper high-sinuosity channel system.

Core data from the low-sinuosity fluvial system indicates that 65% of its volume is composed of channel sandstones with the other 35% percent consisting of finer grained argillaceous overbank mudstones and sandstones. By contrast, the high-sinuosity fluvial system is 30% channel sandstones and 70% fine-grained argillaceous overbank sandstones and flood-plain shales (Davies et al., 1991). Channels within the low-sinuosity fluvial system typically range from 3.7 to 13.7 m in thickness (averaging 8 m in thickness), although the lower amount of mud in the system (as compared to the high-sinuosity system) allows amalgamated channel sandstone units to reach thicknesses of up to 76 m (Dutton et al., 1991; Tye, 1992). The high-

sinuosity fluvial channel sands consist predominantly of migrating point-bar deposits 4 to 5 m in thickness (Davies et al., 1991).

Present-day Travis Peak framework grain compositions average 95% quartz, 4% feldspar, and 1% lithic fragments; a small percentage of additional feldspar may have been lost to dissolution. Present-day average porosity within the formation ranges from 10.5% at 1.8 km depth to 4.4% at 3 km depth, with porosity decreasing steadily as depth increases (Dutton and Diggs, 1992). The most abundant cement within the Travis Peak is quartz, which averages 17% by volume within the clean sandstones (Dutton and Diggs, 1990). Dolomite and ankerite are minor but locally significant cements, averaging 2% by volume in fluvial sandstones and 4% in paralic sandstones (Dutton, 1987). Minor authigenic illite and chlorite are also present.

The most significant structure within the study area (Figure 4.2) is the Sabine Arch. This broad uplift has a vertical relief of about 600 meters and separates the East Texas Salt Basin in the west from the Northern Louisiana Salt Basin to the east (Laubach and Jackson, 1990). While the Travis Peak Formation in East Texas has undergone progressively deeper burial for most of its history, it has experienced two periods of uplift—a brief one in late mid-Cretaceous time, and an ongoing one that began in the Tertiary. This latter event is estimated to have resulted in the erosion of ~450 m of overburden (Figure 4.3) (Dutton and Land, 1988; Jackson and Laubach, 1991; Lander and Laubach, 2015).

Williams et al. (1997) made 76 SIMS measurements of $\delta^{18}\text{O}_{\text{quartz}}$ on 4 Travis Peak Formation sandstone samples from 3 cores, with 15-20 μm diameter spots and 1.3 to 1.8‰ 1σ standard errors. They reported 76 analyses on detrital quartz ($13.7 \pm 4.6\text{‰}$, 1σ), with smaller

grains possessing heavier values (16-23‰) suggestive of a metamorphic source and larger grains possessing lighter values (~12‰) suggestive of a plutonic source. A total of 37 analyses were made on authigenic quartz ($26 \pm 3.5\text{‰}$, 1σ), with values ranging from 22 to 35‰.

2.2 Quartz Bridges

Recent studies of the Travis Peak Formation and other sandstones reveal that vertically-oriented opening-mode fractures can contain 0.5-1 mm fracture-bridging quartz cements (Figure 4.4) (Laubach, 1988, 2003; Laubach et al., 2004a, b; Becker et al., 2010; Fall et al., 2012, 2015, 2016; Hooker et al., 2015). These bridging cements contain many narrow fracture-parallel bands of fluid inclusions that are visible optically, surrounded by quartz that lacks fluid inclusions (Figures 4.5 and 4.6). Quartz deposits contain a range of textures visible with cathodoluminescence, including narrow, commonly symmetrical deposits surrounding fluid inclusion bands (called *gap deposits*, Laubach et al., 2004b) that commonly crosscut each other, and *lateral deposits* that overlap the gap deposits and that typically have zoning that parallels the sides of the bridge. Such crack-seal features are diagnostic of repeated crack opening and cement accumulation (Lander and Laubach, 2015). The patterns indicate that the quartz cement precipitated continuously during episodic fracture opening. For bridges to form, sufficient time in between periods of fracture opening is required for diagenetic quartz to seal the crack produced. The process of bridge formation and the likely rates of quartz accumulation are outlined by Lander and Laubach (2015). Crack-seal features are excellent at preserving detailed fluid inclusion records during the duration of fracture opening and may capture periods of fracture opening that span 40 million years or more.

3. Methods

Crack-seal quartz bridges from the Travis Peak Formation were imaged and analyzed for fluid inclusions at the Jackson School of Geosciences, University of Texas at Austin, as published in Becker et al. (2010) and Fall et al. (2016). From these samples, two doubly-polished thick section chips containing quartz bridges with previously analyzed fluid inclusions were selected for analysis on a Secondary Ion Mass Spectrometer (SIMS). One chip originated from the Holditch SFE No. 2 well (hereafter designated sample SFE2), and the other from the Ashland S.F.O.T. No. 1 well (sample SFOT1) (Figure 4.2). These thick section chips were mounted into epoxy alongside the UWQ-1 quartz standard (Kelly et al., 2007), and cast in a 2.54 cm diameter mold. Mounts were ground and polished to a 0.25 μm diamond grit, given a colloidal alumina finishing polish, and checked for flatness using a reflected light microscope.

As some loss of material was expected during polishing, it was necessary to carefully reimage the sample surface so that proper correlation between previously measured fluid inclusions and subsequent SIMS analyses might be made. This was done prior to SIMS analysis using a Hitachi S3400-N scanning electron microscope (SEM) by collecting backscattered electron (BSE), secondary electron (SE), and cathodoluminescence (CL) imagery. BSE imaging provides growth context for dolomites and ankerites intergrown with quartz cements, as the signal (brightness) recorded in such images correlates with mineral iron content can reveal complex compositional zonation. SE imagery is useful as another check on surface flatness, and CL mapping is effective at revealing quartz cement zonation and distinguishing overgrowth quartz from detrital grains. To aid in interpretation, multiple layers of data and imagery were

imported and combined into a single map within the QGIS software platform (Linzmeier et al., 2018).

Values of $\delta^{18}\text{O}$ were obtained using a CAMECA IMS 1280 large-radius, multi-collector SIMS (secondary ion mass spectrometer) at the WiscSIMS laboratory, Dept. of Geoscience, University of Wisconsin-Madison, using well-established sample preparation and analysis procedures (Kita et al., 2009; Valley and Kita, 2009; Wang et al. 2014). During analysis, samples are exposed to a focused primary beam of $^{133}\text{Cs}^+$ ions under a 10 kV accelerating potential and impact energy of 20 keV. An electron flood gun is used for charge neutralization, and the mount was coated with carbon (~25nm thick) to assist with charge compensation. The impact of $^{133}\text{Cs}^+$ ions with the sample surface excavates an oval-shaped pit in the surface (pits were roughly 9 μm in diameter at their widest and 3 μm deep for this dataset); the sputtered “secondary” ions are accelerated into a double-focusing mass spectrometer that was tuned to simultaneously measure $^{16}\text{O}^-$, $^{18}\text{O}^-$, and $^{16}\text{O}^{17}\text{H}^-$ by 3 faraday cup detectors. The molecular ion species $^{16}\text{O}^{17}\text{H}^-$ is measured to infer the OH content of the quartz and to help verify that hydrous or organic phases were not intersected during analysis.

The ratio of ^{18}O to ^{16}O obtained with the SIMS method is subject to an instrumental mass fractionation, or bias, that requires the use of standards of the same chemical composition and crystal structure for value correction (in this case, quartz standard UWQ-1, $\delta^{18}\text{O} = 12.33\text{‰}$, Kelly et al. 2007). The full corrected dataset is available and may be accessed in Appendices 4.1 and 4.2, and all standard-corrected $\delta^{18}\text{O}$ values are reported in standard permil notation relative to Vienna Standard Mean Ocean Water (VSMOW). Temperatures were related

to $\delta^{18}\text{O}_{\text{quartz}}$ and $\delta^{18}\text{O}_{\text{water}}$ using the low-temperature quartz-water fractionation equation of Clayton et al. (1972) as modified by Friedman and O'Neil (1977).

SIMS pits were imaged by SEM after analysis, and pits that intersected non-quartz phases were not considered further. Unusual spikes in OH^- count rates, most lasting less than 4 seconds but some as long as 12 seconds, were observed in a portion of the analyses, and pits associated with these analyses typically contained small holes or pockets. These OH^- spikes are interpreted to have occurred when SIMS pit excavation liberated small (typically $<2\mu\text{m}$) fluid inclusions from within the quartz. Further evaluation of these analyses revealed that intersecting these inclusions did not affect $\delta^{18}\text{O}$ values during the analysis, and so these data are included in the interpretation. A full discussion of how these OH^- spikes were evaluated can be found in Appendix 4.3.

4. Results

A total of 142 Secondary Ion Mass Spectrometer (SIMS) measurements were made on detrital and authigenic quartz associated with the two prepared fracture-spanning quartz bridges, SFE2 and SFOT1. The precision of these data is reported as two standard deviations of the 8-10 analyses of quartz standard UWQ-1 that bracket each set of 10-15 sample analyses, and is typically $\pm 0.3\text{‰}$ (Appendices 4.1, 4.2). Sample analyses were then compared to previously acquired CL imagery to help place them in their proper petrographic context (Figures 4.4, 4.5, 4.6, and Appendix 4.4). The detrital quartz $\delta^{18}\text{O}$ values analyzed in this study range from 12 to 15.5‰ (Figure 4.7), which is consistent with average detrital values measured by Williams et al. (1997).

Diagenetic quartz cements were subdivided into three groups: 1) Quartz overgrowths, which grew around detrital grains and into the pore space between detrital quartz grains, 2) Gap deposits (bridge quartz), which grew to span fractures via the crack-seal process, and 3) Lateral deposits (bridge-coating quartz), which grew outwards into the fracture space from the bridge quartz, normal to the surface of the quartz bridge itself, and syn- or postkinematically with fracture opening and gap deposit formation. Since gap deposits form sequentially, they will be of different ages depending on where gap deposits occur within the bridge. Likewise, lateral deposits close to the core of the bridge will have been deposited *during* bridge growth (but after the gap deposits they overlap). Some material within lateral deposits will be contemporaneous with some gap deposits, but not gap deposits they are directly overlapping (cf. Laubach et al., 2016, their Figure 4.12.). By using zoning in lateral deposits, it is possible to correlate gap deposits with their time equivalent lateral deposits. Moreover, although lateral deposits overlapping gap deposits are always older than subsequent lateral deposits on the same part of the bridge, all lateral deposits adjacent to gap deposits are not contemporaneous. Furthermore, some lateral deposits toward the exterior of the bridge will be younger than all gap deposits if they formed after the fracture ceased widening.

A portion of the SIMS measurements were made above previously measured fluid inclusion assemblages, so that the fluid history could be reconstructed. Fluid inclusion temperatures range from 126.5 to 143.8 °C in sample SFE2, and from 135.0 to 158.5 °C in sample SFOT1. Aggregating the data from both samples, diagenetic quartz $\delta^{18}\text{O}$ values range from 20.4 to 26.0‰. Quartz overgrowth values range from 20.4 to 25.6‰, and transects of several quartz overgrowths show no obvious systematic trend from earliest cement (grain-

adjacent) to latest cement (porosity-adjacent). Gap deposit quartz $\delta^{18}\text{O}$ values range from 22.1 to 25.0‰, while the range of lateral deposit quartz values is roughly 1‰ higher at 22.9 to 26.0‰. Fluid inclusion temperatures and calculated pore water $\delta^{18}\text{O}$ values from samples SFE2 and SFOT1 show two similar but distinct positive trends (Figure 4.8b). Based upon observations of growth relationships within the quartz, visible in CL, it appears that as these fractures were opening there was a coincident increase in temperature from 128 to 152 °C and $\delta^{18}\text{O}$ from 4.5 to 7.5‰.

5. Burial Modeling

Given the importance of water-rock interaction in modifying pore water $\delta^{18}\text{O}$ values, the possibility that the reproducible high $\delta^{18}\text{O}_{\text{water}}$ values calculated from these quartz bridges are derived from closed system water-rock interaction will be explored via burial modeling. There previously have been attempts to model $\delta^{18}\text{O}$ pore water behavior during the burial of carbonates (Heydari, 1997), and in illite-smectite-rich shales (Land, 1980; Land et al., 1983; Suchecki and Land, 1983; Wilkinson et al., 1992), with successful reproduction of natural trends achieved for relatively simple monomineralic systems. Models such as these often have too many variables to provide a unique solution to a particular dataset, but they are informative in their ability to test different sets of starting assumptions. Here, a 1-dimensional burial model was developed to explore whether simple, closed system quartz-water interaction in a sandstone could explain observed values and trends in pore water $\delta^{18}\text{O}$ with increasing temperature.

5.1 Model Overview

In the model, it is assumed that the change in porosity in quartz-rich sandstones over a small change in burial depth can be broken down into three components reflecting three different compactional processes: 1) mechanical compaction m , 2) grain boundary pressure solution p , and 3) quartz cement precipitation Qtz_{cem} , such that:

$$\Delta\Phi = m + p + Qtz_{cem} \quad [1]$$

Only the pressure solution and cement precipitation components will have an impact on pore water $\delta^{18}O$ values; mechanical compaction processes are here defined as limited to porosity loss through grain rearrangement and breakage, and hence do not play a direct role in pore water chemical alteration. The pressure solution term p may be further broken down into the portion of porosity lost to pressure solution p_{pore} , and the portion of mineral p_{min} dissolved during pressure solution (Figure 4.9). If there is no net loss or gain in silica, then the cement precipitation term Qtz_{cem} and the p_{min} term become equivalent to each other, which means that for any change in porosity from initial porosity Φ_n to new post-compaction porosity Φ_{n+1} , the following relationship may be defined:

$$\Phi_{n+1} = \Phi_n + m + p_{pore} + p_{min} \quad [2]$$

If the rate of change in porosity with depth, the proportion of that change which is due to mechanical compaction, and the relative contributions of p_{pore} and p_{min} to pressure solution p are known for a formation, then it follows that the volume of silica chemically interacting with the pore water through the process of pressure solution and cementation can be estimated. In the absence of external fluid input, the interaction between silica and pore water will drive $\delta^{18}O_{water}$ trends in pure quartz sandstones.

A particular challenge with this approach is determining the relative importance of p_{pore} and p_{min} at any given depth. The model makes the simplifying assumption that these terms are ratioed to porosity such that for any small change in porosity with burial depth:

$$p_{min} = (1 - \Phi_n) * p \quad [3]$$

This relationship is shown visually in Figure 4.9. In this way, the contribution of p_{pore} to porosity loss scales linearly with % porosity. It should be noted, however, that Eqn. 3 does not truly reflect the spatial relationship between sand grains, as the rounded morphology of grains that is common in sandstones will lower the value of p_{min} below that shown in Eqn. 3, particularly during the early stages of burial compaction. This simplifying assumption avoids the difficult spatial problem of determining numerically what the values of p_{pore} and p_{min} will be for a variety of grain orientations, grain shapes, and grain size distributions, at a variety of stages in burial evolution. The result of using Eqn. 3 will be an overestimate of the amount of quartz that interacts with the fluid during pressure solution and cementation, making the model output a useful upper bound for internally mobilized silica.

At each iteration of the model, oxygen atoms from the quartz dissolved at grain boundaries are allowed to fully mix with oxygen in the water (no isotope fractionation), changing the $\delta^{18}O_{water}$ value accordingly, before a volume of quartz cement is precipitated that is equivalent to the volume of quartz initially dissolved at the grain boundaries. The $\delta^{18}O$ value of the newly precipitated overgrowth quartz is calculated using the quartz-water equilibrium fractionation (Clayton et al., 1972; Friedman and O'Neil, 1977) and the temperature gained from a geotherm curve as an additional input. The change that is induced in the $\delta^{18}O_{water}$ by the

cementation process is also calculated and is used as the $\delta^{18}\text{O}$ value for pore water during the next iteration of the model.

As porosity is reduced, water is assumed to leave the system parallel to bedding, with no vertical mixing of pore fluids. This first-order approximation of fluid removal is a reasonable place to start given that within the Travis Peak the most permeable fluid conduits lie in the laterally extensive channel sandstones. No overpressuring of fluids is assumed in the model. As present-day fluid-pressure gradients show no evidence of significant overpressuring in eastern Texas Travis Peak Formation sandstones, this is a reasonable conclusion (Bartberger et al., 2003).

Additional discussion of model assumptions, limitations, and sensitivity to the various input parameters may be found in Appendix 4.5. The R code used to run these simulations is available in Appendix 4.6.

5.2 Formation Input Parameters

The porosity-depth curve for the Travis Peak Formation in eastern Texas was found by averaging data collected by Dutton and Diggs (1992) over present-day depths ranging from 1800 to 3000 m, and then correcting the averaged data 450 m deeper to account for the ~450 m of sediment that is estimated to have been removed during the present period of exposure. Initial porosity within Travis Peak sandstone is thought to have been as high as 40% based on present-day analogues (Houseknecht, 1987; Dutton and Land, 1988); as a higher initial porosity can potentially accommodate higher amounts of pressure solution during burial, and as pressure solution and cementation would be the only way in which model $\delta^{18}\text{O}_{\text{water}}$ would be

changed, this 40% porosity value was chosen for the initial porosity value at 0 m depth.

Additional tie-points to help give the porosity curve its shape were added at 1000 m and 5000 m. Within these constraints, a burial curve for porosity of a hypothetical Travis Peak Formation in the 0-5 km depth range was generated (Figure 4.10a).

The mechanical compaction curve (the proportion of porosity loss attributable to mechanical compaction) is extremely well constrained at the near-surface (where pressure solution processes are virtually nonexistent) and at depths greater than 3 km (where cementation and pressure solution are considered the dominant drivers of porosity loss in sandstones). Based on thin section and core-analysis data, Dutton and Diggs (1992) concluded that mechanical compaction was the dominant cause of porosity loss during the first 1 km of burial, but by 1.5 km, cementation was the dominant driver of porosity loss and mechanical compaction had all but ceased. This approach is further supported by studies investigating the temperature-dependent precipitation rates of α -quartz which indicate that significant volumes of overgrowth quartz are unlikely to directly precipitate at temperatures below $\sim 70^\circ\text{C}$ (Bjorlykke and Egeberg, 1993; Walderhaug, 1994; Lander et al., 2008). A fraction mechanical compaction curve was generated to approximate these constraints (Figure 4.10b).

A geotherm of $40^\circ\text{C}/\text{km}$ was assumed to calculate the quartz-water $\delta^{18}\text{O}$ fractionation during cementation, and for the calculation of depth of quartz precipitation from fluid inclusion temperatures. This geotherm is based on a combination of present-day geothermal gradient data and basin models for organic maturity evolution (Figure 4.10c) (Dutton, 1987). Based upon SIMS data collected in this study and by others (Williams et al., 1997), a value of 13‰ was chosen as the average $\delta^{18}\text{O}$ value for detrital quartz in the Travis Peak Formation.

6. Discussion

6.1 Geochemical Data

The observed trends of increasing temperature from 128 to 152 °C coincident with increasing $\delta^{18}\text{O}_{\text{water}}$ from 4.5 to 7.5‰ (Figure 4.8) are consistent with an interpretation of burial-driven water-rock interaction progressively affecting pore water $\delta^{18}\text{O}$ values. Given that samples SFE2 and SFOT1 were collected ~25km apart, the increasing separation between the two trends at higher temperatures is striking and suggests increasing heterogeneity in pore water chemistry during maximum burial (Figure 4.8). The ~1‰ offset observed between the range of gap deposit quartz $\delta^{18}\text{O}$ values and the range of lateral deposit quartz values in both wells (Figure 4.7) can be explained by the petrographic relationship between those two groups of quartz; the formation of lateral deposit quartz necessitates prior formation of gap deposit quartz, and if fluid $\delta^{18}\text{O}$ values were increasing in this time of maximum burial, the last growth generations of quartz should be highest in $\delta^{18}\text{O}$.

Quartz cement textures demonstrate the temporal equivalence of some quartz trapped fluid inclusions with lateral quartz that lacks fluid inclusions (Figures 4.5, 4.6). Where such equivalences can be shown, isotopic values in equivalent gap and lateral deposits closely match, as expected. Although unsurprising, this is a key observation, since it means that with calibration with fluid inclusion assemblages, isotopic measurements can be used to extend temperature records to quartz filled and quartz lined fractures that lack fluid inclusion assemblages. This can be critical information for using geomechanical data to constrain the history of fracture and fracture pattern development (e.g., Hooker et al., 2018).

6.2 Model Results

To rigorously test the model, nearly 300,000 runs were iteratively performed across all reasonable ranges and combinations of input parameters. Though some of these models resulted in matches to one or two of the available datasets ($\delta^{18}\text{O}_{\text{quartz}}$, $\delta^{18}\text{O}_{\text{water}}$, and % cement), none resulted in simultaneous matches to all three. Matches to all three datasets *can* be achieved if unreasonably early pressure solution (mechanical compaction <0.5 at 0 km), unreasonably high initial $\delta^{18}\text{O}_{\text{water}}$ ($>\sim 5\text{‰}$) and unreasonably high $\delta^{18}\text{O}_{\text{quartz}}$ ($>\sim 18\text{‰}$) are simultaneously selected as inputs. As each of these inputs is considered to be highly unlikely given our current understanding of quartz cement precipitation and empirical data from the Travis Peak Formation, this combination of input conditions is considered untenable. The results of these model runs, as well as sensitivity testing of the model to varying input parameters, can be found in Appendix 4.5.

In general, modeled results fail to match available data because $\delta^{18}\text{O}_{\text{water}}$ and precipitated $\delta^{18}\text{O}_{\text{quartz}}$ both trend too low in $\delta^{18}\text{O}$ at depth, and modeled % cement results are lower than is observed in thin section. This latter mismatch is more severe than it initially appears to be, as the initial use of Eqn. 3 in constructing this model indicates that the model is almost certainly overestimating the percent quartz cement at depth compared to what one would expect from rounded grain morphologies.

6.2.1 Model Behavior Using Best Estimate Inputs

To better elucidate why the model behaves the way it does, an example is provided here that uses the best estimates for inputs for changing porosity with depth (Figure 4.10a),

rates of mechanical compaction with depth (Figure 4.10b), a geotherm of 40°C/km (Figure 4.10c), and an average detrital quartz $\delta^{18}\text{O}$ composition of 13‰. Despite observations suggesting that all of these input parameters are realistic, the model is simultaneously incapable of fitting available $\delta^{18}\text{O}_{\text{quartz}}$, $\delta^{18}\text{O}_{\text{water}}$, and % cement data (Figure 4.11). The failure of this simple model to reproduce the data can be understood as being due to two controlling factors that have been underappreciated in previous literature.

First, dissolving and reprecipitating detrital quartz will drive $\delta^{18}\text{O}_{\text{water}}$ values lower across much of the range of diagenetic temperatures and $\delta^{18}\text{O}_{\text{water}}$ observed in sedimentary basins. Wholesale pressure solution of detrital grains, if done in the absence of cementation, will drive $\delta^{18}\text{O}_{\text{water}}$ towards the $\delta^{18}\text{O}$ value of detrital grains. However, to maintain this condition a sink for silica, internal or external to the system, must be established. In the model this sink is internal to the system and is solely composed of quartz overgrowth precipitation, which will fractionate $\delta^{18}\text{O}$ under equilibrium conditions (Figure 4.1). For much of the range of diagenetic temperatures, precipitated overgrowth quartz will possess higher $\delta^{18}\text{O}$ values than the typical detrital grain $\delta^{18}\text{O}$ compositions from which the silica is originally derived. Because of this, during initial quartz sandstone burial $\delta^{18}\text{O}_{\text{water}}$ will often be driven towards lower values until the difference in $\delta^{18}\text{O}$ value between the dissolving detrital grain and pore water becomes greater than the difference in $\delta^{18}\text{O}$ value between precipitating diagenetic overgrowth quartz and pore water. This is the underlying cause of the modeled initial decrease (at depths <3 km) and subsequent rise (at depths >3 km) in $\delta^{18}\text{O}_{\text{water}}$ in Figure 4.11a.

The second controlling factor that prevents the model from reproducing the data is that, in a closed system, the amount of grain boundary pressure solution must be sufficiently large to

produce the observed volume of cement. The mechanical compaction curve shown in Figure 4.10b, while consistent with current thinking on rates of cementation in sandstones, ultimately does not allow enough silica to be produced to explain the amount of cement that has been observed for Travis Peak sandstones (Figure 4.11c). However, it is also worth noting that modifying the mechanical compaction contribution curve in Figure 4.10b in a way that produces more silica cement only magnifies the impact of the first factor previously discussed above.

6.2.2 Potentially Significant Non-Grain Boundary Influences on Fluid Composition

If a closed system pure quartz sandstone model cannot explain the observed data, it now becomes necessary to find an alternate explanation. One immediate possibility is the influx of significant fluids from outside the formation, or at the very least from outside of the channel sandstones. There is evidence both for and against invoking external fluids. Sourcing of silica within the Travis Peak Formation sandstones remains an unresolved issue; on the basis of 431 thin sections, Dutton and Diggs (1990) concluded that observed grain-boundary pressure solution and stylolites could only account for 20% of the quartz overgrowth cement volume, implying influx of silica from outside of the sandstones and open system behavior. In contrast, salinity measurements made from fluid inclusion assemblages for these same quartz bridges by Becker et al. (2010) hover around 15 wt. % NaCl equivalent and do not change over the duration of quartz bridge development, implying closed system behavior. If the search for alternate influences on $\delta^{18}\text{O}_{\text{water}}$ is limited to the Travis Peak Formation, there are four potentially important diagenetic processes that have not been included in the model—the smectite to illite transition, the dissolution and reprecipitation of carbonates, the reprecipitation of early-precipitated quartz phases, and quartz dissolution along macroscopic

quartz sandstone stylolites. In this section, the potential relative influence of these four, relatively local, diagenetic processes will be weighed and discussed.

The smectite to illite transition is of particular relevance to this discussion because it can release large amounts of silica into the pore water (as much as 11% of the original smectite mass) (Towe, 1962; Boles and Franks, 1979), and is capable of significantly influencing $\delta^{18}\text{O}_{\text{water}}$ towards heavier values (Land et al., 1983; Suchecky and Land, 1983; Wilkinson et al., 1992). The Travis Peak Formation contains numerous argillaceous sandstones and shale beds that bound, and can hydrodynamically isolate, channel sands. This is in contrast with the model described previously, which approximates the burial behavior of a homogeneous pure-quartz sand body. The total estimated volumes of non-channel argillaceous sandstones and mudstones in the Travis Peak ranges from 35 to 70% of the formation, or roughly half. This means that every 10% smectite by mass that was originally contained within the argillaceous sands and muds of the Travis Peak Formation could provide ~1% of the volume of quartz cement observed in clean Travis Peak sandstones, assuming that all of the silica released is transferred directly from the shaley facies into the channel sands. It is also worth noting that the restricted temperature range of the quartz bridge data (~130-150°C) lies above the range of temperatures at which the majority of clay transformation reactions are typically considered to take place (<100°C). So, while silicate reactions in argillaceous sand and mudstones adjacent to the channel sandstones may have played a role in impacting water chemistry and silica sourcing prior to the formation of these quartz bridges, clay reactions are deemed to be an unlikely source of silica for the quartz bridges themselves.

A second factor that must be weighed is the large impact that carbonate diagenesis can have on $\delta^{18}\text{O}_{\text{water}}$. As previously discussed, $\delta^{18}\text{O}_{\text{water}}$ can be driven towards higher values in detrital rocks if the difference between original detrital grain $\delta^{18}\text{O}$ values and $\delta^{18}\text{O}_{\text{water}}$ is larger than the difference between precipitated cement $\delta^{18}\text{O}$ values and $\delta^{18}\text{O}_{\text{water}}$. Because primary carbonate in sedimentary environments forms at surface temperatures (where the fractionation between carbonate minerals and water is relatively large), subsequent carbonate cement precipitation at higher burial temperatures will result in a smaller fractionation factor between carbonate cement and water, making reprecipitating carbonate grains an important lever with which $\delta^{18}\text{O}$ pore water may be driven to higher values. Fe-zoned dolomites with ankeritic overgrowths were observed to occupy pore space in cores SFE2 and SFOT1, and previous authors have reported that dolomite and ankerite cements represent a small but significant component of the Travis Peak sandstones (2% by volume in fluvial sandstones and 4% in paralic sandstones; Dutton, 1987). Euhedral Fe-zonation within these cements does not indicate significant carbonate grain-boundary pressure solution, and so pressure solution between carbonate cements is unlikely to explain observed $\delta^{18}\text{O}_{\text{water}}$ values within these channel sandstones. However, the presence of ankerite cements within the fracture in SFE2 indicates the growth of carbonate cements in Travis Peak sandstones through maximum burial. If these precipitating ankerites are deriving their ions from fluids that interacted with an isotopically heavy mineral source (recrystallizing or dissolving calcite originally precipitated at lower temperatures would be a likely candidate), then the presence of ankerite indicates a means by which $\delta^{18}\text{O}$ water might be driven towards higher values.

A third possible influencing factor is the recrystallization of early low-temperature opaline silica phases. These are known to play active roles in the development of silcretes and low temperature, high- $\delta^{18}\text{O}$ silica cements (Williams and Crerar, 1985; Kelly et al., 2007); if hydrous silica phases were initially present during early burial of the Travis Peak Formation and then later recrystallized to α -quartz, the reequilibration of the overgrowths with pore fluids during recrystallization could have played a significant role in driving $\delta^{18}\text{O}_{\text{water}}$ to higher values. However, all overgrowths observed were syntaxial, and no fibrous CL textures were observed in overgrowths within these samples, as might be expected if these overgrowths were recrystallized from early opaline silica. Modeling for this study was conducted assuming minimal precipitation of quartz cement shallower than 1.5 km, as has been interpreted by prior authors (Dutton and Diggs, 1992). Sources of silica outside of the sandstones cannot be ruled out; the dissolution and reprecipitation of biomineralized silica within the adjacent shales is a distinct possibility. Early reprecipitation of biomineralized silica has been recognized as a significant source of diagenetic silica in shales (Schieber et al., 2000).

A fourth factor that warrants mentioning is the development of stylolites within the sandstone which may have influenced pore water $\delta^{18}\text{O}$ and silica sourcing for cement. Throughout the study area, previous authors have identified stylolites within the Travis Peak Formation, the number of which increases with burial depth and reaches peak abundance below 2440 m (Dutton and Diggs, 1990, 1992). Because stylolites localize pressure solution and silica generation to narrow sub-horizontal zones within a sedimentary rock, they are a major potential source for silica within the Travis Peak. Dutton and Diggs (1990) used compiled thin section data on stylolite frequency and stylolite heights to estimate that only between 4 to 12%

of quartz cement within the Travis Peak could have sourced their silica from pressure solution along stylolites (equivalent to between ~0.6 to 2.3% cement of the rock by volume, compared to the average of 17% cement). The presence of stylolites could help to explain the deficit between model and observed % cement (e.g., Figure 4.11c), particularly if stylolite abundance or silica flux from stylolites were underestimated. However, explaining the mismatch between modeled and observed % cement by increasing the amount of silica sourced from stylolites would do little to explain the observed $\delta^{18}\text{O}_{\text{quartz}}$ and $\delta^{18}\text{O}_{\text{water}}$ trends, due to the chemical processes described above.

6.2.3 Implications for Closed vs. Open System

As aforementioned, no reasonable sets of model inputs were able to reproduce available data. The failure of repeated runs of the closed system model to match available data under an array of conditions suggests that the observed data can only be produced through open system behavior, with silica and water being sourced from somewhere external to the channel sandstones. This implies that a large flux of fluid passed into or through the channel sandstones of the Travis Peak Formation prior to maximum burial. Such a fluid could have served as the source for additional silica, and must have contained $\delta^{18}\text{O}_{\text{water}}$ values inconsistent with the expected $\delta^{18}\text{O}_{\text{water}}$ from quartz-water interaction within the Travis Peak Formation, the fluid being derived from a different history of mineral-water interaction.

The observation that $\delta^{18}\text{O}_{\text{water}}$ varies during quartz bridge growth is in contrast with salinity measurements made from fluid inclusion assemblages for these same quartz bridges by Becker et al. (2010), which hover around 15 wt. % NaCl equivalent and do not change over the duration of quartz bridge development. This simultaneous juxtaposition of one proxy that

implies closed system behavior (i.e., unchanged salinity) with one that implies open system behavior (i.e., varying $\delta^{18}\text{O}_{\text{water}}$) emphasizes the care that must be taken when making closed or open system interpretations. During water-rock interaction, it is not unreasonable to expect some chemical proxies to remain constant while others change, and which proxies will imply closed system behavior is dependent on both the timing of proxy preservation and the extent (both vertical and lateral) of the system as defined by the investigator.

7. Conclusions

Using sequences of quartz deposits progressively accumulated in fractures, new data from the Travis Peak Formation reveal trends of increasingly heavy pore water in response to water-rock interaction during burial. A one-dimensional model created using prior geological constraints on the compaction and cementation history requires that these trends in $\delta^{18}\text{O}_{\text{water}}$ indicate a significant fluid flux into the Travis Peak Formation channel sandstones, which provided an additional source of silica and significantly affected both $\delta^{18}\text{O}_{\text{water}}$ and precipitated $\delta^{18}\text{O}_{\text{quartz}}$. This research demonstrates that a combined study of temperatures from fluid inclusion assemblages and in situ $\delta^{18}\text{O}$ measurements by SIMS on fracture-bridging crack-seal quartz cements can reveal detailed pore water $\delta^{18}\text{O}$ records. By using quartz cement textures to link quartz-trapping fluid inclusions with quartz that lacks fluid inclusions, our work shows how isotopic analysis can extend temperature records to quartz-filled and quartz-lined fractures lacking fluid inclusion assemblages. Measuring such records and testing them against predictive models will allow for improved constraints on water-rock interaction, and provide a new approach to studying burial history.

Appendices

Appendix 4.1 – Condensed SIMS dataset (.xlsx)

Appendix 4.2 – Full SIMS dataset (.xlsx)

Appendix 4.3 – Method used to determine that intersected fluid inclusions do not affect SIMS values in quartz (.doc)

Appendix 4.4.1 – Map of analyzed quartz in SFE2 (zoom in for SIMS pit labels) (.pdf)

Appendix 4.4.2 – Map of analyzed quartz in SFOT1 (zoom in for SIMS pit labels) (.pdf)

Appendix 4.5 – Burial model and sensitivity analysis (.doc)

Appendix 4.6 – R code (.txt)

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References

- Aplin, A.C., and Warren, E.A., 1994, Oxygen isotopic indications of the mechanisms of silica transport and quartz cementation in deeply buried sandstones: *Geology*, v. 22, p. 847–850, doi: 10.1130/0091-7613(1994)022<0847:OIIOTM>2.3.CO;2.d
- Ayalon, A., and Longstaffe, F.J., 1988, Oxygen isotope studies of diagenesis and pore-water evolution in the Western Canada Sedimentary Basin: evidence from the Upper Cretaceous Basal Belly River Sandstone, Alberta: *Journal of Sedimentary Research*, v. 58, p. 489–505.
- Bartberger, C.E., Dyman, T.S., and Condon, S.M., 2003, Potential for deep basin-centered gas accumulation in Travis Peak (Hosston) Formation, Gulf Coastal Basin: U.S. Geological Survey Bulletin 2184–E, 36 p., <http://pubs.er.usgs.gov/publication/b2184E> (accessed August 2016).
- Becker, S.P., Eichhubl, P., Laubach, S.E., Reed, R.M., Lander, R.H., and Bodnar, R.J., 2010, A 48 m.y. history of fracture opening, temperature, and fluid pressure: Cretaceous Travis Peak Formation, East Texas basin: *Geological Society of America Bulletin*, v. 122, p. 1081–1093, doi: 10.1130/B30067.1.
- Bethke, C.M., 1986, Hydrologic constraints on the genesis of the Upper Mississippi Valley Mineral District from Illinois basin brines: *Economic Geology*, v. 81, p. 233–249.
- Bethke, C.M., Reed, J.D., and Oltz, D.F., 1991, Long-range petroleum migration in the Illinois Basin: *AAPG Bulletin*, v. 75, p. 925–945.
- Boles, J.R., and Franks, S.G., 1979, Clay diagenesis in Wilcox Sandstones of Southwest Texas: implications of smectite diagenesis on sandstone cementation: *Journal of Sedimentary Research*, v. 49, p. 55–70.
- Bowen, G.J., 2010, Isoscapes: spatial pattern in isotopic biogeochemistry: *Annual Review of Earth and Planetary Sciences*, v. 38, p. 161–187, doi: 10.1146/annurev-earth-040809-152429.
- Clayton, R.N., O'Neil, J.R., and Mayeda, T.K., 1972, Oxygen isotope exchange between quartz and water: *Journal of Geophysical Research*, v. 77, p. 3057–3067, doi: 10.1029/JB077i017p03057.
- Davies, D.K., Williams, B.P.J., and Vessell, R.K., 1991, Reservoir models for meandering and straight fluvial channels; examples from the Travis Peak Formation, East Texas: v. 41, p. 152–174, <http://archives.datapages.com/data/gcags/data/041/041001/0152.htm>.
- Denny, A.C., Kozdon, R., Kitajima, K., and Valley, J.W., 2017, Isotopically zoned carbonate cements in Early Paleozoic sandstones of the Illinois Basin: $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records of

- burial and fluid flow: *Sedimentary Geology*, v. 361, p. 93–110, doi: 10.1016/j.sedgeo.2017.09.004.
- Dutton, S.P., 1987, Diagenesis and burial history of Lower Cretaceous Travis Peak Sandstone, east Texas: The University of Texas at Austin, Bureau of Economic Geology Report of Investigations, v. 164, p. 58.
- Dutton, S.P., and Diggs, T.N., 1990, History of quartz cementation in the Lower Cretaceous Travis Peak Formation, East Texas: *Journal of Sedimentary Research*, v. 60, p. 191–202.
- Dutton, S.P., and Diggs, T.N., 1992, Evolution of porosity and permeability in the Lower Cretaceous Travis Peak Formation, East Texas: *AAPG Bulletin*, v. 76, p. 252–269.
- Dutton, S.P., and Land, L.S., 1988, Cementation and burial history of a low-permeability quartzarenite, Lower Cretaceous Travis Peak Formation, East Texas: *GSA Bulletin*, v. 100, p. 1271–1282, doi: 10.1130/0016-7606(1988)100<1271:CABHOA>2.3.CO;2.
- Dutton, S. P., Laubach, S. E., Tye, R. S., Baumgardner, R. W., Jr., and Herrington, K. L., 1991, Geologic characterization of low-permeability gas reservoirs, Travis Peak Formation, East Texas: The University of Texas at Austin, Bureau of Economic Geology Report of Investigations, no. 204, p. 89.
- Fall, A., Eichhubl, P., Bodnar, R.J., Laubach, S.E., and Davis, J.S., 2015, Natural hydraulic fracturing of tight-gas sandstone reservoirs, Piceance Basin, Colorado: *Geological Society of America Bulletin*, v. 127, p. 61–75, doi: 10.1130/B31021.1.
- Fall, A., Eichhubl, P., Cumella, S.P., Bodnar, R.J., Laubach, S.E., and Becker, S.P., 2012, Testing the basin-centered gas accumulation model using fluid inclusion observations: Southern Piceance Basin, Colorado: *AAPG Bulletin*, v. 96, p. 2297–2318, doi: 10.1306/05171211149.
- Fall, A., Ukar, E., and Laubach, S.E., 2016, Origin and timing of Dauphiné twins in quartz cement in fractured sandstones from diagenetic environments: Insight from fluid inclusions: *Tectonophysics*, v. 687, p. 195–209, doi: 10.1016/j.tecto.2016.08.014.
- Friedman, I., and O'Neil, J.R., 1977, Chapter K.K. Compilation of stable isotope fractionation factors of geochemical interest, *in* Fleischer, M. ed., *Data of Geochemistry*, U. S. Geological Survey Professional Paper, v. 440, p. 1–12.
- Graham, C.M., Valley, J.W., and Winter, B.L., 1996, Ion microprobe analysis of $^{18}\text{O}/^{16}\text{O}$ in authigenic and detrital quartz in the St. Peter Sandstone, Michigan Basin and Wisconsin Arch, USA: contrasting diagenetic histories: *Geochimica et Cosmochimica Acta*, v. 60, p. 5101–5116, doi: 10.1016/S0016-7037(96)00286-4.

- Harwood, J., Aplin, A.C., Fialips, C.I., Iliffe, J.E., Kozdon, R., Ushikubo, T., and Valley, J.W., 2013, Quartz cementation history of sandstones revealed by high-resolution SIMS oxygen isotope analysis: *Journal of Sedimentary Research*, v. 83, p. 522–530.
- Heydari, E., 1997, Hydrotectonic models of burial diagenesis in platform carbonates based on formation water geochemistry in North American sedimentary basins, *in* Basin-Wide Diagenetic Patterns: Integrated Petrologic, Geochemical, and Hydrologic Considerations, SEPM Special Publication 57, p. 53–79, http://archives.datapages.com/data/sepm_sp/SP57/Hydrotectonic_Models_of_Burial.html.
- Hooker, J.N., Laubach, S.E., and Marrett, R., 2018, Microfracture spacing distributions and the evolution of fracture patterns in sandstones. *Journal of Structural Geology* v. 108, p. 66–79. doi.org/10.1016/j.jsg.2017.04.001
- Hooker, J.N., Larson, T.E., Eakin, A., Laubach, S.E., Eichhubl, P., Fall, A., and Marrett, R., 2015, Fracturing and fluid flow in a sub-décollement sandstone; or, a leak in the basement: *Journal of the Geological Society*, v. 172, p. 428–442, doi: 10.1144/jgs2014-128.
- Houseknecht, D.W., 1987, Assessing the Relative Importance of Compaction Processes and Cementation to Reduction of Porosity in Sandstones: *AAPG Bulletin*, v. 71, p. 633–642.
- Hyodo, A., Kozdon, R., Pollington, A.D., and Valley, J.W., 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*, v. 384, p. 168–180, doi: 10.1016/j.chemgeo.2014.06.021.
- Jackson, M.L., and Laubach, S.E., 1991, Structural history and origin of the Sabine Arch, east Texas and northwest Louisiana: University of Texas at Austin, Bureau of Economic Geology, Geological Circular, v. 91-3, 47 p.
- Kelly, J.L., Fu, B., Kita, N.T., and Valley, J.W., 2007, Optically continuous silcrete quartz cements of the St. Peter Sandstone: High precision oxygen isotope analysis by ion microprobe: *Geochimica et Cosmochimica Acta*, v. 71, p. 3812–3832.
- Kita, N.T., Ushikubo, T., Fu, B., and Valley, J.W., 2009, High precision SIMS oxygen isotope analysis and the effect of sample topography: *Chemical Geology*, v. 264, p. 43–57, doi: 10.1016/j.chemgeo.2009.02.012.
- Land, L.S., 1980, The Isotopic and Trace Element Geochemistry of Dolomite: The State of The Art, *in* Concepts and Models of Dolomitization, SEPM Special Publication 28, p. 87–110.
- Land, L.S., 1983, The application of stable isotopes to studies of the origin of dolomite and to problems of diagenesis of clastic sediments, *in* SEPM Short Course, Stable isotopes in sedimentary geology, v. 10, p. 4.1-4.22.

- Lander R.H., and Laubach, S.E., 2015, Insights into rates of fracture growth and sealing from a model for quartz cementation in fractured sandstones. *Geological Society of America Bulletin* v. 127 (3-4), p. 516-538. doi: 10.1130/B31092.1
- Laubach, S.E., 1988, Subsurface fractures and their relationship to stress history in East Texas basin sandstone: *Tectonophysics*, v. 156, p. 37–49, doi: 10.1016/0040-1951(88)90281-8.
- Laubach, S.E., 2003, Practical approaches to identifying sealed and open fractures: *AAPG Bulletin*, v. 87, p. 561–579.
- Laubach, S. E., and Jackson, M. L. W., 1990, Origin of arches in the northwestern Gulf of Mexico basin: *Geology*, v. 18, no. 7, p. 595–598.
- Laubach, S.E., Reed, R.M., Olson, J.E., Lander, R.H., and Bonnell, L.M., 2004a, Coevolution of crack-seal texture and fracture porosity in sedimentary rocks: cathodoluminescence observations of regional fractures: *Journal of Structural Geology*, v. 26, p. 967–982, doi: 10.1016/j.jsg.2003.08.019.
- Laubach, S.E., Lander, R., Bonnell, L., Olson, J., and Reed, R., 2004b, Opening histories of fractures in sandstone: in Cosgrove, J.W., and Engelder, T., editors, *The initiation, propagation, and arrest of joints and other fractures*, Geological Society of London Special Publication 231, 1-9.
- Laubach, S.E., Fall, A., Copley, L.K., Marrett, R., Wilkins, S.J., 2016, Fracture porosity creation and persistence in a basement-involved Laramide fold, Upper Cretaceous Frontier Formation, Green River Basin, USA: *Geological Magazine* 153, 887-910.
- Lee, M., Aronson, J.L., and Savin, S.M., 1989, Timing and conditions of Permian Rotliegende sandstone diagenesis, Southern North Sea: K/Ar and Oxygen Isotopic Data: *AAPG Bulletin*, v. 73, p. 195–215.
- Linzmeier, B. J., Kitajima, K., Denny, A. C., and Cammack, J. N., 2018, Making maps on a micrometer scale, *Eos*, v. 99, <https://doi.org/10.1029/2018EO099269>.
- Marchand, A.M.E., Haszeldine, R.S., Macaulay, C.I., Swennen, R., and Fallick, A.E., 2000, Quartz cementation inhibited by crestal oil charge: Miller deep water sandstone, UK North Sea: *Clay Minerals*, v. 35, p. 205–214.
- McBride, E.F., Land, L.S., and Mack, L.E., 1987, Diagenesis of eolian and fluvial feldspathic sandstones, Norphlet Formation (Upper Jurassic), Rankin County, Mississippi, and Mobile County, Alabama: *AAPG Bulletin*, v. 71, p. 1019–1034.
- Millán, M.I., Machel, H., and Bernasconi, S.M., 2016, Constraining Temperatures of Formation and Composition of Dolomitizing Fluids In the Upper Devonian Nisku Formation (Alberta, Canada) With Clumped Isotopes: *Journal of Sedimentary Research*, v. 86, p. 107–112.

- Milliken, K.L., Land, L.S., and Loucks, R.G., 1981, History of burial diagenesis determined from isotopic geochemistry, Frio Formation, Brazoria County, Texas: AAPG Bulletin, v. 65, p. 1397–1413.
- Pollington, A.D., Kozdon, R., and Valley, J.W., 2011, Evolution of quartz cementation during burial of the Cambrian Mount Simon Sandstone, Illinois Basin: In situ microanalysis of $\delta^{18}\text{O}$: Geology, v. 39, p. 1119–1122.
- Pollington, A.D., Kozdon, R., Anovitz, L.M., Georg, R.B., Spicuzza, M.J., and Valley, J.W., 2016, Experimental calibration of silicon and oxygen isotope fractionations between quartz and water at 250 °C by in situ microanalysis of experimental products and application to zoned low $\delta^{30}\text{Si}$ quartz overgrowths: Chemical Geology, v. 421, p. 127–142, doi: 10.1016/j.chemgeo.2015.11.011.
- Schieber, J., Krinsley, D., and Riciputi, L., 2000, Diagenetic origin of quartz silt in mudstones and implications for silica cycling: Nature, v. 406, p. 981–985, doi:10.1038/35023143.
- Śliwiński, M.G., Kozdon, R., Kitajima, K., Denny, A., and Valley, J.W., 2016, Microanalysis of carbonate cement $\delta^{18}\text{O}$ in a CO_2 -storage system seal: Insights into the diagenetic history of the Eau Claire Formation (Upper Cambrian), Illinois Basin: AAPG Bulletin, v. 100, p. 1003–1031.
- Suchecky, R.K., and Land, L.S., 1983, Isotopic geochemistry of burial-metamorphosed volcanogenic sediments, Great Valley sequence, northern California: Geochimica et Cosmochimica Acta, v. 47, p. 1487–1499, doi: 10.1016/0016-7037(83)90308-3.
- Towe, K.M., 1962, Clay mineral diagenesis as a possible source of silica cement in sedimentary rocks: Journal of Sedimentary Research, v. 32, p. 26–28.
- Tye, R.S., 1992, Fluvial sandstone reservoirs of the Travis Peak Formation, East Texas Basin, in Miall, A.D. and Tyler, N. eds., The three-dimensional facies architecture of terrigenous clastic sediments, and its application for hydrocarbon discovery and recovery, SEPM Concepts in Sedimentology and Paleontology, v. 3, p. 172–188, http://archives.datapages.com/data/sepm_sp/csp3/Fluvial-Sandstone_ReservoirsOp.htm.
- Valley, J.W., and Kita, N.T., 2009, *In situ* oxygen isotope geochemistry by ion microprobe: Mineralogical Association of Canada Short Course, v. 41, p. 19–63.
- Valley, J.W., Graham, C.M., Harte, B., Eiler, J.M., and Kinny, P.D., 1998, Ion microprobe analysis of oxygen, carbon, and hydrogen isotope ratios, in McKibben, M.A. ed., Applications of Microanalytical Techniques to Understanding Mineralizing Processes, Society of Economic Geologists, Reviews in Economic Geology 7, p. 73–98.
- Wang, X.-L., Coble, M.A., Valley, J.W., Shu, X.-J., Kitajima, K., Spicuzza, M.J., and Sun, T., 2014, Influence of radiation damage on Late Jurassic zircon from southern China: Evidence

- from in situ measurements of oxygen isotopes, laser Raman, U–Pb ages, and trace elements: *Chemical Geology*, v. 389, p. 122–136, doi: 10.1016/j.chemgeo.2014.09.013.
- Wilkinson, M., Crowley, S.F., and Marshall, J.D., 1992, Model for the evolution of oxygen isotope ratios in the pore fluids of mudrocks during burial: *Marine and Petroleum Geology*, v. 9, p. 98–105, doi: 10.1016/0264-8172(92)90007-2.
- Williams, L.B., Hervig, R.L., and Dutton, S.P., 1997, Constraints on paleofluid compositions in the Travis Peak Formation, East Texas: evidence from microanalyses of oxygen isotopes in diagenetic quartz, *in* Basin-Wide Diagenetic Patterns: Integrated Petrologic, Geochemical, and Hydrologic Considerations, SEPM Special Publication 57, p. 169-280, http://archives.datapages.com/data/sepm_sp/SP57/Constraints_on_Paleofluid_Compositions.html.
- Worden, R.H., and Burley, S.D., 2003, Sandstone diagenesis: the evolution of sand to stone, *in* Burley, S.D. and Worden, R.H. eds., *Sandstone Diagenesis: Recent and Ancient*, Oxford, UK, Blackwell Publishing Ltd., p. 1–44, <http://onlinelibrary.wiley.com.ezproxy.library.wisc.edu/doi/10.1002/9781444304459.ch/summary>.

Figures

Figure 4.1. The equilibrium relationship between $\delta^{18}\text{O}$ of water, temperature, and $\delta^{18}\text{O}$ of precipitating quartz (Clayton et al., 1972; Friedman and O'Neil, 1977). If temperature or pore water $\delta^{18}\text{O}$ changes during quartz precipitation, this change may be preserved as a corresponding change in the $\delta^{18}\text{O}$ value of quartz. Four hypothetical trends are shown. (1) Trend of $\delta^{18}\text{O}_{\text{quartz}}$ values in response to an increase in temperature at constant $\delta^{18}\text{O}_{\text{water}}$. (2) Trend of $\delta^{18}\text{O}_{\text{quartz}}$ values in response to an increase in $\delta^{18}\text{O}_{\text{water}}$ values at constant temperature. (3) Constant $\delta^{18}\text{O}_{\text{quartz}}$ over a prolonged period of quartz growth if temperature and $\delta^{18}\text{O}_{\text{water}}$ both increase at proportionate rates. (4) The inverse of trend 3, where temperature and $\delta^{18}\text{O}_{\text{water}}$ decrease at proportionate rates.

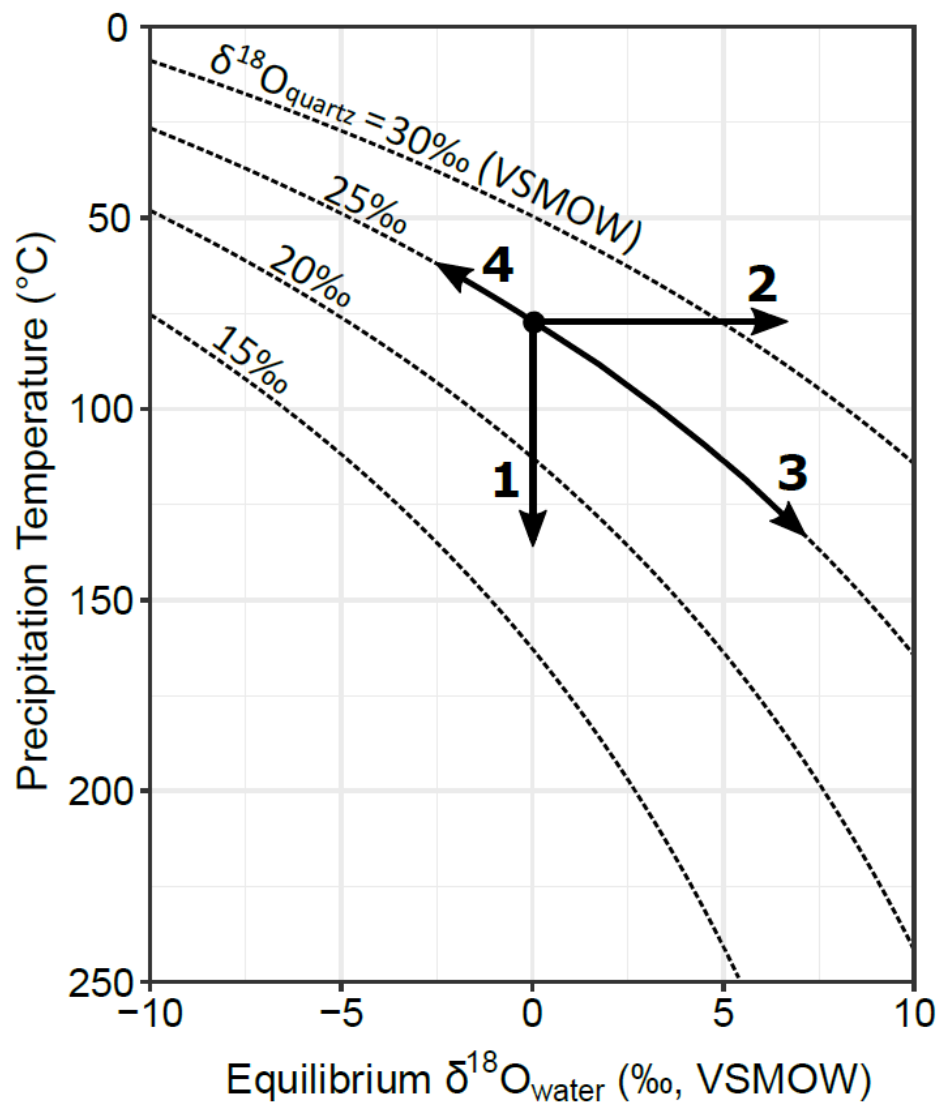


Figure 4.2. The study area in east Texas, with sample locations and important structures marked. Locations of quartz bridge samples are denoted with stars, and the wells used to help constrain model porosity burial curves are marked with dots. Modified after Dutton and Diggs (1992).

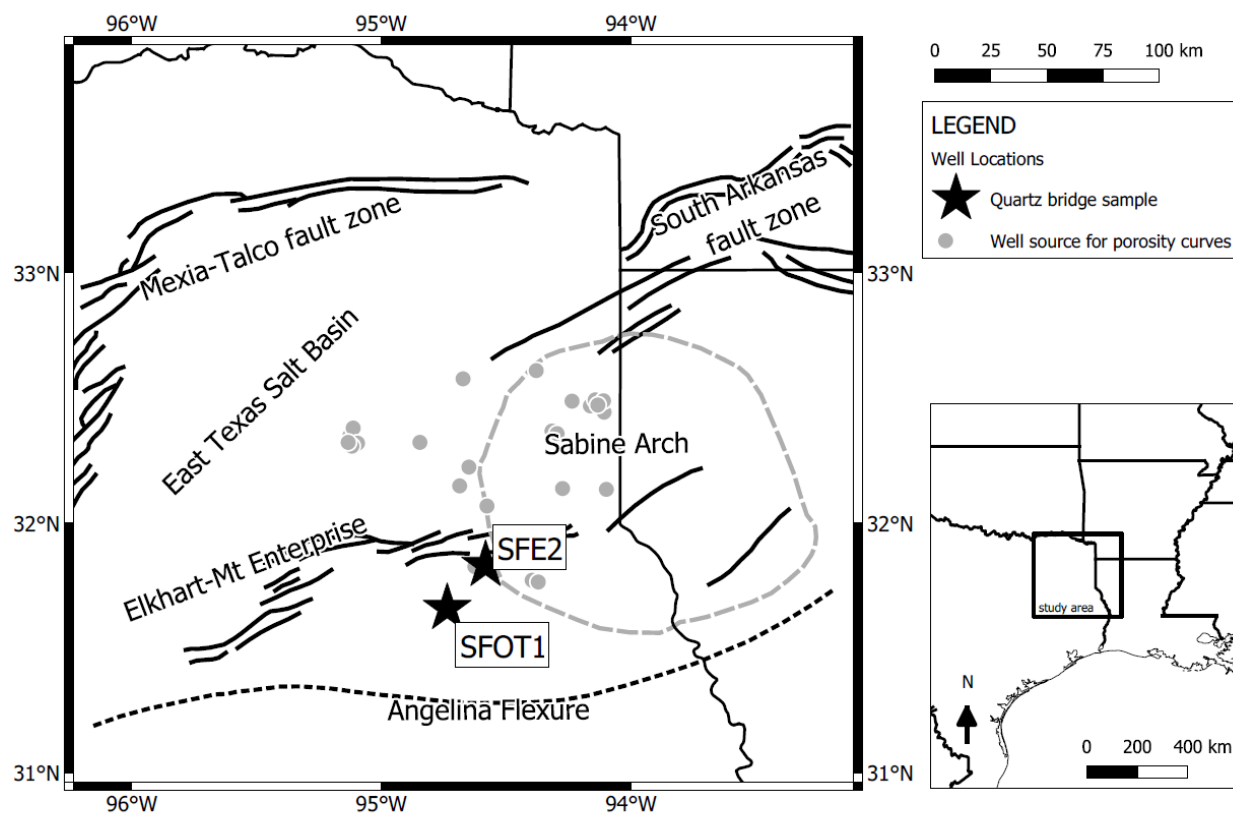


Figure 4.3. Burial history for the Travis Peak Formation in well SFE2. Uplift over the last 40 million years is thought to have removed ~450 m of overburden. Burial curve modified after Dutton and Land (1988) and Lander and Laubach (2015). Range of fracture formation from Becker et al., 2010.

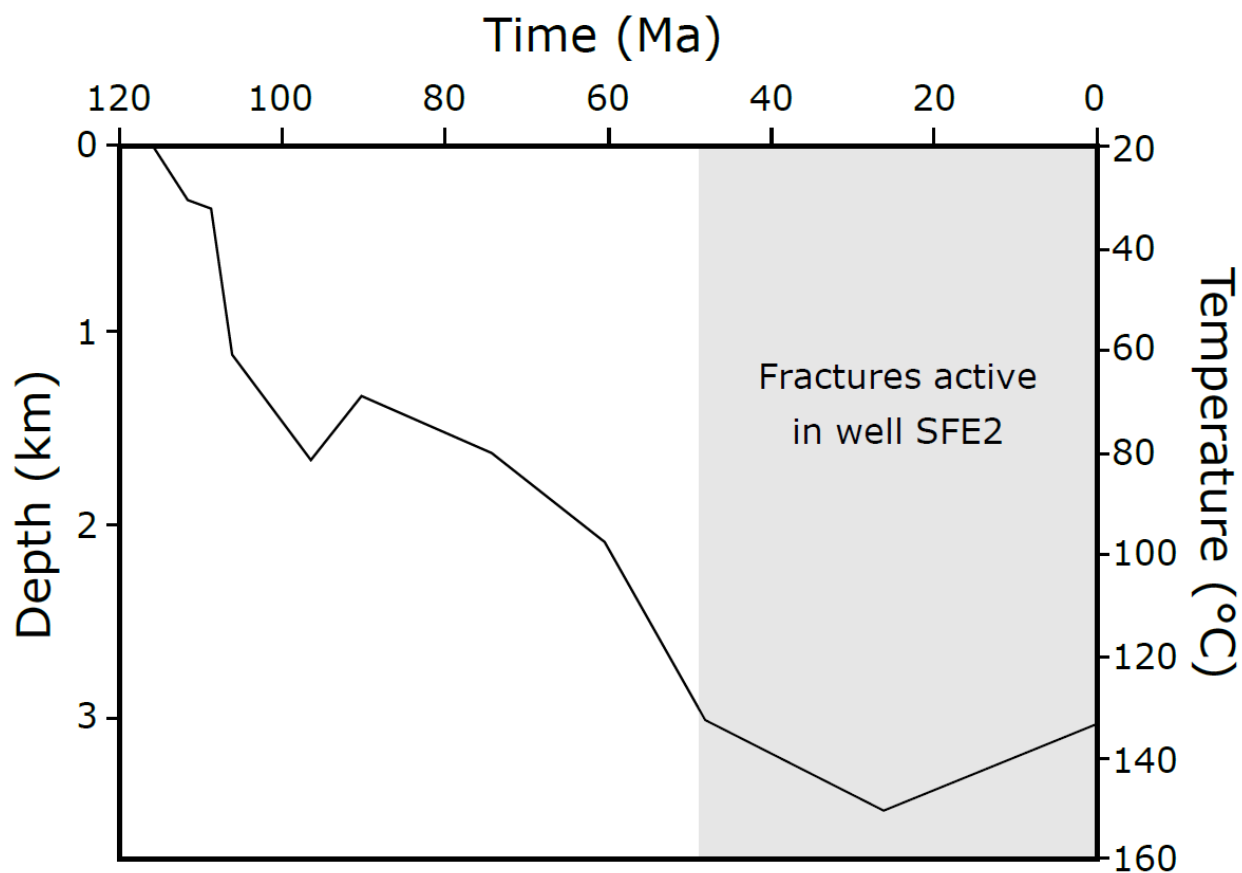


Figure 4.4. Fractures containing quartz bridges from wells SFE2 and SFOT1. **(a)** Transmitted light (plain-polarized) imagery. Dots were placed with red marker on the samples to aid the eye in identifying the ends of quartz bridges analyzed for fluid inclusions and by SIMS. **(b)** Backscattered electron maps of the same areas shown in (a). **(c)** Schematic petrography of the areas shown in (a) and (b). Study areas detailed in Figures 4.5 and 4.6 are outlined.

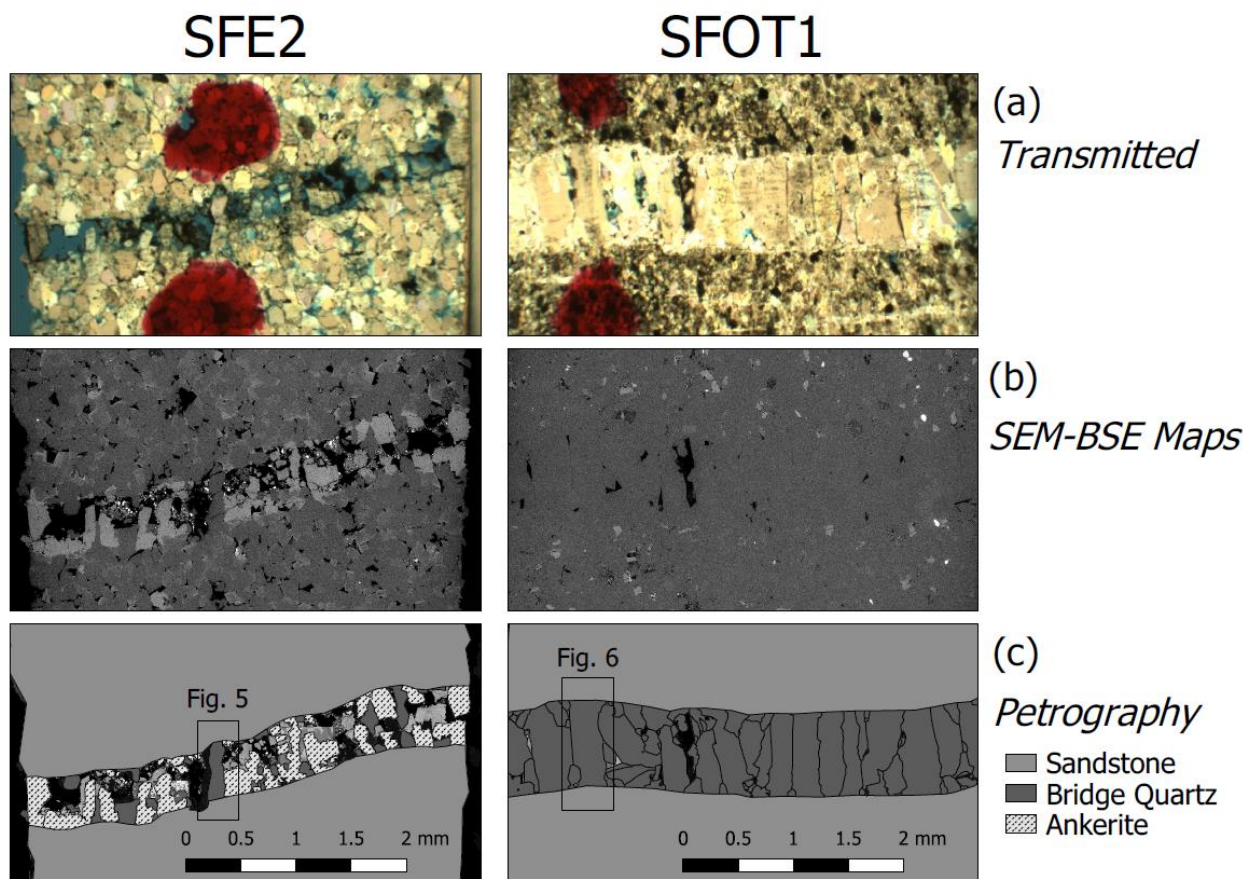


Figure 4.5. (next page) **(a)** Composited color SEM-CL image map of sample SFE2. CL imagery has not been smoothed across individual 180 μm images and boundaries between images are clearly visible. White lines denote fluid inclusion assemblages for which temperature ranges were acquired (Fall et al., 2016), a representative subset of which is reported in white text in the figure (in degrees Celsius). **(b)** Schematic petrographic map of sample SFE2. SIMS analyses are demarcated with white ovals; a representative subset of these analyses have their $\delta^{18}\text{O}$ values provided.

Fig. 5a - SFE2 composite color CL

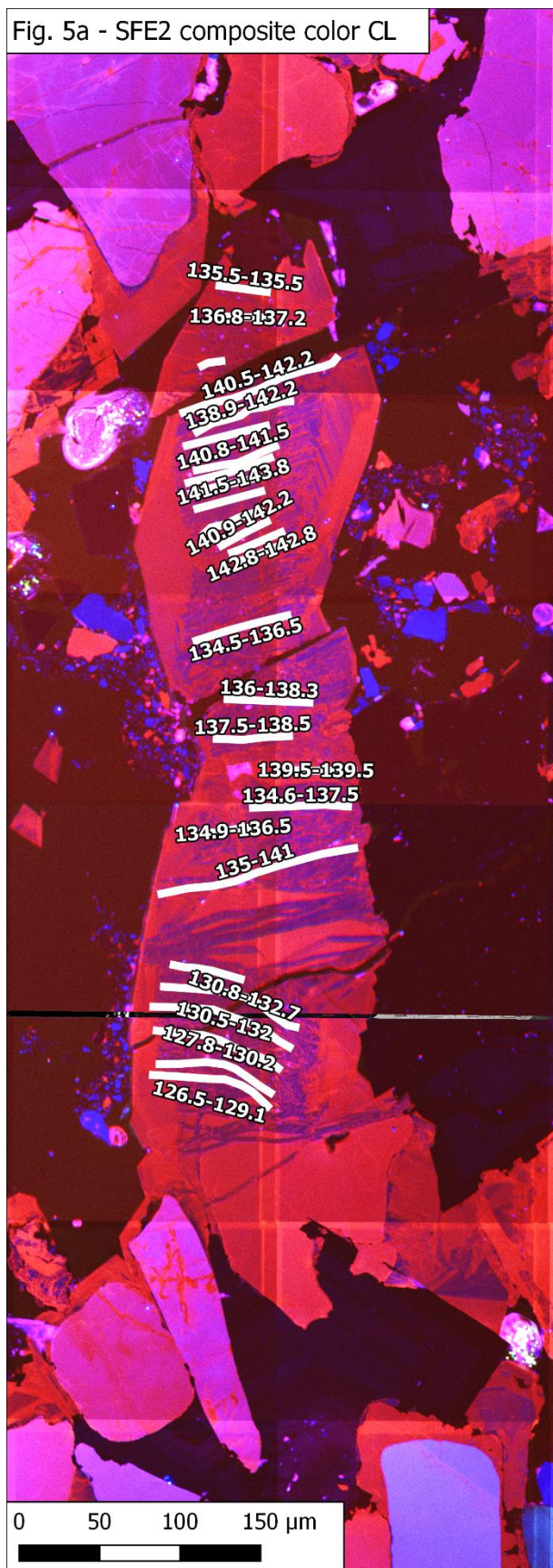


Fig. 5b - SFE2 petrography

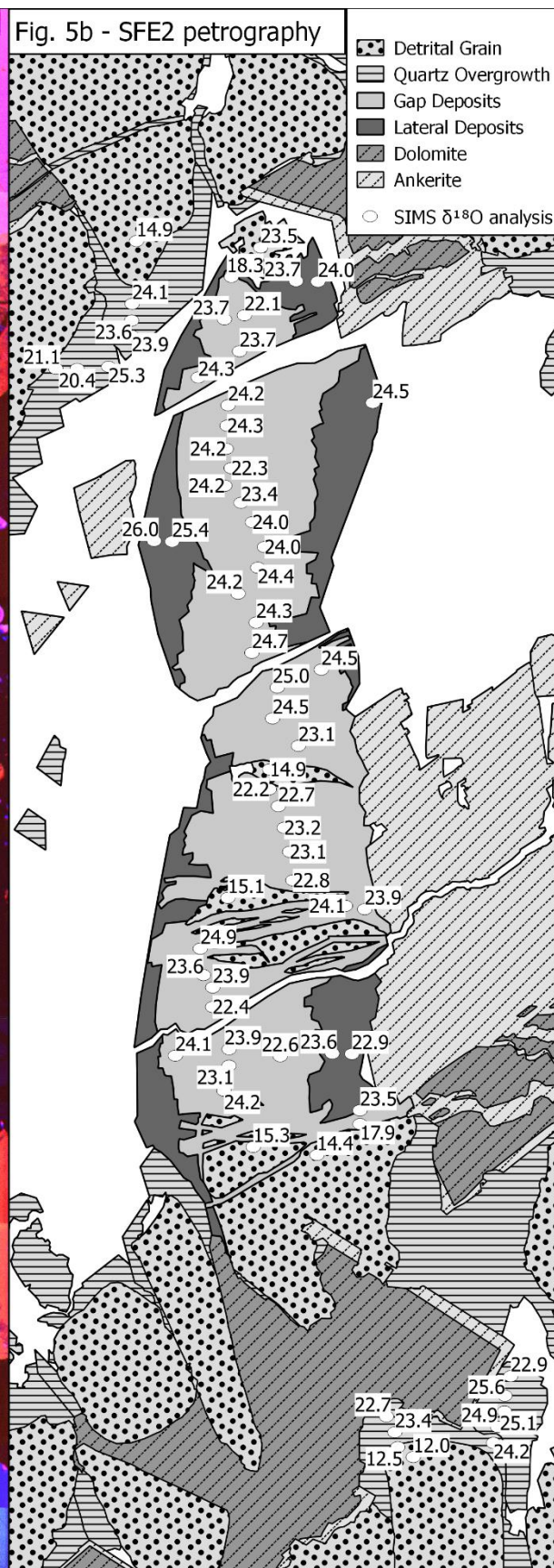


Figure 4.6. (next page) **(a)** SEM-CL (no filters) image map of sample SFOT1. CL imagery has not been smoothed across individual 200 μm images and boundaries between images are clearly visible. White lines denote fluid inclusion assemblages for which temperature ranges were acquired, a representative subset of which is reported in white text in the figure (in degrees Celsius). **(b)** Schematic petrographic map of sample SFOT1. SIMS analyses are demarcated with white ovals; a representative subset of these analyses have their $\delta^{18}\text{O}$ values provided.

Fig. 6a - SFOT1 composite CL (no filters)



Fig. 6b - SFOT1 petrography

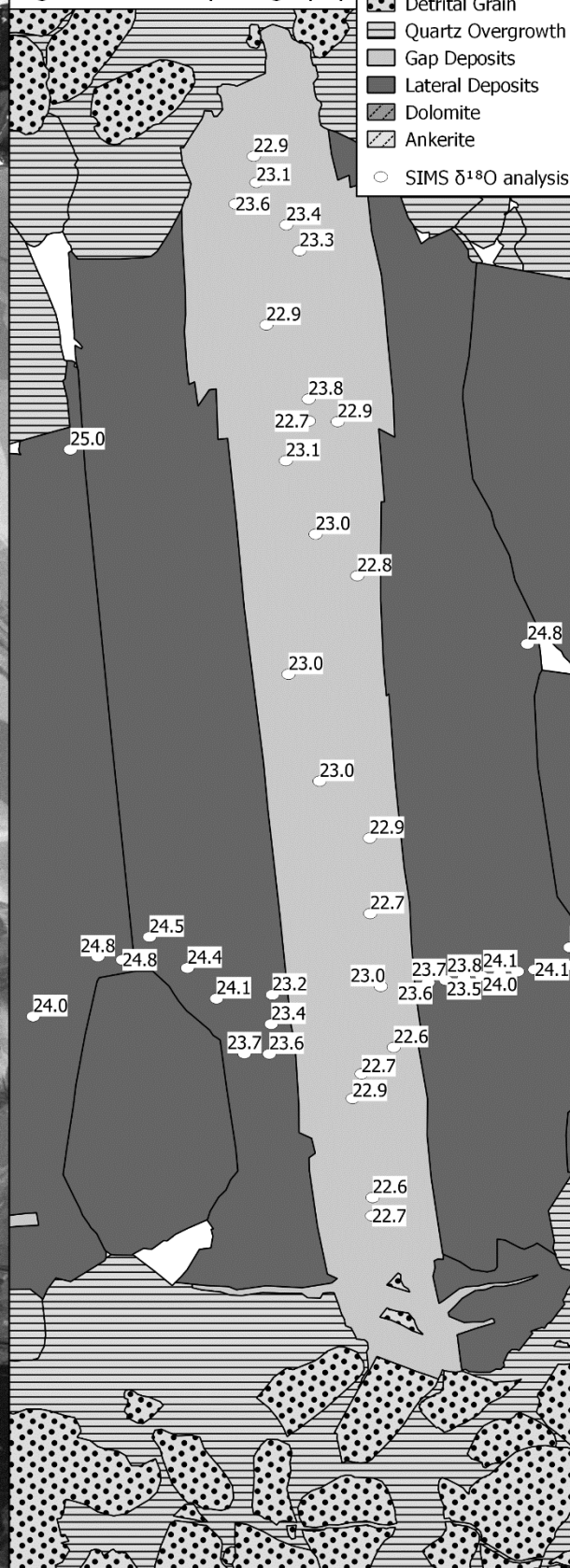


Figure 4.7. Histograms of SIMS $\delta^{18}\text{O}_{\text{quartz}}$ data for the Travis Peak Formation. Detrital quartz grains were analyzed in sample SFE2. Gap deposits (bridge quartz) are fracture-spanning and grew normal to the fracture plane. Lateral deposits (bridge-coating quartz) grew perpendicular to the quartz bridge using the gap deposits as a substrate. **(a)** Quartz analyses from sample SFE2. **(b)** Quartz analyses from sample SFOT1.

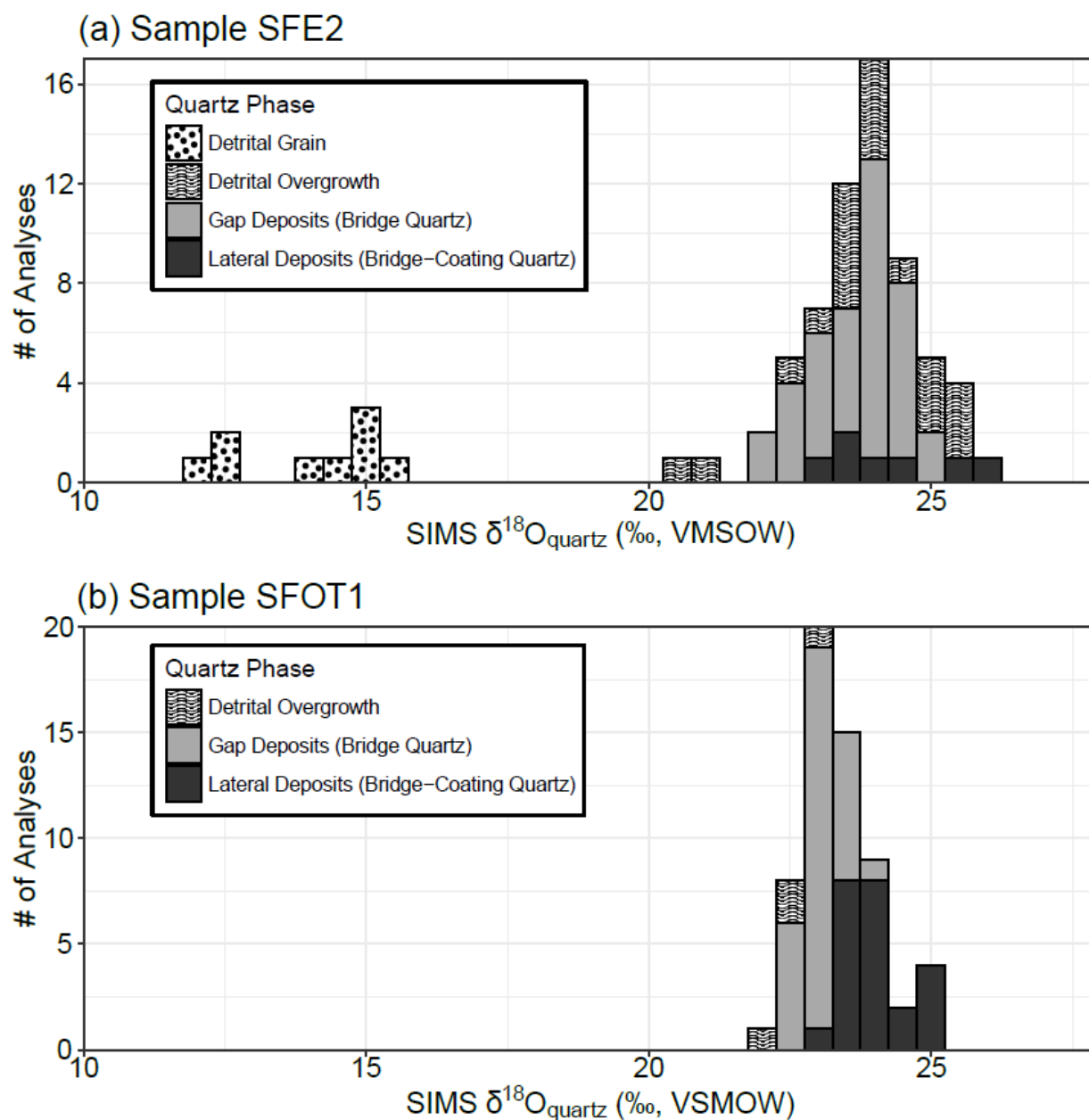


Figure 4.8. Combined data from adjacent SIMS pits and fluid inclusions for the two analyzed quartz bridges. **(a)** Fluid inclusion assemblage (FIA) temperature ranges plotted against adjacent single SIMS $\delta^{18}\text{O}_{\text{quartz}}$ analyses. Included are the equilibrium fractionation lines for quartz precipitating from 5, 6, or 7‰ water. Horizontal error bars are the $\delta^{18}\text{O}$ value 2SD precision for SIMS data. Vertical error bars are the variability of temperatures measured from the FIA. **(b)** Average fluid inclusion assemblage temperatures plotted against $\delta^{18}\text{O}_{\text{water}}$ values calculated assuming quartz equilibrium fractionation. Horizontal bars are the 2SD external precision for $\delta^{18}\text{O}$ if applied to the full range of temperatures measured for the FIA. Vertical error bars are as in (a). The linear regression for SFE2 is $y = 4.94x + 106.37$; the linear regression for SFOT1 is $y = 8.80x + 89.57$.

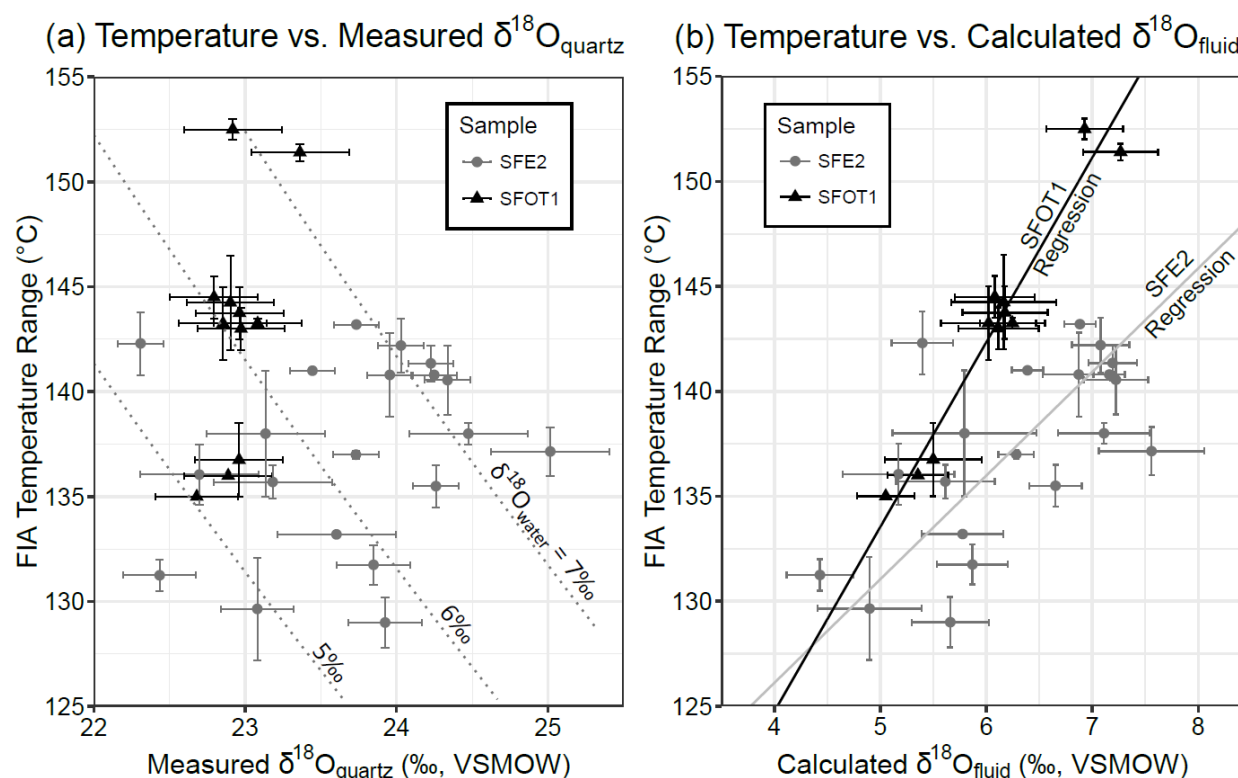
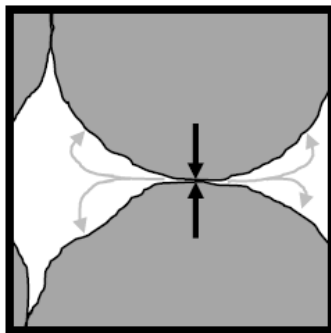


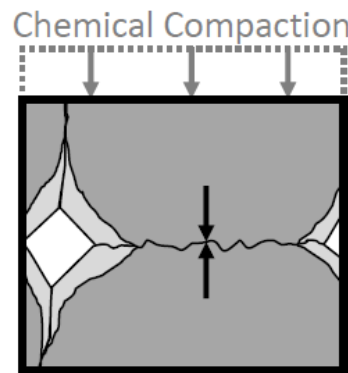
Figure 4.9. (a) Schematic diagram showing idealized chemical compaction in a pure quartz sandstone. Pressure solution occurs at grain boundaries and mobilizes silica into the pore space, where it precipitates as cement. **(b)** Schematic diagram showing what occurs in each burial step of the model, for the condition in which there is no mechanical compaction ($m = 0$). Grey shades represent quartz and white is porosity (Φ). During each compaction event, original volume is lost due to pressure solution from the pore space (p_{pore}) and in the mineral phase (p_{min}), from the regions denoted with dotted lines. Pore volume is reduced by p_{pore} and by the precipitation of quartz cement (Qtz_{cem}). The removal of p_{min} leaves the remaining mass of quartz Qtz_{rem} , but is transferred over to Qtz_{cem} such that $p_{min} = Qtz_{cem}$. The result is no net change in the volume of quartz ($Qtz_n = Qtz_{cem} + Qtz_{rem}$), but a net loss in porosity ($\Phi_n - \Phi_{n+1}$) equal to $p_{pore} + Qtz_{cem}$.

(a) Sandstone Chemical Compaction

depth = 0 (sand)

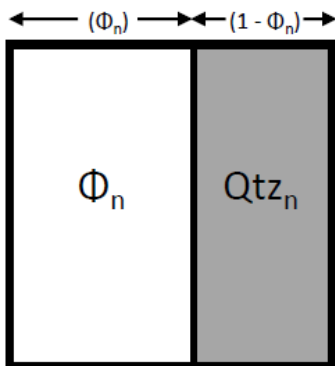


depth >> 0

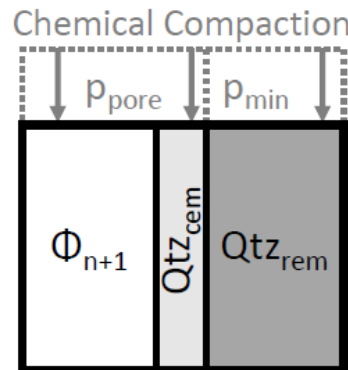


(b) Computational Burial Model

depth = n



depth = n + 1



$$Qtz_n = Qtz_{n+1} = Qtz_{cem} + Qtz_{rem}$$

$$Qtz_{cem} = p_{min}$$

Figure 4.10. Inputs of the burial model. **(a)** Model porosity curve for the Travis Peak sandstones, created by combining average porosity data from the Travis Peak with constraints from analogous formations. **(b)** Fraction of porosity that is lost to mechanical compaction. **(c)** The input geotherm of 40°C/km, assuming an average surface temperature of 25°C.

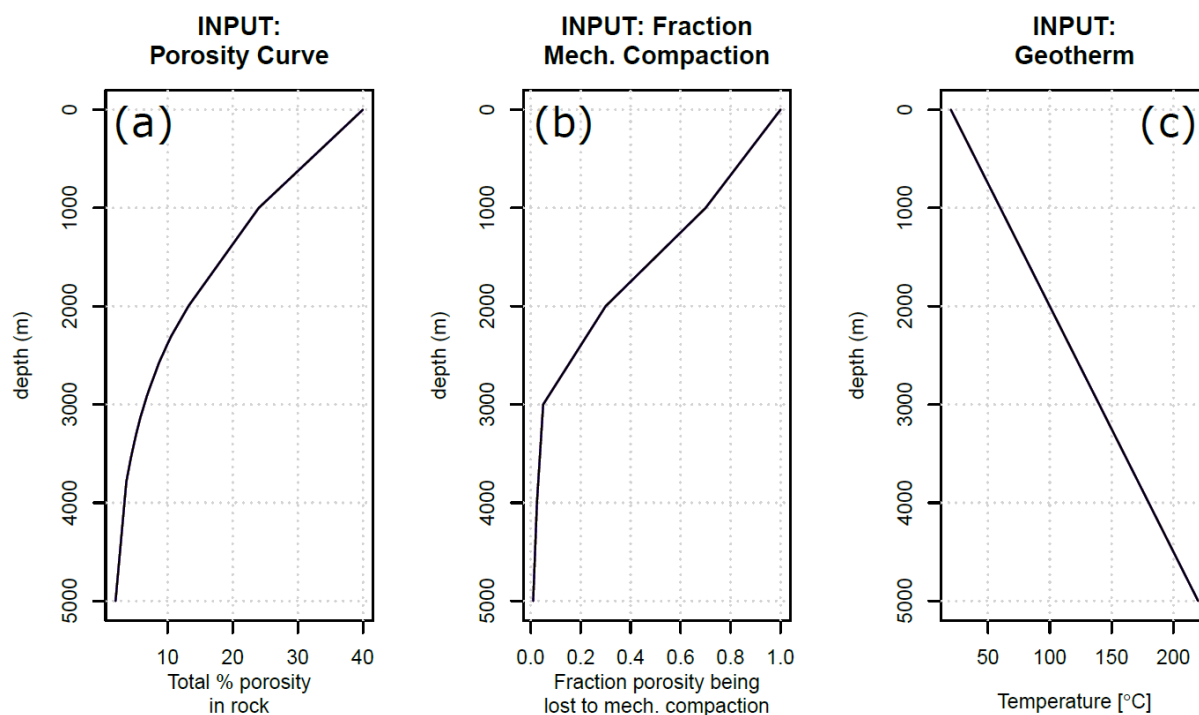
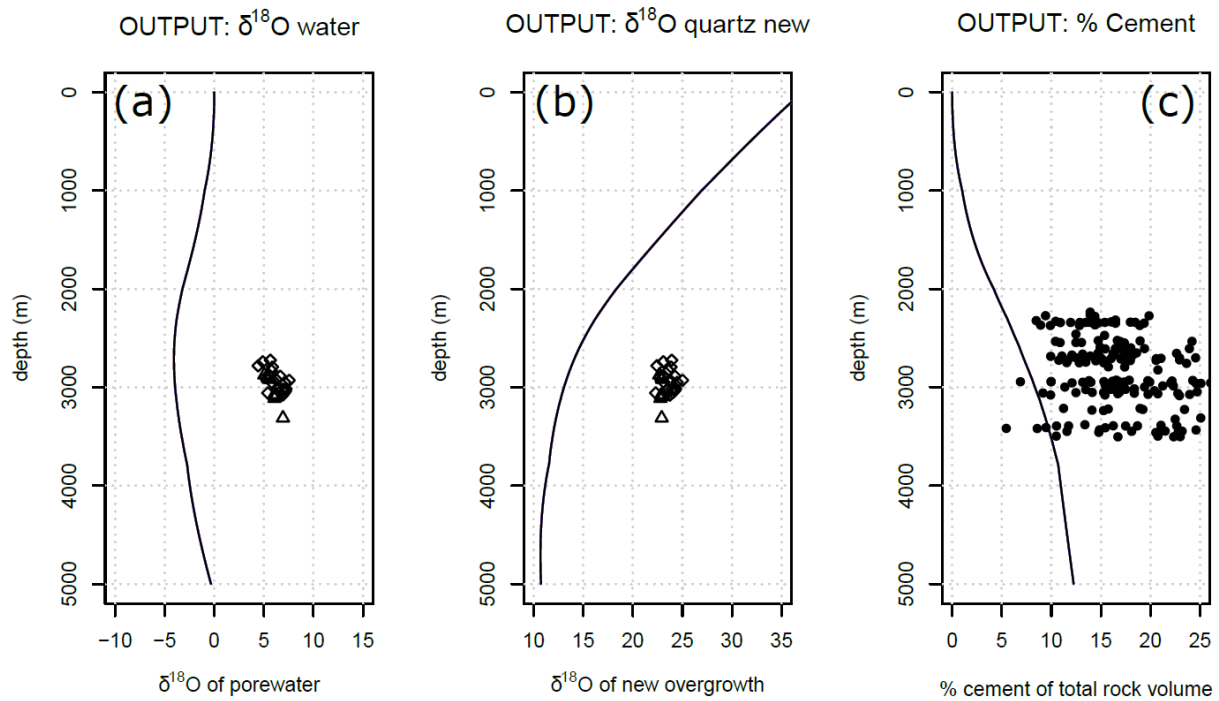


Figure 4.11. Results of the burial model, using the inputs provided in Figure 4.10 and an initial water $\delta^{18}\text{O}$ value of 0‰. Setting the initial $\delta^{18}\text{O}$ of pore water to have a higher value is still insufficient to fit the data; see Appendix 4.5 for details. **(a)** The predicted pore water $\delta^{18}\text{O}$ trend with burial depth in the Travis Peak Formation. Calculated quartz bridge $\delta^{18}\text{O}_{\text{water}}$ data are plotted for comparison. **(b)** The predicted $\delta^{18}\text{O}_{\text{quartz}}$ value of newly precipitated quartz overgrowths at any given depth. Quartz bridge $\delta^{18}\text{O}_{\text{quartz}}$ values measured by SIMS are plotted for comparison. **(c)** Predicted trend with depth of the % of total rock volume composed of cement. Black dots are Travis Peak data collected by Dutton and Diggs (1992).



Samples at UW

Sample descriptions and locality information for each sample may be found in corresponding chapters.

Sample	Sample Type	Chapter
24883-3743.4	SIMS Mount	1
20249-6013.4	SIMS Mount	1
17272-7591.5	SIMS Mount	1
17676-8738.4	SIMS Mount	1
16586-9812.5	SIMS Mount	1
17015-10354.4	SIMS Mount	1
21668-10225.8	SIMS Mount	1
21668-10233.5	SIMS Mount	1
12785-11315.5	SIMS Mount	1
22493-11122.9	SIMS Mount	1
22493-11159	SIMS Mount	1
E701-9922.8A	SIMS Mount	2, 3
E701-9922.8B	SIMS Mount	2, 3
21706-11087.5	SIMS Mount	2, 3
12785-11351.25	SIMS Mount	2, 3
17015-10422.7	SIMS Mount	2, 3
16586-9791.3	SIMS Mount	2, 3
SFE2/SFOT1	SIMS Mount	4