

Authigenic minerals archive elemental cycle and redox fluctuation during early diagenesis

Dissertation

with the aim of achieving a doctoral degree (Dr. rer. nat.)
at the Faculty of Mathematics, Informatics and Natural Sciences
Department of Earth System Sciences
at University of Hamburg

Submitted by

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Hamburg, 2026

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07.09.2026

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Contribution to publications/manuscripts

Study I

Zhang, Q.Y., Lin, Z.Y., Strauss, H., Chen, T.T., Lu, Y., Goedert, J.L., Peckmann, J., 2025. Characterizing ancient seep environments by in-situ sulfur isotope composition of authigenic pyrite. *Chemical Geology* 683, 122767. <https://doi.org/10.1016/j.chemgeo.2025.122767>.

I contributed the methodology, extensive literature researches, discussion, preparing all table and figures, writing – original draft and revising.

Study II

Zhang, Q.Y., Zhang, H, Lin, Z.Y., Mihailova, B, van de Schootbrugge, B., Peckmann, J., 2026. Disentangling the complex paragenetic sequence of glendonite by mineral phase analysis with Fourier transform infrared spectroscopy. *Marine Geoscience and Energy Resources*. Under review.

I contributed the methodology, experiments, extensive literature researches, discussion, preparing all table and figures, writing – original draft and revising.

Study III

Zhang, Q.Y., Lin, Z.Y., Peckmann, J., 2026. Sulfur isotope and trace element variations in pyrite from corroded seep carbonates: records of redox condition changes and episodic methane seepage. Preparing for submission.

I contributed the methodology, sample treatment, experiments, extensive literature researches, discussion, preparing all table and figures, writing – original draft.

Abstract

Early diagenesis encompasses the processes of elemental cycling and the dissolution and formation of minerals in surficial marine sediments. These processes are typically mediated by bacterial decomposition of organic matter. Oxygen is generally depleted within the first few centimeters below the sediment–water interface, leading to a redox transition from oxic to suboxic and ultimately to reduced conditions. The diverse authigenic minerals formed during early diagenesis can faithfully record coeval redox conditions and elemental distribution patterns, even though they may constitute only a minor fraction of the total sediment. Furthermore, investigations of early diagenesis in modern marine sediments are greatly facilitated by pore water extraction and analysis. However, pore water cannot be recovered from ancient strata. Consequently, authigenic minerals serve as critical proxies for reconstructing past sedimentary environments.

Seepage activity represents a particular hotspot characterized by intensive biogeochemical processes during early diagenesis, occurring either in the bottom water column or within the sediment. Seepage activities play a major role in mitigating the massive release of methane from marine sediments into the ocean and, potentially, the atmosphere, thereby helping to prevent the intensification of the greenhouse effect. The most critical process governing methane consumption during seepage activity is sulfate-driven anaerobic oxidation of methane, which primarily produces pyrite and authigenic carbonates (e.g., calcite, aragonite). However, the formation of seep-related carbonates can be interrupted by aerobic oxidation of CH_4 or H_2S . The substantial amounts of H^+ generated by these reactions favor carbonate dissolution over precipitation. Once oxygen is depleted and the environmental conditions return to a reduced state, pyrite and authigenic carbonates can form again. As the most important sulfide mineral in seep environments, pyrite faithfully records the contemporaneous evolution of pore-water sulfur isotopes and trace element concentrations. In addition, ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) forms when temperatures are just above the freezing point of water in seepage-impacted or organic matter-enriched sediment and subsequently transforms into glendonite upon burial. Glendonite is therefore indicative to provide direct evidence of cold paleoclimate. The calcite varieties within glendonite also archive the coeval availability of trace elements and the carbon and oxygen isotopic signatures of the fluids. Collectively, these authigenic minerals provide meaningful insights into the complex geochemical processes occurring during early diagenesis in ancient strata.

Although significant advances have been made in the study of authigenic minerals formed during early diagenesis, particularly in relation to seepage activities, existing analytical methods have largely focused on bulk sample analysis. For example, the determination of pyrite content in bulk sediments or authigenic carbonates is commonly conducted via chromium-reducible sulfur extraction. However, an increasing number of recent studies suggest that pyrite in sediments or authigenic carbonates can exhibit varying habits (e.g., framboids, euhedral crystals) at small spatial scales (e.g., hundreds of micrometers). Consequently, information pertaining to individual pyrite habit becomes homogenized in bulk measurements. Similarly, carbon and oxygen isotope analyses of bulk authigenic carbonates and glendonite are typically performed using micro-drilling techniques. Yet, carbonate phases may also vary over small scales due to complex cementation and later-phase infilling of voids left by earlier phases. Therefore, high-resolution in-situ analysis is

critical for elucidating the formation processes of these authigenic minerals during early diagenesis.

Glendonites for phase specific analysis collected from ancient seepage-impacted strata in Siberia, Russia. They are typically composed of multiple calcite varieties, and electron microprobe analysis (EMPA) and Fourier-transform infrared spectroscopy (FTIR) requiring micro-area analysis were conducted on these calcite phases. The calcite varieties, in paragenetic order, include replacive, light, fibrous (subclassified as botryoidal and gerbil tail), and blocky calcite. The replacive calcite exhibits the lowest Mg and Fe contents and contains abundant organic matter inclusions, suggesting it formed by dehydration of original ikaite at or near the seafloor. The formation of subsequent calcite varieties was thus controlled by transient availability of trace elements and redox conditions in pore water during burial. Blocky calcite displays heterogeneous fabric and variable Mg and Fe contents, likely formed over an extended duration. FTIR spectra confirm that all calcite varieties are characteristic of calcite but show discernible vibrational shifts, particularly at ν_4 ($\sim 709\text{ cm}^{-1}$) and ν_2 ($\sim 876\text{ cm}^{-1}$). It is suggested that both cationic substitution of Mg^{2+} and Fe^{2+} at Ca^{2+} sites and potential variations in the carbon and oxygen isotopic composition of CO_3^{2-} influence the shape of the FTIR spectra of each calcite variety. Consequently, FTIR represents a promising tool for unraveling the full spectrum of elemental cycling and carbon–oxygen isotope variations during the formation of individual calcite varieties in glendonites during early diagenesis.

Pyrite for phases specific analysis is enclosed in the bulk ancient seep authigenic carbonate collected from Whiskey Creek (USA), Beauvoisin (France), and Willapa Bay (USA). In situ sulfur isotope and trace element analysis are conducted on the pyrite, respectively. The $\delta^{34}\text{S}$ values of framboidal pyrite are predominantly negative, with only a few spots showing slightly positive values, indicating variable degrees of the engulfment effect during framboid formation due to carbonate cementation across sampling sites. In contrast, euhedral pyrite crystals in seep carbonates from Whiskey Creek and Beauvoisin exhibit slightly positive $\delta^{34}\text{S}$ values, whereas those from Willapa Bay show markedly negative $\delta^{34}\text{S}$ values. These negative values are attributed to the replenishment of seawater sulfate during and after corrosion events, facilitated by frequent exchange between seawater and porewater. This diversity in $\delta^{34}\text{S}$ values highlights the predominant role of seawater sulfate input in modulating the sulfur isotope signatures of pyrite during early diagenesis. Regarding trace elements, framboids in Willapa Bay seep carbonates display significantly higher contents of Mn, Co, Ni, Cu, Zn, Cd, As, Sb, Mo, and Pb compared to euhedral crystals, suggesting enhanced input and dissolution of organic matter and ferromanganese oxides under reduced conditions. The lower contents of these elements in euhedral crystals are reasonably interpreted as reflecting reduced availability of organic matter and ferromanganese oxides during their formation. However, contrasting Mo and U contents between framboids and euhedral crystals indicate a shift from sulfidic-reduced to less reduced conditions, attributed to the ingress of O_2 -bearing seawater into the seep carbonates during corrosion events. Thus, trace element contents can effectively reflect variations in both substrate availability and redox conditions during pyrite formation in early diagenesis.

Zusammenfassung

Die frühe Diagenese umfasst Prozesse innerhalb von Elementkreisläufen sowie die Auflösung und Neubildung von Mineralen in marinen Oberflächensedimenten. Diese Prozesse werden typischerweise durch den bakteriellen Abbau organischer Substanz angetrieben. Sauerstoff ist im Allgemeinen bereits innerhalb der ersten Zentimeter unterhalb der Sediment-Wasser-Grenzfläche erschöpft, was zu einem Redox-Übergang von oxischen über suboxische bis hin zu reduzierten Bedingungen führt. Die vielfältigen authigenen Minerale, die während der frühen Diagenese gebildet werden, können gleichzeitige Redox-Bedingungen und Elementverteilungsmuster aufzeichnen, selbst wenn sie nur einen geringen Anteil am Gesamtsediment ausmachen. Darüber hinaus werden Untersuchungen zur frühen Diagenese in rezenten Meeressedimenten durch die Gewinnung und Analyse von Porenwässern erheblich erleichtert. Porenwasser kann jedoch nicht aus fossilen Gesteinsabfolgen gewonnen werden. Folglich dienen authigene Minerale als wichtige Proxies für die Rekonstruktion vergangener Sediment-Milieus.

Fluidtransport stellt einen besonderen Faktor dar, der durch intensive biogeochemische Prozesse während der frühen Diagenese gekennzeichnet ist und entweder in der bodennahen Wassersäule oder innerhalb des Sediments auftritt. Die mikrobielle Umsetzung von in Fluiden enthaltenen reduzierten Verbindungen spielt eine bedeutende Rolle bei der Abschwächung der massiven Freisetzung von Methan aus marinen Sedimenten in den Ozean und potenziell in die Atmosphäre und trägt somit dazu bei, eine Verstärkung des Treibhauseffekts zu verhindern. Der kritischste Prozess, der den Methankonsum an submarinen Fluidaustritten steuert, ist die Sulfat-getriebene anaerobe Oxidation von Methan, die hauptsächlich Pyrit und authigene Karbonate (z. B. Calcit, Aragonit) produziert. Die Bildung von Fluidaustritt-assoziierten Karbonaten kann jedoch durch die aerobe Oxidation von CH_4 oder H_2S unterbrochen werden. Die durch diese Reaktionen erzeugten erheblichen Mengen an H^+ -Ionen begünstigen die Karbonat-Auflösung gegenüber der Ausfällung. Sobald Sauerstoff aufgebraucht ist und die Umweltbedingungen wieder in einen reduzierten Zustand zurückkehren, können Pyrit an Fluidaustritten zeichnen. Pyrit die gleichzeitige Entwicklung der Porenwasser-Schwefelisotope und Spurenelementkonzentrationen getreu auf. Darüber hinaus bildet sich Ikait ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$), wenn die Temperaturen knapp über dem Gefrierpunkt von Wasser liegen, in Fluidaustritt-beeinflusstem oder Sediment in Sediment mit hohen Gehalten organischer Substanz. Ikait wandelt sich im Zuge der Versenkung in Glendonit um. Glendonit ist daher geeignet, direkte Hinweise auf ein kaltes Paläoklima zu liefern. Die Calcit-Varietäten innerhalb des Glendonits archivieren zudem die gleichzeitige Verfügbarkeit von Spurenelementen sowie die Kohlenstoff- und Sauerstoffisotopensignaturen der Fluide. Gemeinsam liefern diese authigenen Minerale aufschlussreiche Einblicke in die komplexen geochemischen Prozesse, die während der frühen Diagenese in fossilen Abfolgen abliefen.

Obwohl bedeutende Fortschritte bei der Untersuchung authigener Minerale, die während der frühen Diagenese gebildet werden, insbesondere im Zusammenhang mit Fluidaustritten erzielt wurden, konzentrieren sich die vorhandenen Analysemethoden weitgehend auf die Gesamtprobenanalyse. Beispielsweise wird die Bestimmung des Pyrit-Gehalts in Sedimenten und Sedimentgesteinen oder authigenen Karbonaten üblicherweise mittels chromreduzierender Schwefelextraktion durchgeführt. Eine zunehmende Zahl aktueller Studien deutet jedoch darauf hin, dass Pyrit in Sedimenten oder authigenen Karbonaten auf

kleinen räumlichen Skalen (z. B. hundert von Mikrometern) unterschiedliche Kristallformen (z. B. Framboide, idiomorph-kristallin) aufweisen kann. Folglich werden Informationen, die den einzelnen Pyrit-Habitus betreffen, in Gesamtmessungen homogenisiert. In ähnlicher Weise werden Kohlenstoff- und Sauerstoffisotopenanalysen an Gesamtproben authigener Karbonate und Glendoniten typischerweise mit Mikrobohrtechniken durchgeführt. Dennoch können Karbonat-Phasen aufgrund komplexer Zementation und späterer Verfüllung von Hohlräumen, die von früheren Phasen hinterlassen wurden, ebenfalls auf kleinen Skalen variieren. Daher ist eine hochauflösende In-situ-Analyse entscheidend für die Aufklärung der Bildungsprozesse dieser authigenen Minerale während der frühen Diagenese.

Für eine phasenspezifische Analyse wurden Glendonite aus fossilen, Fluidaustrittsbeeinflussten Abfolgen in Sibirien (Russland) untersucht. Sie setzen sich typischerweise aus mehreren Calcit-Varietäten zusammen, an denen Elektronenstrahlmikroanalysen (ESMA) und Fourier-Transform-Infrarotspektroskopie (FTIR) mit Mikrobereichsanalyse durchgeführt wurden. Die Calcit-Varietäten umfassen in paragenetischer Reihenfolge verdrängenden, hellen, faserigen (unterteilt in botryoidalen und "Gerbil Tail"-Typ) sowie blockigen Calcit. Der frühe, Ikait-ersetzende Calcit weist die niedrigsten Mg- und Fe-Gehalte auf und enthält zahlreiche Einschlüsse organischer Substanz, was auf seine Bildung durch Dehydratisierung des ursprünglichen Ikaites an oder nahe dem Meeresboden hindeutet. Die Bildung der nachfolgenden Calcit-Varietäten wurde folglich durch die transiente Verfügbarkeit von Spurenelementen und die Redox-Bedingungen im Porenwasser während der Einbettung gesteuert. Blockiger Calcit zeigt ein heterogenes Gefüge und variable Mg- und Fe-Gehalte und bildete sich wahrscheinlich über einen längeren Zeitraum. FTIR-Spektren bestätigen, dass alle Calcit-Varietäten für Calcit charakteristisch sind, jedoch erkennbare Schwingungsverschiebungen aufweisen, insbesondere bei ν_4 ($\sim 709\text{ cm}^{-1}$) und ν_2 ($\sim 876\text{ cm}^{-1}$). Es wird angenommen, dass sowohl der kationische Ersatz von Mg^{2+} und Fe^{2+} auf Ca^{2+} -Positionen als auch potenzielle Variationen in der Kohlenstoff- und Sauerstoffisotopenzusammensetzung von CO_3^{2-} die Form der FTIR-Spektren jeder Calcit-Varietät beeinflussen. Folglich stellt FTIR eine vielversprechende Methode dar, um das gesamte Spektrum der Elementkreisläufe und Kohlenstoff-Sauerstoff-Isotopenvariationen während der Bildung einzelner Calcit-Varietäten in Glendoniten im Zuge der frühen Diagenese zu entschlüsseln.

Für die phasenspezifische Analyse wurde Pyrit, der in Gesamtproben fossiler Fluidaustritts-Karbonate aus Whiskey Creek (USA), Beauvoisin (Frankreich) und Willapa Bay (USA) eingeschlossen ist, hinsichtlich seiner In-situ-Schwefelisotope bzw. seiner Spurenelement--Verteilung untersucht. Die $\delta^{34}\text{S}$ -Werte des framboidalen Pyrits sind überwiegend negativ, wobei nur wenige Messpunkte leicht positive Werte aufweisen, was auf unterschiedliche Grade eines Einschlusseffekts während der Framboidbildung infolge der Karbonat-Zementation an den Probenahme-Standorten hindeutet. Im Gegensatz dazu zeigen idiomorph-kristalline Pyritkristalle in Fluidaustritts-Karbonaten aus Whiskey Creek und Beauvoisin leicht positive $\delta^{34}\text{S}$ -Werte, während solche aus Willapa Bay deutlich negative $\delta^{34}\text{S}$ -Werte aufweisen. Diese negativen Werte werden auf die Auffrischung von Meerwassersulfat während und nach Korrosionsereignissen zurückgeführt, begünstigt durch einen häufigen Austausch zwischen Meerwasser und Porenwasser. Diese Vielfalt der $\delta^{34}\text{S}$ -Werte unterstreicht

die vorherrschende Rolle des Meerwassersulfat-Eintrags bei der Modulierung der Schwefelisotopensignaturen von Pyrit während der frühen Diagenese. Hinsichtlich der Spurenelemente zeigen Framboide in Fluidaustritts-Karbonaten aus Willapa Bay deutlich höhere Gehalte an Mn, Co, Ni, Cu, Zn, Cd, As, Sb, Mo und Pb im Vergleich zu idiomorph-kristallinen Kristallen, was auf einen verstärkten Eintrag und Abbau von organischer Substanz und Ferromanganoxiden unter reduzierten Bedingungen hindeutet. Die niedrigeren Gehalte dieser Elemente in den idiomorph-kristallinen Kristallen werden folgerichtig als Widerspiegelung einer verringerten Verfügbarkeit von organischer Substanz und Ferromanganoxiden während ihrer Bildung interpretiert. Die gegenläufigen Mo- und U-Gehalte zwischen Framboiden und idiomorph-kristallinen Kristallen deuten jedoch auf einen Wechsel von sulfidisch-reduzierten zu weniger reduzierten Bedingungen hin, der auf das Eindringen von O₂-haltigem Meerwasser in die Fluidaustritts-Karbonate während Korrosionsereignissen zurückgeführt wird. Somit können Spurenelementgehalte sowohl Variationen in der Substratverfügbarkeit als auch in den Redox-Bedingungen während der Pyritbildung in der frühen Diagenese effizient widerspiegeln.

Chapter 1 General introduction

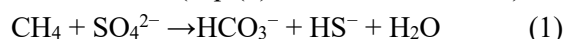
1.1 Early diagenesis

Early diagenesis is defined as the suite of chemical, biological, and physical modifications that sediments undergo following deposition (Berner, 1980; Burdige, 2020). These processes predominantly occur within the upper intervals of superficial sediments (less than several hundred meters in thickness), where significant compaction has not yet occurred and pore spaces remain saturated with water (Berner, 1980; Nagra, 2024). The upper temperature limit of early diagenesis is conventionally placed at approximately 75 °C (Hesse and Schacht, 2011) or even lower, near 50 °C (Burdige, 2018), above which most microbial metabolic activity ceases and temperatures become sufficient to supply the activation energies necessary for thermocatalytic reactions. It has been widely suggested that the remineralization of sedimentary organic matter serves as the direct or indirect driving force behind many early diagenetic reactions (Van Cappellen et al., 1993; Hesse and Schacht, 2011; Burdige, 2020). These reactions generally include aerobic oxidation of organic matter, nitrate, ferromanganese oxide and sulfate reduction and release and uptake of phosphate with burial (Froelich et al., 1979). Moreover, microbes are recognized as the primary mediators of organic matter degradation during early diagenesis in marine sediments (Ahmed et al., 1992; Deming and Baross, 1993; Ruddy, 1997).

Marine sediments are primarily composed of inorganic detrital material (e.g., silicate, and Fe-Mn oxides; Shaw et al., 1990; Morton and Hallsworth, 2007), biogenic material (e.g., calcite and opal; Hover et al., 2001; Hesse and Schacht, 2011), and authigenic material (e.g., various carbonate phases including glendonite, pyrite, phosphorites, and barite; Poulton and Canfield, 2006; Blöthe et al., 2015; Jørgensen et al., 2019; Graul et al., 2023; Iakimov et al., 2023; Nagra, 2024). Since authigenic minerals mainly form during early diagenesis, it plays a crucial role in interpreting the cycling of key elements—such as C, S, Fe, Mn, and P—during complex biogeochemical processes within the sediment (Van Cappellen et al., 1993; Manceau et al., 2014; Jørgensen et al., 2019). Elements are initially released from organic matter, detrital and biogenic particles and are subsequently remobilized into authigenic minerals via biotic or abiotic processes once these particles reach the sediment surface (Graybeal and Heath, 1984; Pellegrino et al., 2023). Thermodynamic principles indicate that the dissolution of organic matter, detrital and biogenic material occurs successively, leading to the stratigraphic zoning within the sediment (Berner, 1980; Coleman, 1985; Henrich, 1989; Hashim et al., 2024; Schultz and Huggert, 2025). Corresponding to the biogeochemical reactions, these chemical zones are typically divided as oxic, nitrogenous, manganous, ferruginous, sulfidic and methanic (Canfield and Thamdrup, 2009). The following formed variable authigenic minerals thus distribute in different chemical zones. In addition, although various authigenic minerals can form during early diagenesis in marine sediments, many of them (e.g., carbonate, pyrite, phosphorites, and barite) typically occur in low abundance in sediments containing low organic matter content (Mänd et al., 2018; Loyd and Smirnov, 2022; Pellegrino et al., 2023; Gu et al., 2025). Moreover, PH gradient during microbial reactions exerts a magnificent influence during the formation of authigenic minerals (Curtis, 1987). Fluctuations in the redox front, modulated by sedimentation rate, also play a critical role in further regulating the formation of these authigenic minerals (Buckley and Cranston, 1988; Lucotte et al., 1994; Curtis, 1995). Notably, seawater diffusion

also supplies a substantial proportion of elements during the formation of certain authigenic minerals (e.g., sulfides and barite; Berner, 1981; Jewell, 2000; Griffith and Paytan, 2012).

Seepage activity is a unique geological phenomenon which are widely documented in both modern passive and active continental margins (Judd and Hovland, 2009; Ni et al., 2025) and have also been identified in ancient strata throughout the Phanerozoic (Peckmann and Thiel, 2004; Birgel et al., 2008; Oppo et al., 2020). Large-scale methane emissions resulting from the destabilization of gas hydrates in seep areas and their release into the atmosphere are considered a potential trigger or catalyst for climate warming during geological history (Judd et al., 2002; Ruppel and Kessler, 2017). However, the majority of the released methane is consumed by sulfate-driven anaerobic oxidation of methane (SD-AOM), a process mediated by a consortium of methanotrophic archaea and sulfate-reducing bacteria in seep environments (Eq. (1); Boetius et al., 2000).



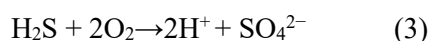
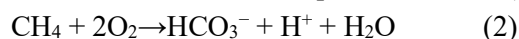
Authigenic minerals forming in seep environments are typically more complex than those in normal marine sediments due to the continuous supply of additional hydrocarbon components (e.g., CH_4) from deep sedimentary layers (Badesab et al., 2020; Zan et al., 2022). These authigenic minerals typically form under sequentially changing redox conditions, ranging from oxic (e.g., gypsum), weakly reduced (e.g., glauconite), reduced (sulfidic: authigenic carbonate, pyrite, barite; or sulfide-free: vivianite, apatite), to methanic (e.g., magnetite). Gypsum discovered in seep environments is interpreted as an oxidized product of pre-existing pyrite when seep activity wanes or ceases (Lin Z et al., 2016a; Pierre, 2017; Wittig et al., 2024). However, glauconite is far less reported from seep environments due to its strict formation requirements, but its presence is robust evidence for weakly reducing conditions (Zhang et al., 2022; Nicolas, 2024). Moreover, authigenic carbonate and pyrite are the most common products of seep activity, as abundant CO_3^{2-} and HS^- generated by SD-AOM subsequently combines with Ca^{2+} and Fe^{2+} in porewater, respectively (Greinert et al., 2001; Feng et al., 2010; Borowski et al., 2013). Meanwhile, barite is occasionally observed in seep settings and characteristic Ba fronts in sediment record the modern and past position of SMTZ (Dickens, 2001; Torres et al., 2003; Feng et al., 2022). However, barite tends to dissolve under low sulfate concentrations in porewater, which challenges its role as a widespread mineral in seep environments (Feng and Chen, 2007; Zan et al., 2022). In addition, vivianite and apatite typically precipitate below the SMTZ and have garnered increasing research interest as they may represent the primary phosphorus sink during seep activity (Egger et al., 2015; Chen Q et al., 2023). Particularly, sedimentary vivianite formation could serve as a mineralogical marker of iron-mediated anaerobic oxidation of methane, signaling low-sulfate availability against methanogenic and ferruginous backdrop (Liu et al., 2018). Last but not least, magnetite has long been considered to dissolve in H_2S -bearing zones (Canfield and Berner, 1987; Roberts, 2015), particularly within the sulfate–methane transition zone (SMTZ) (Riedinger et al., 2005). Nevertheless, recent studies have proposed that magnetite can also form below the SMTZ or in the methanogenic zone (Lin et al., 2020, 2024; Gaikwad et al., 2021), thereby enhancing our understanding of paleomagnetic signals in seep environments. Whereas, these authigenic minerals will not all occur simultaneously in the seep sediment. Instead, they are controlled by local sedimentary conditions and appear in the form of mineral assemblages.

1.2 Targeted authigenic minerals

Authigenic carbonate, pyrite, and glendonite commonly exhibit multiple phases or habits, indicating dynamically changing redox conditions and pore-water geochemistry—a characteristic that is evidently lacking in other authigenic minerals. Thus, analysis focusing on each phase of these authigenic minerals is favorable to rebuild their formative history and further advancing our understanding of elemental cycle and redox condition shift during early diagenesis.

1.2.1 Authigenic carbonate

In seep environments, authigenic carbonate precipitates extensively due to the efficient supply of CO_3^{2-} from sulfate-driven anaerobic oxidation of methane (SD-AOM) and subsequent combination with Ca^{2+} in pore water under elevated alkalinity (Eq. (1); Ritger et al., 1987; Suess, 2020). Attributed to dynamical episodes and variable methane flux of seepage activity, this carbonate typically exhibits a chaotic fabric and comprises multiple phases of carbonate minerals, including aragonite, Mg-calcite, and dolomite, which vary with burial depth (Savard et al., 1996; Buggisch and Krumm, 2005; Chen et al., 2007; Li J. et al., 2018). Furthermore, seep carbonate often contains abundant fossils such as bivalve shells, fecal pellets, and foraminifera, providing critical evidence for reconstructing seep communities (Kiel and Peckmann, 2007; Torres et al., 2010; Mazumdar et al., 2011; Hryniewicz et al., 2021). In contrast, aerobic oxidation of CH_4 or H_2S generated by recurring methane (or hydrocarbon) pulses (Campbell et al., 2002; Jean-Philippe et al., 2017) or by biotic benthic activity (Kuechler et al., 2011; Pierre et al., 2014) can induce corrosion of seep carbonate due to the substantial release of H^+ from these processes (Eq. (2) and (3); Himmler et al., 2011; Crémière et al., 2012). Such corroded seep carbonates typically display irregular corrosion surfaces, thereby recording dynamic episodes of seep activity (Beauchamp et al., 1989; Machel, 1989; Campbell et al., 2002).



The carbon isotope composition of seep carbonates typically exhibits $\delta^{13}\text{C}$ values lower than -30% , indicative of a direct biogenic methane-derived origin and widely recognized as a key proxy for seep activity (Buggisch and Krumm, 2005; Roberts et al., 2010; Himmler et al., 2015). Nevertheless, the characteristic strongly negative $\delta^{13}\text{C}$ signature may be absent in some cases, which necessitates a more integrative approach incorporating mineralogy, petrography, biology, and isotope geochemistry (Stakes et al., 1999; Kiel and Peckmann, 2007; Roberts et al., 2010). Recent advances have demonstrated the utility of combined multiple conventional (e.g., $\delta^{13}\text{C}$, $\delta^{18}\text{O}$) and progressive isotope systems (e.g., $\Delta 47$, and $\delta^{44}\text{Ca}$) in constraining fluid sources and precipitation temperatures, while also underscoring the importance of analyzing individual carbonate phases (e.g., aragonite, Mg-calcite) (Loyd et al., 2016; Thiagarajan et al., 2020; Staudigel et al., 2024).

Glendonite is a pseudomorph of ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$), a mineral that initially forms under low-temperature, high-alkalinity, and phosphate-rich conditions (Suess et al., 1982; Swainson and Hammond, 2001; Papadimitriou et al., 2014; Zhou et al., 2015) and rapidly decomposes at temperatures above 7°C (Pauly, 1963). Glendonites are now frequently

reported from both modern marine sediments and ancient strata at middle to high latitudes (Qu et al., 2017; Rogov et al., 2017; Muramiya et al., 2022). They have also been widely documented in seepage-impacted setting during early diagenesis and suggests a dependent formation mechanism coupled from seep activity (Greinert and Derkachev, 2004; Selleck et al., 2007; Teichert and Luppold, 2013; Morales et al., 2017; Giunti and Bojanowski, 2025). In their bulk form, glendonites typically exhibit bladed, rosette, or stellate habits, which are interpreted as reflecting the duration and intensity of cold climatic conditions (Rogov et al., 2023).

The voids left by the dissolution of primary ikaite are subsequently filled by later mineral phases, primarily calcium carbonate, resulting in characteristic paragenetic sequences (Huggett et al., 2005; Bloem, 2019; Vasileva et al., 2021). Several models have been proposed to explain these diagenetic processes (Greinert and Derkachev, 2004; Teichert and Luppold, 2013; Vickers et al., 2018). These carbonate phases often display heterogeneous textures, variable trace element and organic matter contents, and diverse carbon and oxygen isotopic compositions (Frank et al., 2008; Vasileva et al., 2019; Vickers et al., 2020; Rogov et al., 2023). Such variability suggests that glendonite formation is a complex process occurring under fluctuating pore-water chemical conditions. Consequently, reconstructing the formation history of glendonites in ancient strata and interpret the synchronous sedimentary environment requires careful focus on individual phases (Peckmann, 2017; Vickers et al., 2018; Bloem, 2019).

1.2.2 Pyrite

Pyrite could form in both bulk authigenic carbonate and sediments (e.g., silty clay), and thus serves as the critical indicator of seepage activity (Wang et al., 2015; Lin et al., 2016a; Yu et al., 2025). The H₂S produced via the sulfate-driven anaerobic oxidation of methane (SD-AOM; Eq. (1)) or organoclastic sulfate reduction (OSR; Eq. (4)) further reacts with porewater Fe²⁺ to form stable pyrite as the final sulfide phase (Sweeney and Kaplan, 1973; Butler et al., 2004; Schoonen, 2004). It has been suggested that framboidal pyrite rapidly crystallizes under supersaturated conditions with respect to pyrite, through nucleation processes sustained by continuous supplies of sulfur and iron (Rickard, 2012, 2021). However, as supersaturation decreases, limited sulfur and iron availability inhibits framboid formation but allows continuous growth of euhedral crystals (Raiswell, 1982; Strauss, 1997; Rickard, 2012; Farquhar et al., 2013). These euhedral crystals form either by continued growth of microcrystals within primary framboids as long as they remain in contact with the porewater, or by direct formation with distinct morphologies within the porewater during diagenesis (Merinero et al., 2008; Karamova et al., 2025).



Compared to conventional bulk sulfur isotope analysis methods (e.g., chromium-reducible sulfur; Canfield et al., 1986), which extract pyrite without accounting for its diverse morphological habits (e.g., framboids, euhedral crystals; Li N. et al., 2016, 2018; Miao et al., 2023), in-situ sulfur isotope analysis with a spatial resolution of several tens of micrometers offers a more robust and insightful approach to deciphering the evolution of sulfur isotopes in seep environments (Li et al., 2019; Gong et al., 2023; Wood, 2023). It is generally accepted that framboids are more enriched in ³²S compared to later-stage euhedral crystals (Seal, 2006;

Lin et al., 2016b, 2017). However, in sediments characterized by well-replenished sulfate but limited iron supply, both framboids and euhedral crystals may show negative $\delta^{34}\text{S}$ values (Passier et al., 1997). Collectively, these studies indicate that the $\delta^{34}\text{S}$ values of pyrite in both ancient and modern seep environments are potentially controlled by multiple factors, including the availability of sulfate and iron, and the nature of organic matter and hydrocarbon (methane) substrates.

The trace element composition of pyrite has recently been employed to interpret redox conditions, element sources, and immobilization pathways in marine seep environments (Miao et al., 2022; Chen et al., 2023, 2024; Smrzka et al., 2024; Song et al., 2026). These trace elements are commonly categorized as conservative and nutrient-type elements characterized by long oceanic residence times (e.g., Mo, As, Sb, Cd, Ni, Cu, U, and Zn) and scavenged-type elements with short residence times (e.g., Co, Pb, and Mn) (Smrzka et al., 2019; Large et al., 2022). The delivery of trace elements to sedimentary pore waters during seepage activity is governed by the degradation of organic matter, the reductive dissolution of ferromanganese oxides and seawater diffusion. Once in pore waters, trace elements are partitioned among three main transient sources: organic matter, ferromanganese oxides, and terrigenous aluminosilicate clay minerals (Smrzka et al., 2019, 2020). Labile organic matter is consumed by either oxygen or ferromanganese oxides under reduced condition, leading to a marked increase in the concentrations of associated trace elements in pore waters (Little et al., 2015). However, the incorporation of different elements into pyrite varies considerably (Huerta-Diaz and Morse, 1992; Deditius et al., 2008; Berner et al., 2012), primarily due to: (1) differences in water-exchange reaction kinetics relative to Fe. For example, Cu, Pb, and Zn precipitate as discrete metal sulfide inclusions prior to pyrite formation, whereas Co and Ni tend to substitute for Fe or S sites within the pyrite lattice (Morse and Luther, 1999; Sternbeck et al., 2000; Gregory et al., 2015); (2) source availability. Recent studies have reported high Mn contents in pyrite formed from SD-AOM (Lin et al., 2022; Gong et al., 2025; Yu et al., 2025), which has been attributed to elevated degrees of pyritization of iron under conditions of depleted amorphous iron phases and a high $\text{Mn}^{2+}/\text{Fe}^{2+}$ ratio in pore waters under reducing conditions (Morse and Arakaki, 1993; Morse and Luther, 1999).

1.3 Objective

The phases variation in glendonite strictly originate from the decomposition of ikaite, representing a unidirectional process (Rogov et al., 2021). Similarly, pyrite initially precipitates as framboids and subsequently grows progressively into euhedral crystals (Sawlowicz, 1993). Particularly, glendonite include four varieties of calcite and pyrite show textures in framboids and euhedral crystals under optical microscope observation in our study. Consequently, pyrite and glendonite serve as ideal authigenic minerals for reconstructing changing precipitation environments during early diagenesis through phase-specific analysis. Notably, studies focusing on the glendonite and pyrite in modern marine environments have enabled the interpretation of their formation mechanisms when combined with concomitant pore-water geochemical data (e.g., Raven et al., 2016; Muramiya et al., 2022; Jiang et al., 2024). However, such an approach is not feasible for ancient analogues, as the original pore water is no longer preserved. Nevertheless, phase-specific analyses of ancient glendonite and pyrite specimens can significantly advance our understanding of elemental cycling and redox condition shifts

during early diagenesis. Therefore, investigating the implications of glendonite and pyrite for ancient marine sedimentary environments requires high-resolution analytical approaches.

To thoroughly explore the formative processes of glendonite in ancient strata, bulk glendonite samples from Siberia (Russia) were selected for high-resolution in-situ analysis (Table 1). Fourier transform infrared (FTIR) reflection micro-spectroscopy and electron probe microanalysis (EPMA) were conducted over areas of several tens of square micrometers to decipher the influence of trace elements on phase formation (i.e., calcite varieties). Analogically, authigenic carbonate containing abundant pyrite from Beauvoisin (France), as well as from Whiskey Creek and Willapa Bay (USA), were selected to conduct secondary ion mass spectroscopy (SIMS) and laser ablation (multicollector) inductively coupled plasma mass spectrometry (LA-(MC)-ICP-MS) (Table 1) and interpret sulfur isotope and trace element patterns during the formation of framboids and euhedral crystals at a small scale (tens of micrometers).

Table 1 Information of minerals in this thesis

Minerals	Locations	Methods	Targeted phases
Glendonite	Siberia, Russia	EMPA, FTIR	Calcite varieties
	Beauvoisin, France	CRS, SIMS	Framboids; Euhedral crystals
Pyrite	Whiskey Creek, USA	CRS, SIMS	Framboids; Euhedral crystals
	Willapa bay, USA	LA-(MC)-ICP-MS	Framboids; Euhedral crystals

1.4 Reference: General introduction

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Chapters 2 Disentangling the complex paragenetic sequence of glendonite by mineral phase analysis with Fourier transform infrared spectroscopy

Under review in Marine Geoscience and Energy Resources

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Abstract: Glendonite, a pseudomorph of ikaite (metastable hexahydrate of calcium carbonate), serves as paleotemperature proxy indicative of near-freezing conditions in ancient sedimentary environments. While glendonite principally has great potential as a climate proxy, its applicability as a geochemical archive of cold house conditions is hampered by the circumstance that glendonite typically consists of a mosaic of successively formed mineral phases replacing former ikaite. This study employs Fourier transform infrared (FTIR) reflection micro-spectroscopy and electron microprobe analysis (EMPA) to characterize the paragenetic sequence of Jurassic glendonite from Siberia (Russia), which had previously been used as an archive of climate change and episodes of methane seepage in polar settings. FTIR analysis reveals that the Siberian glendonite consists of a complex mosaic of four calcite varieties, (1) replacive calcite, (2) light calcite, (3) fibrous calcite, and (4) blocky calcite. All calcite varieties reveal low magnesium (Mg) contents (< 2.0 wt.%), consistent with the ikaite-glendonite transformation for replacive calcite and with mineral formation under shallow to deeper burial conditions for the other calcite varieties. Progressive iron (Fe) enrichment from replacive calcite to fibrous calcite reflects a shift from sulfidic to post-sulfidic, probably methanic, porewater conditions, attributed to preferential uptake of Fe during sulfide mineral formation during diagenesis under sulfidic conditions as evidenced by abundant pyrite within the Siberian glendonite aggregates and the surrounding host rocks. Blocky calcite, representing the latest-stage diagenetic variety, exhibits variable Fe contents (0.0-1.5 wt.%) and textures, suggesting that the large, equant crystals are genetically heterogeneous and probably formed over prolonged periods of time. FTIR spectra suggest minor amounts of Mg^{2+} and Fe^{2+} cationic substitution at the Ca site for replacive, light, and fibrous calcite, which is evidenced by the change in the positions of the $\nu_4(\text{CO}_3)$ and $\nu_2(\text{CO}_3)$ IR reflection signals near 709 and 876 cm^{-1} . This work is setting the stage for a better utilization of the information stored in the widespread pseudomorphs of ikaite, highlighting the potential of FTIR reflection spectroscopy to assist phase specific, high-resolution geochemical analysis of the complex crystal mosaic of

glendonite.

1. Introduction

Glendonite is widely recognized as a calcite pseudomorph after ikaite, a metastable hydrous calcium carbonate mineral that typically forms at low temperatures just above the freezing point of water (Dieckmann et al., 2008; Tollefsen et al., 2018; Whiticar et al., 2022). Glendonite serves as a paleoenvironmental proxy for reconstructing cold-climate conditions throughout the Phanerozoic (Brysch, 2018; Popov et al., 2019; Vickers et al., 2020; Rogov et al., 2021). The transformation of ikaite to glendonite can be caused by rising temperature during burial and changing porewater conditions (e.g., Mg/Ca ratio, pH; Purgstaller et al., 2017; Qu et al., 2017; Vickers et al., 2024). In brief, the hexahydrate mineral ikaite disintegrates into less soluble calcium carbonate phases upon the release of water molecules at increasing temperature, while the composition of the resulting anhydrous calcium carbonate minerals is controlled by variable porewater conditions (e.g., Purgstaller et al., 2017). The distinct morphologies of the crystal aggregates of glendonite typically involve blade, rosette, and stellate habits depending on the duration and intensity of cold climates (Rogov et al., 2023 and reference therein). Among the different environments in which the precursor mineral forms, methane-seep associated glendonite exhibits exceptionally low $\delta^{13}\text{C}$ values ($< -30\text{‰}$), providing evidence of hydrocarbon fluid migration in the depositional environment and a potential connection with gas hydrate dynamics (Greinert and Derkachev, 2004; Teichert and Luppold, 2013; Morales et al., 2017; Peckmann, 2017; Vasileva et al., 2024). Occurrences of glendonite in sedimentary sequences may therefore offer constraints on past climate feedback mechanisms.

Glendonite can comprise multiple mineral phases, typically dominated by calcite but sometimes associated with other minerals like authigenic quartz (Teichert and Luppold, 2013; Morales et al., 2017; Qu et al., 2017; Vasileva et al., 2019). It has commonly been observed that the initially forming replacive calcite is postdated by the sequential precipitation of other mineral phases; since the recrystallization of ikaite into replacive calcite results in a loss of volume, the pore space generated by this recrystallization is successively filled by later-formed mineral phases (Huggett et al., 2005; Vickers et al., 2018, 2020; Muramiya et al., 2022; Rogov et al., 2023; Counts et al., 2024). Geochemical signatures like trace-element and isotopic compositions ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) as well as organic constituents typically vary among these mineral phases, but the complex crystal mosaic and the small size of crystals hinder conventional phase-specific analysis (Qu et al., 2017; Mikhailova et al., 2021; Vasileva et al., 2022; Counts et al., 2024). While the geochemical composition of replacive calcite may reflect the conditions at or close to the seafloor, excepted for changes resulting from the recrystallization of ikaite to replacive calcite (e.g., Lázár et al., 2025), all subsequently formed mineral phases will necessarily reflect the evolution of the diagenetic environment. Therefore, to use the full potential of glendonite as a climate archive, replacive calcite has to be targeted individually, avoiding any sampling of interwoven later phases.

Since glendonite is frequently enriched in organic constituents producing strong photoluminescence background under visible-laser irradiation (McCreery, 2001; Smith and Dent, 2005) and thus, compromising the application of Raman spectroscopy, micro-area analytical techniques with limited material requirements and low susceptibility to luminescence interference are needed. Fourier transform infrared reflectance (FTIR) spectroscopy has great potential for this application, because in contrast to Raman spectroscopy it does not suffer from any

photoluminescence. Moreover, the utilization of FTIR reflection micro-spectroscopy allows for probing spatial areas of linear size of an order of 10 micrometers directly from open-cover thin sections. Ikaite shows wavenumber and intensity vibrational modes similar to those of calcite (Coleyshaw et al., 2003; Gunasekaran et al., 2006) and recent studies have indicated that the phase transformation from synthetic ikaite to calcite can be recognized with FTIR spectroscopy, resulting in characteristic peak shifts in the internal CO₃ vibrational modes (ν_2 , ν_3 , and ν_4 ; Purgstaller et al., 2017; Lázár et al., 2023). However, current analytical limitations persisted for the analysis of glendonite to date, probably caused by the compositional heterogeneity of its crystal mosaic (Németh et al., 2022). Still, recent advances have demonstrated the high sensitivity of FTIR to carbonate mineral variations through several key mechanisms including the dynamics of cation substitution (Henry et al., 2017; Korchef, 2019; Stanienda-Pilecki and Łukowiec, 2025), organic-inorganic interactions (Long et al., 2011; Tao, 2013; Pearson et al., 2020), and carbon and oxygen isotope heterogeneities (Xu et al., 2018; King et al., 2023). These findings provide the foundation to establish FTIR micro-spectroscopy as a viable tool for resolving phase-specific compositional differences in glendonite.

To evaluate the potential utility of FTIR reflection micro-spectroscopy for phase identification of organic matter-rich geomaterials, samples of Jurassic glendonite from Siberia, Russia (Morales et al., 2017), were analyzed through wavelength-dispersive electron microprobe analysis (EMPA) and FTIR spectroscopy. A paragenetic sequence of four calcite varieties is described herein, comparing element composition with vibrational modes in FTIR spectra to elucidate the similarities and differences of the respective mineral phases of glendonite. This approach of separating the highly interconnected mineral phases of glendonite's crystal mosaic is setting the stage for an advanced use of glendonite as an archive of paleoenvironmental change and diagenetic evolution.

2. Materials and methods

2.1 Sample information

The Siberian glendonite samples studied herein derive from Jurassic marine depositional environments, representing shelf settings of different water depths spanning from shoreface to offshore environments. The respective strata expose Lower to Middle Jurassic marine sandstone, siltstone, and mudstone and macrofossils include abundant wood debris and bivalves, as well as a few belemnites, gastropods, brachiopods, and ammonites (Morales et al., 2017; Vasileva et al., 2019). A total of twelve glendonite specimens, showing spindle-shaped and stellate morphologies, was sampled from late Pliensbachian (Anabar Bay) and late Bajocian (Cape Kystatym) formations (Fig. 1) by Mikhail Rogov in the years 2008 to 2013. Morales et al. (2017) suggested that methane seepage exerted a key control on glendonite formation in the study area. Glendonite from the study areas exhibit negative $\delta^{13}\text{C}_{\text{VPDB}}$ values ranging from -44.5‰ to -0.4‰ and gas inclusion data confirm the presence of methane and longer-chain hydrocarbon gases, suggesting a thermogenic source for methane (Morales et al., 2017). Photographs of typical glendonite crystal aggregates studied herein are shown in Figure 2. The Siberian glendonite aggregates are of spindle-shaped (Fig. 2a) or stellate (Fig. 2b) shape and a few centimeters in size.

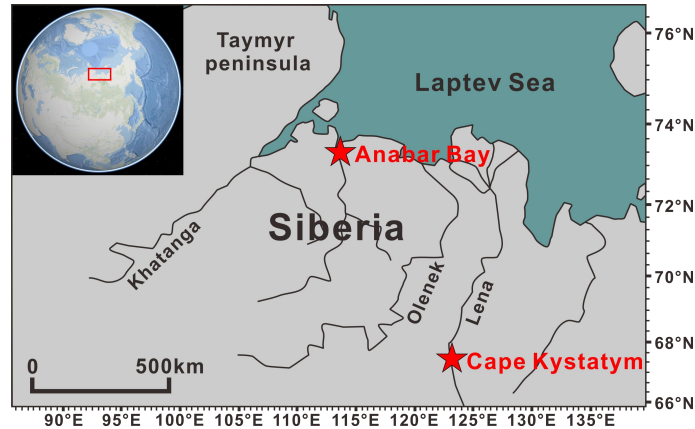


Fig. 1. Sample locations (marked with stars) of Jurassic glendonite in northern Siberia close to the Laptev Sea; the insert shows the study area (marked by a rectangle) on a planetary-hemisphere scale.

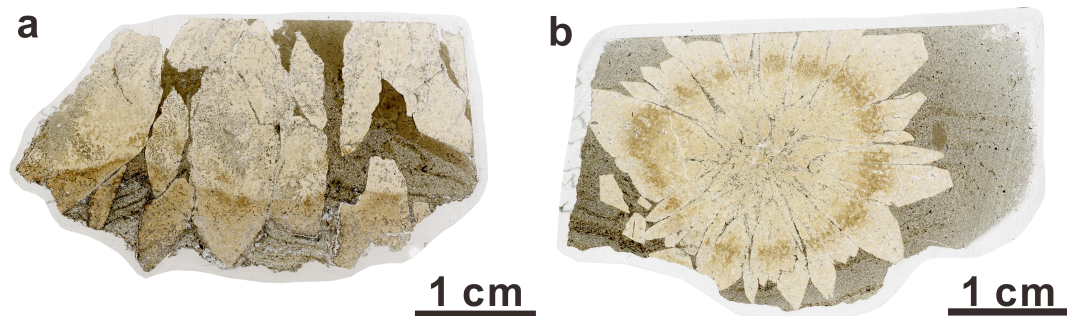


Fig. 2. Thin-section scans of Siberian glendonite showing spindle-shaped (a; sample W23A-1) and stellate (b; sample W22B2) textures.

2.2 EMPA and chemical-element mapping

Calcium, Mg, and Fe contents in the glendonite samples were determined with a wavelength-dispersive EMPA, averaging over ca. 50 points from each sample, using a Cameca Microbeam SX100 system operating at an accelerating voltage of 15 kV, a beam current of 20 nA, and a defocused beam (spot diameter 10 μm on the sample surface) to avoid possible mobilization of light elements. The standards used were MgO for Mg and andradite for Ca and Fe. Backscattered electron (BSE) images as well as elemental mapping for Ca, Fe, Mg, and P were conducted with a lateral resolution of ca. 1 μm . The detection limits were approximately 120, 300, and 400 ppm for Mg, Ca, and Fe, respectively.

2.3 FTIR analysis

Fourier transform infrared (FTIR) reflectance spectra in the range 620-7000 cm^{-1} were collected with a Bruker Invenio FTIR spectrometer equipped with a Hyperion 2000 IR microscope, using a LN-MCT-D316-025 detector and an objective with 15 $\times$ magnification. Spectra were recorded in a normal-incidence geometry with an instrumental spectral resolution of 2 cm^{-1} and peak position accuracy 0.5 cm^{-1} , averaging over 64 scans. The background single-channel signal was measured from a gold wafer. A rectangular aperture was used to restrict the infrared beam to the size of the spatial area to be probed. For standardization, a calcite specimen

from the collection of the Museum of Nature Hamburg – Mineralogy, Leibniz Institute for the Analysis of Biodiversity Change, was firstly analyzed with EMPA, which revealed Mg and Fe contents below the detection limit, and then used to collect a reference FTIR reflection spectrum. The peak positions were determined using the peak-picking option in the OPUS software package.

3. Results

3.1 Mineral phases of glendonite

The paragenetic sequence of the studied Siberian glendonite is made up of different varieties of calcite, starting from (1) replacive calcite and followed by (2) light calcite, (3) fibrous calcite, and (4) blocky calcite (Table 1 and Fig. 3). Replacive calcite is typified by abundant inclusions of organic matter and in some cases by crystal zonation (Fig. 3a). Light calcite is represented by large homogenous crystals, typically in direct contact with replacive calcite. Fibrous calcite forms crystal aggregates with variable texture, with isopachous rims and botryoids representing one end-member variety (Fig. 3a and b) and whiskers projecting from a central strand representing the second end-member variety (Fig. 3b-d, and 4). Herein, the latter variety of fibrous calcite is referred to as gerbil tail calcite. The crystal tips of whiskers of gerbil tail calcite are apparently covered by organic substances as suggested by their intense autofluorescence (Fig. 4). Similar observations have been made for other glendonite occurrences (Rogov et al., 2023) and ooids (Suarez-Gonzalez and Reitner, 2021; Pei et al., 2024), suggesting an origin from organomineralization, in accord with a classification of the Siberian gerbil tail calcite as pseudo-fossils. The varieties of fibrous calcite formed on crystal surfaces of replacive calcite and light calcite, filling part of the porosity between the two earlier varieties of calcite (Fig. 3 and 4). Later blocky calcite cement filled much of the remaining porosity. Most of the crystals of blocky calcite are of equant shape, are large, and translucent but with faint yet variable shading. Pyrite is widely distributed in glendonite and the surrounding host rocks, showing framboidal and euhedral morphologies.

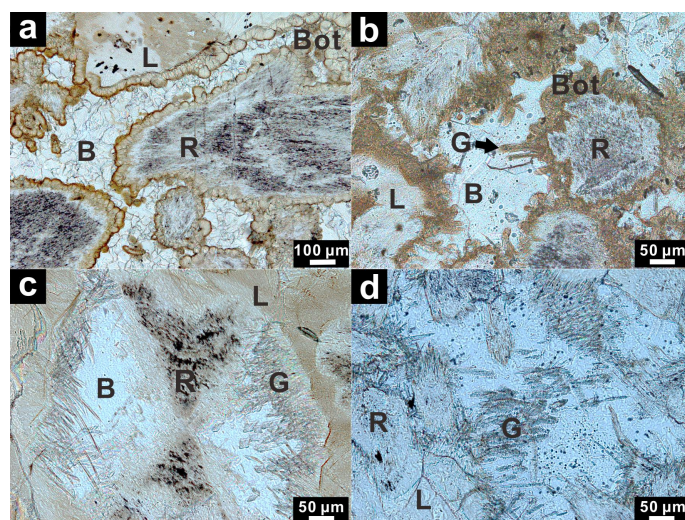


Fig. 3. Transmission-light optical micrographs (plane-polarized light) of mineral varieties composing Siberian glendonite: (a; sample W17.2) botryoidal calcite distributed along the margin of early replacive and light calcite; (b; sample W16) botryoidal and gerbil tail calcite; (c; sample W22B2) gerbil tail calcite projecting from the surface of light calcite; and (d; sample W23A-1)

gerbil tail calcite partially filling a cavity. R: replacive calcite; L: light calcite; Bot: botryoidal variety of fibrous calcite; G: gerbil tail variety of fibrous calcite; B: blocky calcite (same hereafter)

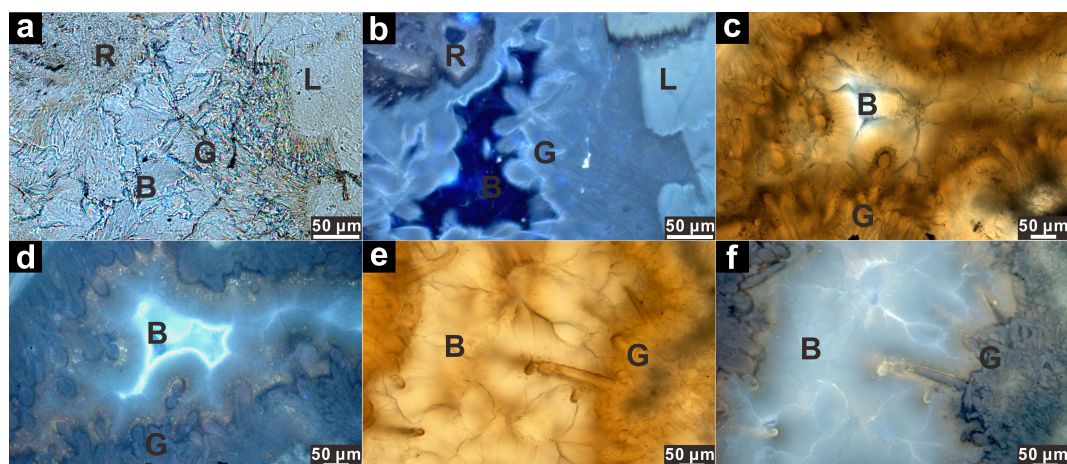


Fig. 4. Photomicrographs of gerbil tail calcite. (a, c; sample 1, and e; sample W16). Spatial relationships among various gerbil tail and other types of calcite under plane-polarized, transmitted light. (b, d, and f) Corresponding fluorescence images of a, c, and e, respectively.

3.2 Element patterns

Calcium is the main cation of all calcite varieties (> 30 wt.%; Table 1; Fig. 5). Element contents of Mg, Fe, and P vary among calcite varieties (Table 1; Fig. 5). Replacive calcite is typified by low Mg (0.0-0.5 wt.%) and Fe (0.0-0.1 wt.%) contents. Light calcite shows overall higher contents with a narrow range of Mg (0.6-0.9 wt.%) and Fe (0.0-0.4 wt.%) contents. Magnesium and Fe contents for fibrous (0.4-1.0 wt.% and 0.0-1.5 wt.%) and blocky (0.4-1.1 wt.% and 0.0-1.5 wt.%) calcite vary.

Table 1 Mineral phases information in glendonite

Paragenetic sequences	Mineral phases		Description	Element contents (wt.%)			FTIR peaks (cm ⁻¹)	
				Ca	Mg	Fe	v ₄	v ₂
1	Replacive calcite (R)		Whitish calcite crystals contain dark organic matter impurities	38.2-39.6	0.0-0.5	0.0-0.1	710, 711	877, 878, 881
2	Light calcite (L)		Brownish calcite show well crystallization	37.3-39.2	0.6-0.9	0.0-0.4	710, 711	879, 880, 883
3	Fibrous calcite (F)	Botryoidal calcite (Bot)	Isopachous and tiny calcite crystals show brown color and poor crystallization	30.9-39.0	0.4-1.0	0.0-1.5	710, 711	874, 877, 878, 879, 880
		Gerbil tail calcite (Ger)	Non-isopachous and tiny crystals; colorless to brownish calcite reveal poor crystallization					
4	Blocky calcite (B)		Colorless to yellowish calcite reveal inhomogeneous crystallization	35.0-39.0	0.4-1.1	0.0-1.5	710, 711	876, 877, 878, 879, 882

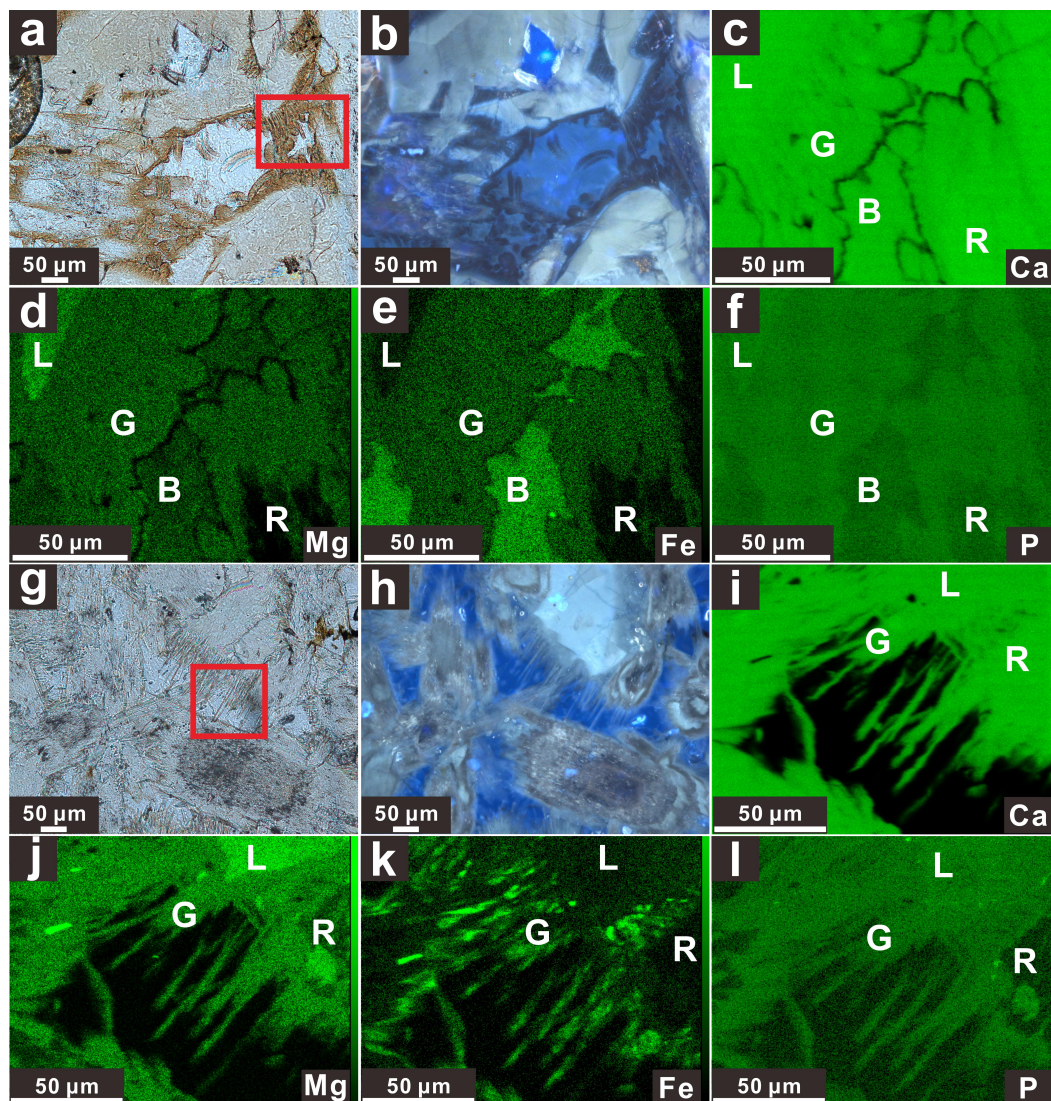


Fig. 5. Paragenetic sequences in different areas of glendonite under plane-polarized, transmitted light (a; sample 1, and g; sample W23A-1) and corresponding fluorescence images (b and h). The red boxes in (a) and (g) indicate the areas of element mapping shown in (c-f) and (i-l), respectively; the corresponding chemical element is indicated in the lower right corner of the map.

3.3 FTIR reflection spectra

Representative FTIR spectra of the four calcite varieties found in Siberian glendonite, along with the spectrum of a reference calcite, are shown in Figure 6. FTIR reflection signals above 2000 cm^{-1} were not detected. It should be highlighted that in IR reflection spectra, both longitudinal optical (LO) and transverse optical (TO) vibrational modes are detected, in contrast to IR spectra measured in transmission, where only TO vibrational modes are detected. The band near $1430\text{--}1520\text{ cm}^{-1}$ is due to the CO_3 antisymmetrical stretching (ν_3), the signal near 876 cm^{-1} originates from CO_3 out-of-plane bending (ν_2), and that near 709 cm^{-1} from CO_3 in-plane bending (ν_4 ; Nakamoto, 2008). The difference in the relative intensities among the samples is due to the

different orientation of the crystals analyzed in the probe areas. The interference fringes in the spectral baseline are due to the fact that the thickness of the analyzed thin sections is similar to the wavelength of the probe radiation. Evidently, the spectra of the four mineral varieties observed in Siberian glendonite match the spectra of reference calcite, thus confirming that these are calcite varieties, but there are discernible shifts in the peaks near 709 and 876 cm^{-1} (see Table 1 and Fig. 6), arising from $\nu_4(\text{CO}_3)$ and $\nu_2(\text{CO}_3)$, the wavenumbers of which are known to be sensitive to the presence of Mg^{2+} and Fe^{2+} substituting for Ca (Bishop et al., 2021).

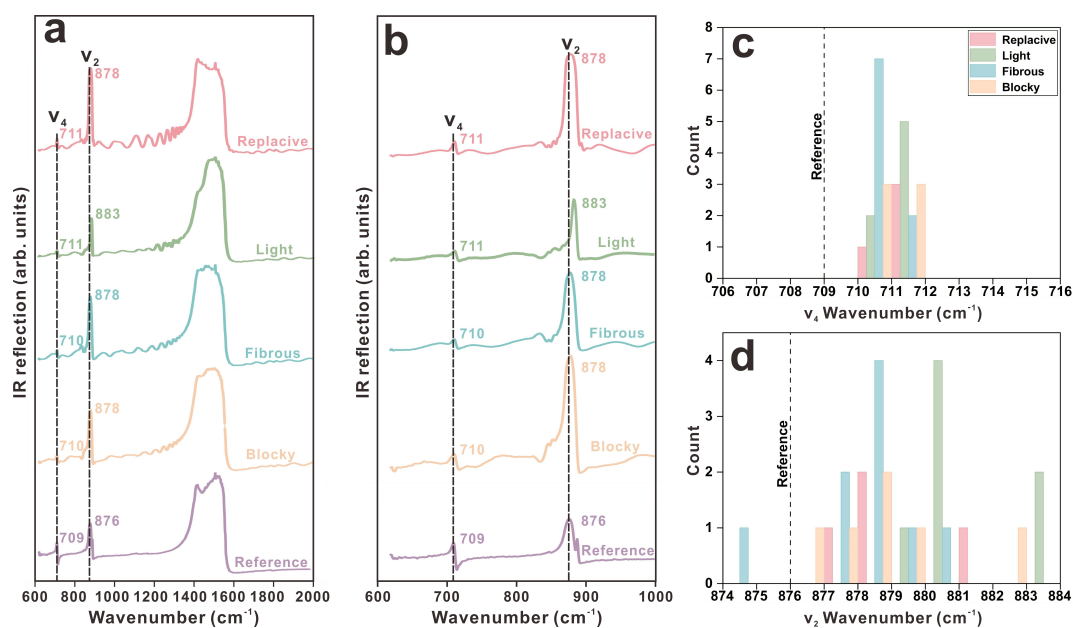


Fig. 6. FTIR spectra and wavenumbers frequency of mineral phases in Siberian glendonite between 600 and 2000 cm^{-1} (a) and on an enlarged scale (b), showing better the IR reflection signals due to $\nu_4(\text{CO}_3)$ and $\nu_2(\text{CO}_3)$ vibrational modes; the spectra are vertically offset for better visualization. Histograms of $\nu_4(\text{CO}_3)$ and $\nu_2(\text{CO}_3)$ wavenumbers are shown in (c) and (d), respectively.

4. Discussion

4.1 Early diagenetic formation of glendonite at shallow sediment depth

Former studies on glendonite already documented phase-dependent variations of element compositions (e.g., Mg, Fe), reflecting dynamic porewater chemistry during recrystallization and mineralization (Vasileva et al., 2022; Schultz et al., 2023). Magnesium contents of the Siberian glendonite studied herein exhibits marked heterogeneity across its paragenetic calcite varieties (Fig. 7), with replacive calcite (derived from ikaite recrystallization) consistently displaying the lowest Mg contents – a pattern also observed during previous investigations (Teichert and Luppold, 2013; Mikhailova et al., 2021). It has been suggested that two main factors account for the low Mg contents of replacive calcite: (1) crystallization at low temperatures with multiple factors resulting from porewater composition inhibiting Mg^{2+} incorporation into the ikaite lattice, and (2) preferential Mg^{2+} ion exclusion during ikaite-calcite transformation (Zhou et al., 2015; Vickers et al., 2024). In contrast, light calcite reveals elevated Mg contents compared to replacive calcite (Fig. 5d and j, 7), consistent with precipitation from Mg-enriched fluids possibly generated through progressive ikaite dissolution (Vickers et al., 2024). Therefore, both replacive and light

calcite may record a genetic link to precursor ikaite. However, the highest Mg contents (≤ 1.0 wt.%) in light and fibrous calcite of the studied Siberian glendonite remain substantially lower than typical contents in glendonite (> 3 wt.%) reported globally (Teichert and Luppold, 2013; Qu et al., 2017; Mikhailova et al., 2021). The low Mg contents therefore suggest diagenesis under shallow burial conditions with limited Mg^{2+} availability. Blocky calcite represents a distinct, late-stage paragenetic variety with complex Mg incorporation pathways influenced by burial and possibly alteration processes (Teichert and Luppold, 2013; Mikhailova et al., 2021). Its textural and compositional variability suggests that blocky calcite is of variable origin in the Siberian glendonite, having formed over an extended time interval and reflecting changing conditions during burial diagenesis.

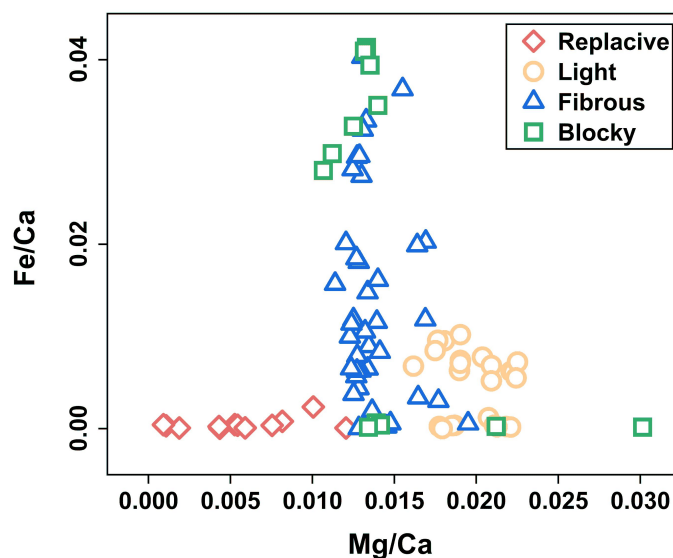


Fig. 7. Scatter plot of element/Ca ratios of calcite varieties of Siberian glendonite.

Iron enrichment in glendonite is frequently associated with late-stage diagenetic processes (McLachlan et al., 2001; Teichert and Luppold, 2013; Counts et al., 2024). Our analytical data obtained for fibrous and blocky calcite reflect substantial variability of Fe contents (≤ 1.5 wt.%) compared to replacive and light calcite (Fig. 7). In marine sedimentary systems, dissolved iron is typically rapidly immobilized by dissolved sulfide generated through organoclastic sulfate reduction and sulfate-driven anaerobic oxidation of methane within the sulfate-methane transition zone (SMTZ), resulting in the formation of authigenic carbonate with low iron contents in sulfidic sediments (Coleman et al., 1997; Riedinger et al., 2017). The widespread occurrence of authigenic pyrite in glendonite-bearing sequences provides petrographic evidence of a porewater environment shaped by microbial sulfate reduction. Replacive calcite displays exceptionally low Fe contents (≤ 0.1 wt.%), suggesting recrystallization from ikaite occurred within the sulfidic zone where iron incorporation was inhibited by sulfide complexation. In contrast, light calcite exhibits slightly elevated Fe contents (≤ 0.4 wt.%), indicating some iron partitioning into authigenic carbonate during early glendonite formation under conditions of reduced sulfide availability (Vickers et al., 2018). Progressive Fe enrichment in fibrous and blocky calcite implies precipitation from iron-rich, later diagenetic fluids conducive to iron substitution in carbonate lattices (Qu et al., 2017; Li et al., 2018). The heterogeneous Fe distribution within fibrous calcite

suggests either (1) temporal variation in sulfide availability during crystallization or (2) micro-scale geochemical gradients in sulfide concentrations during mineral formation.

The observed low Mg contents across all calcite varieties of the studied Siberian glendonite coupled with Fe enrichment in later-stage calcites represents a pattern similar to glendonite specimens documented from the De Kalk Formation (Great Karoo Basin, South Africa), which developed in environments typified by low sedimentation rates represented by a pyrite-bearing carbonaceous mudstone lithofacies (McLachlan et al., 2001). Such element partitioning between mineral phases demonstrates significant potential for constraining glendonite formation and paleoenvironmental conditions through geochemical analyses.

4.2 FTIR discriminates calcite varieties of glendonite

The FTIR spectra among all mineral phases of the studied Siberian glendonite confirms that all phases are calcite (Fig. 6; cf. Gunasekaran et al., 2006). The FTIR reflection signals arising from $\nu_4(\text{CO}_3)$ and $\nu_2(\text{CO}_3)$ vibrational modes are better resolved compared to the broad band generated by the $\nu_3(\text{CO}_3)$ antisymmetric stretching mode; besides, the latter can be compromised by atmospheric water interference artifacts and potential influence from organic matter (Andersson et al., 2014). This circumstance positions the ν_2 and ν_4 modes as superior proxies for evaluating effects of cation substitution, organic-inorganic interaction, and stable isotope composition (e.g., Long et al., 2011; Tao, 2013; Xu et al., 2018) when applying FTIR spectroscopy to calcite. The wavenumber distributions of ν_2 and ν_4 vibrational modes of light calcite of the Siberian glendonite (Fig. 6) consistently exhibit slightly higher wavenumbers in both bands than for the other calcite varieties. As effects from temperature and incidence of angles are excluded during analysis, the distribution patterns of ν_4 and ν_2 vibration might be impacted by other diagnostic factors (e.g., cation substitution, carbon and oxygen isotope composition).

Cation substitution effects on FTIR spectra of calcite are primarily controlled by effective ionic radii (e.g., Ca^{2+} : 1.18 Å; Mn^{2+} : 0.83 Å; Fe^{2+} : 0.78 Å; Mg^{2+} : 0.72 Å; Fe^{3+} : 0.64 Å; Shannon, 1976), which govern the vibrational peak shifts of the carbonate group (Zhuravlev and Atuchin, 2020; Bishop et al., 2021). Natural and synthetic carbonates are typified by an increase in ν_4 and ν_2 wavenumbers correlated with smaller cation radii (Bishop et al., 2021). However, experiments with synthetic calcite with low Mg^{2+} contents ($\text{Mg}:\text{Ca} = 0:1-1:4$) demonstrated minimal ν_2 (871-872 cm^{-1}) and ν_4 (711-713 cm^{-1}) band shifts despite Mg incorporation (2-12 mol%; Purgstaller et al., 2016). Notably, Loste et al. (2003) reported opposing trends in synthetic calcite with higher Mg content (3-47 mol%): ν_2 shifted from 868 to 851 cm^{-1} , while ν_4 increased from 712 to 717 cm^{-1} , although potential interference from amorphous calcium carbonate complicated the interpretation of patterns. A recent study focusing on natural low- and high-magnesium calcite further confirmed an increase in the ν_2 (874 cm^{-1} for low-Mg and 876 cm^{-1} for high-Mg calcite) and ν_4 (712 cm^{-1} for low-Mg and 719 cm^{-1} for high-Mg calcite) vibrational modes with higher Mg contents (Stanienda-Pilecki and Łukowiec, 2025). Furthermore, recent studies on Mg incorporation into synthetic calcite demonstrated that higher concentrations of L-aspartic acid (0-7.5 mM) in solution enhance Mg partitioning into the calcite crystal structure, while inducing ν_2 vibrational band shifts (869-874 cm^{-1}) at constant Mg^{2+} concentrations (Tao, 2013). However, such effects remained unobserved in systems containing polyacrylic acid or dextran sulfate sodium at constant Mg/Ca ratios (Long et al., 2011). Although some of the calcite varieties of the Siberian glendonite (Figs 4, 5) exhibit distinct fluorescence patterns and elevated phosphorus

contents – particularly light and fibrous (gerbil tail) calcite – no precise identification of organic matter composition and contents was pursued in our study. However, all of these observations collectively suggest that low Mg contents (maximum 1.1 wt.% in blocky calcite) cannot be the only factor causing the observed discernible ν_2 and ν_4 shifts (Table 1; Fig. 6; ν_4 : 2 cm^{-1} and ν_2 : 9 cm^{-1}). Iron substitution similarly influences calcite's FTIR signatures (Simpson, 1998; Korchef, 2019). Böttcher et al. (1997) documented $< 2 \text{ cm}^{-1}$ peak displacements in natural carbonates with $< 1 \text{ mol\% Fe}^{2+}/\text{Mn}^{2+}$, particularly for ν_2 vibrations. The maximum Fe content (1.5 wt.%) detected in calcite varieties of Siberian glendonite thus appears insufficient to solely cause the observed vibrational band shifts, suggesting additional controlling mechanisms, which will require more detailed investigations in the future.

Systematic variation of $^{13}\text{C}/^{12}\text{C}$ ratios in calcite causes nonlinear, mode-dependent shifts in the relative positions and intensities of infrared-active vibrational modes as documented by combined experimentally-produced and simulated FTIR spectra, demonstrating sensitivity to even minor isotope variability on a small scale (Xu et al., 2018). Oxygen isotope substitution experiments further demonstrated that variability of $^{16}\text{O}/^{18}\text{O}$ ratios induces measurable peak displacement in the dominant vibrational bands of the carbonate group (King et al., 2023). Siberian glendonite from the study area exhibits bulk $\delta^{13}\text{C}_{\text{VPDB}}$ values ranging from -44.5‰ to -0.4‰ , and $\delta^{18}\text{O}_{\text{VPDB}}$ values from -14.7‰ to -0.8‰ (Morales et al., 2017), with systematic variation among specimens. Although we did not determine the carbon and oxygen isotope composition of the calcite varieties of glendonite in this study – due to the small scale of crystals and the complex intermeshing of phases – the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of calcite from glendonite documented by previous studies are highly variable suggesting a dominant carbon source from different organic compounds and variable porewater environments (Greinert and Derkachev, 2004; Frank et al., 2008; Qu et al., 2017; Vickers et al., 2018; Vasileva et al., 2019). Such a phase-dependent isotopic divergence underscores the critical role of microenvironmental redox conditions in the diagenesis of glendonite (Geptner et al., 2014). Therefore, the wavenumber distribution patterns observed for Siberian glendonite (Fig. 6c, d) agree with a partial attribution of the vibrational shifts to coupled carbon-oxygen isotope effects. Future investigations should integrate refined spectral interpretations coupled with high-resolution geochemical analyses (e.g., cation speciation, isotopic composition) to unleash the full potential of FTIR analysis for utilizing the paleoenvironmental information archived in the complex paragenetic sequence of glendonite.

5. Conclusions

To elucidate the successive formation process resulting in the complex crystal mosaic of glendonite, its individual mineral phases were analyzed with electron microprobe analysis (EMPA) and Fourier transform infrared spectroscopy (FTIR). The paragenetic sequence of Jurassic glendonite from Siberia (Russia) was found to consist of four calcite varieties including replacive calcite, light calcite, fibrous calcite, and blocky calcite. Our results demonstrate that glendonite is typified by structural and compositional complexity compared to its precursor ikaite. While systematic quantification of Mg and Fe contents in discrete mineral phases enables preliminary assessment of the corresponding formation environments, the observed shifts in FTIR reflection signals, particularly those arising from $\nu_4(\text{CO}_3)$ and $\nu_2(\text{CO}_3)$ vibrational modes, are apparently only partially caused by substitution effects. Variability of carbon and oxygen isotope composition of calcite varieties is probably an additional driver of the observed peaks shifts of

FTIR spectra. Irrespective of what is causing such peak shifts, FTIR allows to characterize the individual phases forming the crystal mosaic of glendonite, setting the stage for the full exploitation of the geochemical information stored in in this pseudomorph of ikaite.

Acknowledgments

We thank Mikhail Rogov (Moscow) for providing the Siberian glendonite samples studied herein, Stefanie Heidrich (Hamburg) for help with electron microprobe analysis, Magnus Ivarsson (Stockholm) for discussion of the classification of gerbil tail calcite, and Stefan Peters, curator of the Museum of Nature Hamburg – Mineralogy, Leibniz Institute, for the Analysis of Biodiversity Change, for providing a reference calcite sample. Qinyi Zhang acknowledges funding provided by a China Scholarship Council fellowship (file No. 202304910070). Comments by two anonymous reviewers helped to improve this article.

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Chapter 3 Characterizing ancient seep environments by in-situ sulfur isotope composition of authigenic pyrite

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Characterizing ancient seep environments by in-situ sulfur isotope composition of authigenic pyrite



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Keywords: Ancient seep deposits; Carbonate authigenesis; Authigenic pyrite; Sulfur stable isotopes

Abstract:

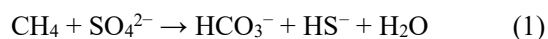
Authigenic pyrite commonly coexists with authigenic carbonate forming at marine methane seeps. Both pyrite and carbonate minerals are by-products of sulfate-driven anaerobic oxidation of methane (SD-AOM), the dominant biogeochemical process at seeps. The sulfur isotopic composition of pyrite has been extensively used to study the sulfur cycle and seepage activity in modern seep environments. However, to what extent $\delta^{34}\text{S}_{\text{py}}$ values can aid the interpretation of ancient seep environments is poorly known. To improve on this knowledge gap, secondary ion mass spectroscopy (SIMS) was applied to investigate the sulfur isotope patterns of different types of pyrite (framboidal and euhedral) on a microscale from seep deposits of Beauvoisin (Jurassic, France) and Whiskey Creek (Eocene, USA), which is supplemented by the sulfur isotope measurement of bulk pyrite (chromium reducible sulfur; CRS). Framboids of the Beauvoisin seep deposits show low $\delta^{34}\text{S}_{\text{py}}$ values (-40.1‰ to -23.9‰), those of the Whiskey Creek deposit exhibit a wider range of values (-40.7‰ to 9.9‰). Most of the euhedral pyrite from both sites is typified by higher $\delta^{34}\text{S}_{\text{py}}$ values (4.4‰ to 5.7‰ for Beauvoisin; 0.4‰ to 3.6‰ for Whiskey Creek). The $\delta^{34}\text{S}_{\text{CRS}}$ values of Beauvoisin deposits (-23.0‰ to 1.80‰) are also lower than those of Whiskey Creek (-10.8‰ to 2.9‰). The large variations in $\delta^{34}\text{S}_{\text{py}}$ values, reflecting different types of pyrite, suggest that pyrite formed episodically over a prolonged period of seepage during early diagenesis. Overall, high rates of sulfate reduction and high replenishment of the pore water pool of sulfate with seawater sulfate at active methane seeps controlled the crystal habit and the sulfur isotope composition of the studied pyrite. Higher $\delta^{34}\text{S}_{\text{py}}$ values of euhedral pyrite record progressively sulfate-limited conditions where sulfate consumption by SD-AOM exceeded sulfate replenishment – as observed for later-stage pyrite extracted from modern seepage-affected

sediment with $\delta^{34}\text{S}_{\text{py}}$ values higher than 100‰. The lack of such extremely high $\delta^{34}\text{S}_{\text{py}}$ values within the studied seep limestones is probably not only controlled by the degree of replenishment of seawater sulfate but also by the engulfment of pyrite by authigenic seep carbonate, impeding the formation of later stages of pyrite. Overall, the identified sulfur isotope patterns of pyrite preserved in the Beauvoisin and Whiskey Creek seep deposits resemble observations made on pyrite from modern seeps, confirming that the sulfur isotopic composition of pyrite can serve as a potent tool for reconstructing the biogeochemical cycling of sulfur in ancient seep environments.

Key words: Ancient seep deposits; Carbonate authigenesis; Authigenic pyrite; Sulfur stable isotopes

Introduction

Marine hydrocarbon seeps are common phenomena along continental margins where hydrocarbons, mostly methane, migrate to the seafloor through and from deep sedimentary reservoirs (Boetius and Wenzhöfer, 2013). Methane and other reduced compounds contained in the seepage fluids are the source of energy for the lush chemosynthesis-based communities living at modern marine seeps, with different groups of metazoans adapted to this environment since at least the Silurian (Bowden et al., 2013; Kiel and Peckmann, 2019; Smrzka et al., 2019). Seepage of hydrocarbons is also thought to have influenced current and past global warming (Dickens, 2011; Ruppel and Kessler, 2017). At seeps, sulfate-driven anaerobic oxidation of methane (SD-AOM) is the dominant biogeochemical process, mediated by a consortium of methanotrophic archaea and sulfate-reducing bacteria (Eq 1; Boetius et al., 2000).



This process produces dissolved bicarbonate, favoring precipitation of carbonate minerals including aragonite, low-Mg calcite, high-Mg calcite, and dolomite at marine seeps (Feng et al., 2014; Lu et al., 2021). Authigenic carbonates also form at oil seeps, where the oxidation of methane and other reduced organic compounds increases pore water alkalinity (Smrzka et al., 2019; Akam et al., 2021; Krake et al., 2022). Seep carbonates have also been reported from the rock record (Peckmann and Thiel, 2004; Bristow and Grotzinger, 2013). Ancient seep deposits represent an excellent archive documenting the evolution of biogeochemical processes and past metazoan life in chemosynthesis-based ecosystems (e.g., Hryniewicz, 2022).

During SD-AOM, in addition to bicarbonate, hydrogen sulfide is released into pore water and subsequently converted into iron sulfide minerals and finally pyrite (FeS_2) in the presence of reactive iron (Jørgensen et al., 2004). Authigenic pyrite is common in seepage-affected sediments (Zhang et al., 2014; Lin et al., 2016a) and commonly enclosed within seep carbonates (Peckmann et al., 2001; Chen et al., 2021). Apart from SD-AOM, organoclastic sulfate reduction (OSR), using organic matter as a substrate, leads to pyrite formation (Berner, 1984; Canfield, 1991). As a diagenetically stable iron sulfide mineral in the sediment, pyrite can record sedimentary sulfur cycling and variations in local environmental conditions, typically expressed by various crystal habits and sulfur isotopic compositions (Lin et al., 2016b, 2016a; Chang et al., 2022). In marine sediments not affected by seepage, pyrite formed by OSR typically reveals low $\delta^{34}\text{S}$ values (Wortmann et al., 2001; Canfield and Teske, 1996); organic matter contents and sedimentation

rates have been shown to affect the sulfur stable isotope composition of pyrite (e.g., Pasquier et al., 2017; Jørgensen, 2021). In contrast, many studies reported ^{34}S enriched authigenic pyrite from modern seep environments (Peckmann et al., 2001; Lin et al., 2016a, 2017a, 2018, 2024; Wu et al., 2019; Miao et al., 2021), with ^{34}S enrichment apparently caused by higher rates of sulfate reduction compared to OSR (Deusner et al., 2014), low sulfate replenishment (Gong et al., 2018), and quantitative conversion of seawater sulfate to sulfide (Borowski et al., 2013). Since pyrite formation – strictly speaking, the formation of iron mono sulfide minerals and their subsequent recrystallization into pyrite – is a cumulative process in seep environments, occurring at different stages of diagenesis, the sulfur isotope composition of the resultant composite pyrite reflects the mixture of pyrite forming under changing environmental conditions. Lin et al. (2016a) investigated in-situ sulfur isotope compositions of authigenic pyrite consisting of a sequence of intergrown stages of pyrite formation by applying secondary ion mass spectroscopy (SIMS). The pyrite was extracted from modern seepage-affected sediments and was found to consist of a sequence of pyrite phases with different crystal habits and highly variable $\delta^{34}\text{S}_{\text{py}}$ values, representing a much wider range of values than the range of $\delta^{34}\text{S}_{\text{py}}$ resulting from bulk analyses. The SIMS approach helped to understand the effects of SD-AOM on the local pore water pool of sulfate and the diagenetic history of pyritization at methane seeps (Lin et al., 2016a). To decipher the relationship between co-existing carbonate minerals and pyrite at modern seeps, Chen et al. (2021) analyzed the in-situ $\delta^{34}\text{S}_{\text{py}}$ composition of pyrite enclosed in seep carbonate from the South China Sea, suggesting pore water sulfate composition impacted the sulfur isotope composition of pyrite.

Although pyrite with different crystal habits is common in ancient seep carbonates, sulfur isotope analysis of individual pyrite aggregates on a microscale is lacking to date. This hampers our understanding of the pyritization history and the dynamics of the biogeochemical cycling of sulfur at ancient seeps and, thus, the application of the pyrite sulfur isotope proxy to the reconstruction of the environmental conditions at seeps in the geological past. In this study, we investigated the in-situ sulfur isotope compositions of authigenic pyrite enclosed in two ancient seep deposits, the Beauvoisin site in southeastern France and Whiskey Creek site from Washington State, USA. In comparison with pyrite sulfur isotope patterns of modern seeps, we conclude that the characteristic evolution from framboidal to euhedral crystals along with a gradually developing trend toward more positive $\delta^{34}\text{S}_{\text{py}}$ values is a common phenomenon in both ancient – dating back at least to the Jurassic – and modern seep environments, confirming that the analysis of the sulfur isotopic composition of composite pyrite aggregates is a useful tool for reconstructing local environments and biogeochemical processes at ancient seeps.

1. Geological setting

The Beauvoisin ancient seep site is situated in southeastern France (Fig. 1A). Previous studies recognized a seep origin of the Beauvoisin carbonate deposits based on low $\delta^{13}\text{C}$ values of authigenic carbonate, molecular fossils of methanotrophic archaea with low $\delta^{13}\text{C}$ values (as low as -76‰), and chemosymbiotic bivalves (Gaillard et al., 1992; Peckmann et al., 1999; Senowbari-Daryan et al., 2007; Kiel et al., 2010). The seep deposits occur in a thick succession (up to 2,500 m) of Jurassic black shales of the Terres Noires Formation in Lower Oxfordian to Upper Oxfordian strata (Gaillard et al., 1985). Two main levels of seep deposits were recognized. The lower level with marlstones contains abundant, large and well-exposed seep deposits (Early to

Middle Oxfordian) and the upper level corresponds to a limestone/marl alternation with scarce and smaller limestone bodies (Middle Oxfordian); in this study, pyrite enclosed in the seep deposits of the lower level is analyzed. The Beauvoisin seep sites may have been impacted by oil seepage in addition methane seepage and a wide range of $\delta^{13}\text{C}_{\text{carbonate}}$ values has been reported (-37.0‰ to 15.1‰ ; Peckmann et al., 1999; Louis-Schmid et al., 2007; Tribovillard et al., 2013).

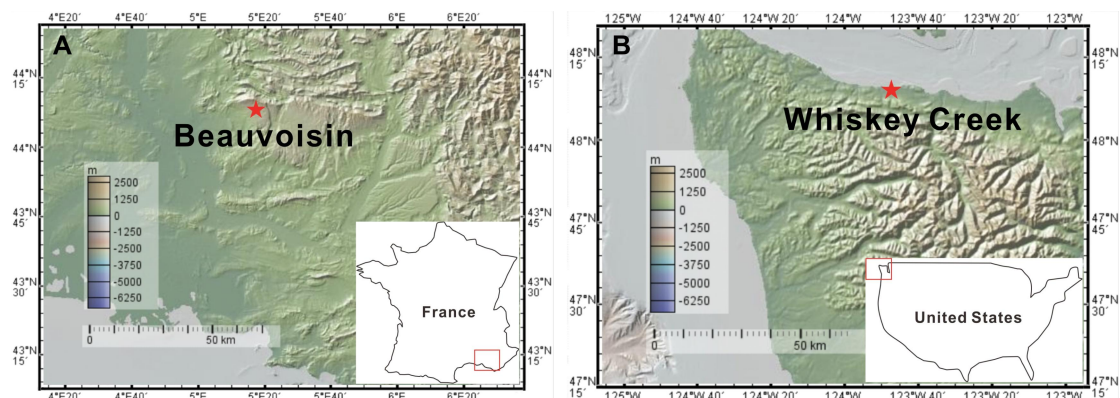


Fig. 1. Geographic setting of the Beauvoisin (A) and Whiskey Creek (B) seep deposits, magnified from the red boxes marked in the maps of France and the United States of America. Sample locations are marked by red stars. Map made with GeoMapApp (www.geomapapp.org) / CC BY / CC BY (Ryan et al., 2009).

The Whiskey Creek site is located in Clallam County, on the north side of the Olympic Peninsula in Washington State (Fig. 1B). The Whiskey Creek seep deposit appears to derive from the late Eocene lowermost part of the Pysht Formation (Goedert et al., 2003). The Whiskey Creek limestones contain a seep fauna (Goedert et al., 2003; Kiel et al., 2023) and exhibit a chaotic fabric produced by a variety of processes having occurred during early diagenesis (bioturbation, concretionary carbonate formation, early in-situ brecciation, carbonate corrosion) and late diagenesis (fracturing of the rock). The formation of the authigenic carbonate phases making up most of the Whiskey Creek limestones was induced by SD-AOM as revealed by negative $\delta^{13}\text{C}_{\text{carbonate}}$ values as low as -36.0‰ and ^{13}C depleted biomarkers of the microbial consortium performing SD-AOM (Goedert et al., 2003; Peckmann et al., 2003). The good preservation of lipid biomarkers in the studied Phanerozoic Beauvoisin and Whiskey Creek seep deposits excludes high thermal alteration and metamorphic overprinting during burial (cf. Peckmann et al., 1999; Goedert et al., 2003).

2. Material and methods

2.1 Chromium reducible sulfur and $\delta^{34}\text{S}_{\text{CRS}}$ measurement

Rock samples from Beauvoisin and Whiskey Creek were selected for this study because the presence of abundant pyrite was previously documented (Peckmann et al., 1999, 2003). The lithologies used for chromium reducible sulfur (CRS) are shown in Figure 2. Targeted microfacies of the Beauvoisin and Whiskey Creek samples consisted of microcrystalline carbonate enclosing abundant pyrite. Selected portions of the microcrystalline matrix were micro-drilled and subsequently powdered (Fig. 2). Sulfide sulfur from bulk samples was liberated as hydrogen sulfide by wet chemical, sequential extraction (Canfield et al., 1986; Rice et al., 1993). Acid-

volatile sulfides (AVS, mainly FeS) were liberated with HCl (25%) for 1 h at room temperature: no AVS was detected for the samples. The remaining sample powder was reacted with 1 M CrCl₂ at sub-boiling temperatures for 2 h to liberate CRS (mainly pyrite). Released hydrogen sulfide from CRS was precipitated as zinc sulfide by a zinc acetate solution. Zinc sulfide precipitates were subsequently converted to silver sulfide (Ag₂S) using a AgNO₃ solution. Ag₂S precipitates were collected by filtration (<0.45 µm) and dried at 40 °C overnight. For δ³⁴S analysis, Ag₂S precipitates were measured as SO₂ via combustion of ca. 200 µg Ag₂S mixed with an equal amount of V₂O₅ using a ThermoScientific Delta V Advantage mass spectrometer linked to a Flash EA Isolink CN Elemental Analyzer (EA-IRMS) at the Institut für Geologie und Paläontologie, Universität Münster. The measurement was calibrated with international reference materials IAEA-S1 (δ³⁴S = −0.3‰), IAEA-S2 (δ³⁴S = 22.6‰), IAEA-S3 (δ³⁴S = −32.5‰), and NBS 127 (δ³⁴S = 20.3‰; Brand et al., 2014). The isotope ratio is expressed as δ³⁴S (δ³⁴S_{CRS}) values relative to the V-CDT standard. The analytical precision was better than ±0.3‰.

$$\delta^{34}\text{S} (\text{‰}, \text{V-CDT}) = \left[\left(\frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{34}\text{S}/^{32}\text{S})_{\text{V-CDT}}} \right) - 1 \right] \times 1000.$$

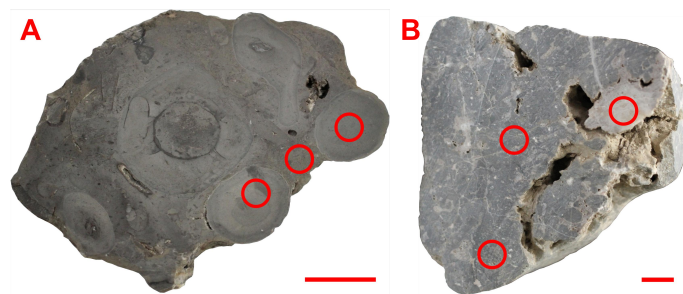


Fig. 2. Selected seep carbonates from Beauvoisin (A) and Whiskey Creek (B). Microdrill areas for CRS determination are marked by red circles. Scale bars represent 2 cm.

2.2 In-situ sulfur isotope analysis

Samples from Beauvoisin and Whiskey Creek with abundant pyrite were selected for high spatial resolution sulfur isotope analysis by secondary ion mass spectrometry (SIMS). Selected carbonate samples were cut and embedded in epoxy discs (25 mm in diameter) together with sulfide standards. After the epoxy was cured, the discs were polished until the pyrite crystals and carbonate minerals were exposed and became visible under an optical microscope. SIMS analyses were carried out with a Cameca IMS1280-HR at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. An off-mount calibration procedure was used. Analytical methods and instrument parameters were described in Li et al. (2019). Pyrite standard UWPY-1 (δ³⁴S = 16.0 ± 0.2‰; Ushikubo et al., 2014) was used as the primary standard, and PPP-1 (δ³⁴S = 5.3 ± 0.2‰; Gilbert et al., 2014) was used as a quality control standard. Pyrrhotite standard YP-136 (δ³⁴S = 1.5 ± 0.1‰; Li et al., 2019) was used to monitor analytical reliability. Standard YP-136 was measured after every five analyses. The isotope ratio is expressed as δ³⁴S (δ³⁴S_{py}) values relative to the V-CDT standard. Analytical precision was better than ±0.2‰.

3. Results

3.1 CRS contents and δ³⁴S_{CRS} values

CRS contents and δ³⁴S_{CRS} values of selected samples from Beauvoisin and Whiskey Creek

are shown in Table S1 and Fig. 3. For Beauvoisin, CRS contents vary from 0.0 wt.% to 0.5 wt.% and $\delta^{34}\text{S}_{\text{CRS}}$ values range from -23.0‰ to 1.8‰ . For Whiskey Creek, CRS contents range from 0.0 wt.% to 2.0 wt.%, corresponding $\delta^{34}\text{S}_{\text{CRS}}$ values vary from -10.8‰ to 2.9‰ .

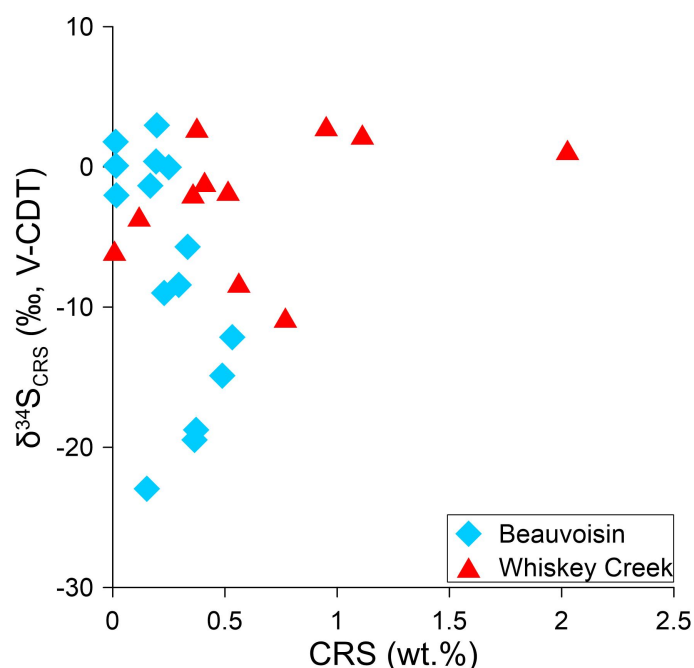


Fig. 3. Chromium reducible sulfur (CRS) contents versus bulk rock $\delta^{34}\text{S}_{\text{CRS}}$ values of seep carbonates from Beauvoisin and Whiskey Creek.

3.2 Pyrite crystal habits and $\delta^{34}\text{S}_{\text{py}}$ values determined by SIMS analysis

3.2.1 Beauvoisin

Typical pyrite crystals (framboids and euhedral pyrite) enclosed in seep limestones from the Beauvoisin site are shown in Figure 4. Beauvoisin seep deposits are typified by abundant microcrystalline carbonate nodules; nodules contain most of the pyrite, which is commonly enriched in the center and along their periphery (Peckmann et al., 1999). The $\delta^{34}\text{S}_{\text{py}}$ values range from -40.1‰ to 5.7‰ (Table S2). Framboids are typically smaller than $20\text{ }\mu\text{m}$. Most framboids are dispersed in the center of nodules and reveal low $\delta^{34}\text{S}_{\text{py}}$ values (Table S2; Fig. 4A; from -40.1‰ to -23.9‰). Euhedral pyrite crystals of variable size (diameters from $3\text{ }\mu\text{m}$ to more than $20\text{ }\mu\text{m}$) are preferentially distributed in the periphery of nodules (Fig. 4B). Most of the euhedral crystals revealed higher $\delta^{34}\text{S}_{\text{py}}$ values, mainly ranging from 4.4‰ to 5.7‰ (Table S2; Fig. 4C). In some instances, largely different sulfur isotope compositions between framboidal pyrite (-26.5‰) and euhedral pyrite (5.7‰) were identified even on a small scale (Fig. 4D).

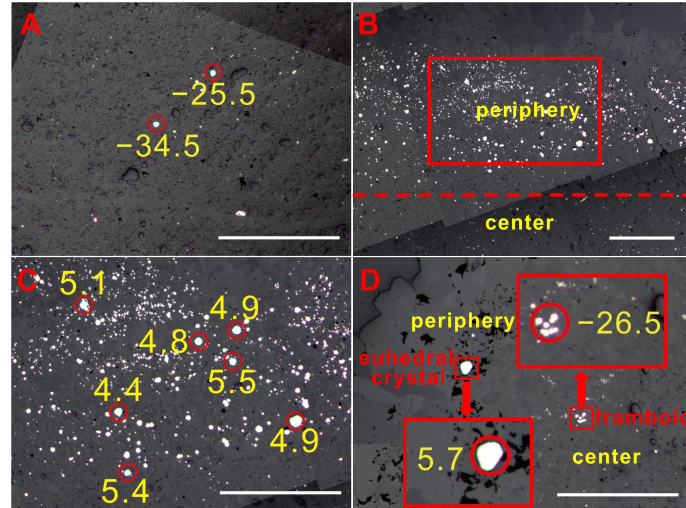


Fig. 4. Photomicrographs of pyrite in seep carbonate from Beauvoisin; reflected light. (A) Framboidal pyrite with low $\delta^{34}\text{S}_{\text{py}}$ values (yellow number). Red circles indicate the areas for SIMS analysis. (B) Pyrite is enriched at the periphery and the center of carbonate nodules. (C) Enlarged area in the red rectangle of B with large euhedral crystals with high $\delta^{34}\text{S}_{\text{py}}$ values. (D) Variable $\delta^{34}\text{S}_{\text{py}}$ values of framboidal and euhedral pyrite on a small scale. Large red rectangles are enlarged from the smaller ones. Scale bars represent 200 μm .

3.2.2 Whiskey Creek

In the Whiskey Creek seep limestones, pyrite is widely distributed within the matrix of angular carbonate aggregates consisting of authigenic micrite (i.e., microcrystalline calcite; Fig. 5). Pyrite occurs as framboidal and euhedral aggregates, characterized by a large variability of sulfur isotope compositions with $\delta^{34}\text{S}_{\text{py}}$ values ranging from -40.7‰ to 9.9‰ (Table S3; Fig. 5A and B). In some instances, framboidal pyrite enriched along the periphery of angular micrite aggregates tends to exhibit pronounced ^{34}S depletion with $\delta^{34}\text{S}_{\text{py}}$ values as low as -40.7‰ (Table S3; Fig. 5C and D). Like the pattern observed for Beauvoisin samples, euhedral pyrite from Whiskey Creek shows higher $\delta^{34}\text{S}_{\text{py}}$ values than most of the framboidal pyrite.

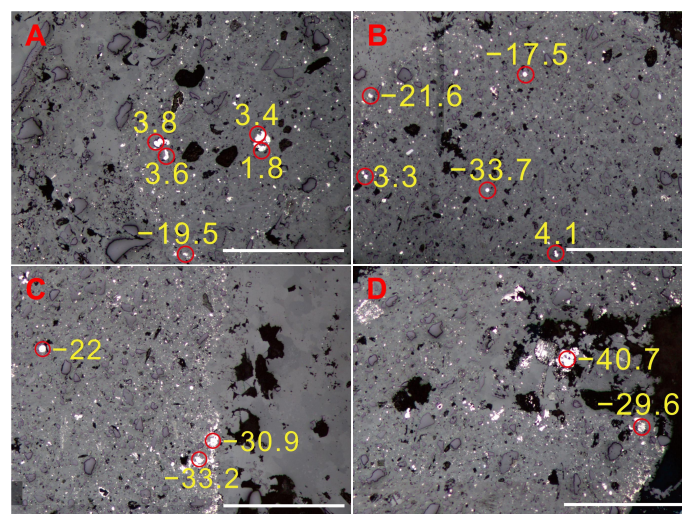


Fig. 5. Photomicrographs of pyrite from the Whiskey Creek deposit and in-situ sulfur isotopic

compositions of pyrite; reflected light. (A) and (B) Pyrite distributed in the microcrystalline carbonate matrix; both negative and positive $\delta^{34}\text{S}_{\text{py}}$ values (yellow numbers) exist. (C) and (D) Angular aggregates of pyrite within the microcrystalline carbonate matrix. Scale bars represent 200 μm .

4. Discussion

Framboidal and euhedral pyrite are common components of ancient and modern seep limestones (e.g., Peckmann et al., 2001; Peckmann and Thiel 2004; Merinero et al., 2008; Chen et al., 2021). The accepted model of framboid formation proceeds through (1) rapid nucleation in solutions supersaturated with respect to iron sulfide minerals and (2) limited crystal growth in diffusion-dominated stagnant sediments (Rickard, 2021). Upon rapid nucleation, supersaturation in the pore water decreases dramatically. Later progressive supply of iron and sulfur might result in overgrowths on existing framboids or precipitation of euhedral pyrite (Taylor and Macquaker, 2000; Merinero et al., 2008; Rickard, 2021). Recent studies on the in-situ sulfur isotope composition of pyrite from modern seep sediments and carbonates found that euhedral crystals, having formed at a later stage, were strongly enriched in ^{34}S , while framboids were depleted in ^{34}S (Lin et al., 2016a, 2017a). Large variability of their sulfur isotopic composition was also identified for pyrite aggregates enclosed in the Beauvoisin and Whiskey Creek limestones studied herein, where euhedral crystals tend to reveal higher $\delta^{34}\text{S}_{\text{py}}$ values than framboids (Fig. 4, 5 and 6).

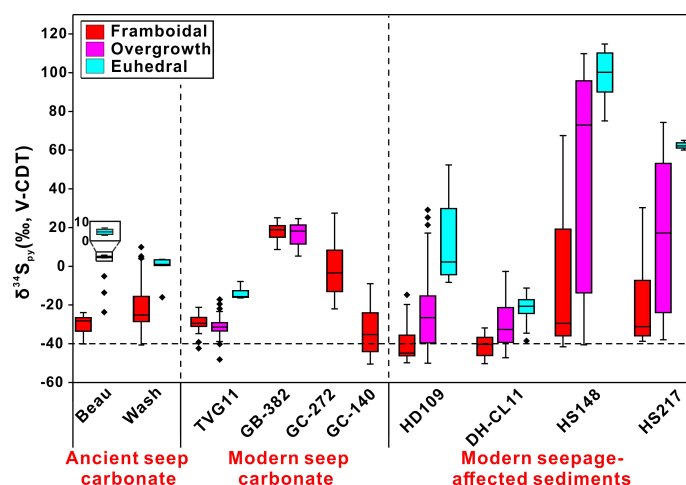


Fig. 6. Box-whisker plot of $\delta^{34}\text{S}$ values of framboidal, overgrowth, and euhedral pyrite measured by secondary ion mass spectroscopy. The data from sites GB382, GC272, GC140, and TVG11 are from Morelli (2019) and Chen et al. (2021), while those from sites HD109, DH-CL11, HS148, and HS217 are from Lin et al. (2016a, 2017a). The black box at left shows the magnified $\delta^{34}\text{S}$ values of euhedral pyrite from Beauvoisin; Beau = Beauvoisin; Whis = Whiskey Creek.

During SD-AOM, the rate of sulfate reduction is sensitive to methane concentration, which results in a range of sulfur isotope fractionation from 20 to 60‰ (Deusner et al., 2014). The sulfur isotopic composition of framboids shows different patterns for the two Phanerozoic study sites (Fig. 6). For the Jurassic Beauvoisin deposits, all framboids have low $\delta^{34}\text{S}_{\text{py}}$ values (from -40.1‰ to -23.9‰ ; Fig. 4 and 6), corresponding to sulfur isotope fractionation of around 57‰ compared to ambient seawater sulfate ($\delta^{34}\text{S} \approx 17\text{‰}$ in the late Jurassic; Kampschulte and Strauss, 2004).

Such significant sulfur isotope fractionation between seawater sulfate and framboidal pyrite falls into the isotope fractionation field during SD-AOM (Deusner et al., 2014).

The ^{34}S depletion in framboids reflects seawater sulfate diffusing to a sufficient degree into a shallow sulfate-methane transition zone (SMTZ) to maintain high rates of SD-AOM (Gong et al., 2018; Chen et al., 2021). In such a case, the dissolved sulfate in pore water at shallow SMTZs will tend to exhibit a sulfur isotope composition close to the composition of seawater sulfate, which eventually converts into sulfide with low $\delta^{34}\text{S}$ values due to the preferential use of isotopically light sulfate during SD-AOM (Jørgensen, 1979; Deusner et al., 2014). However, pyrite formed by OSR also tends to show low $\delta^{34}\text{S}$ values (Canfield and Teske, 1996) and it is consequently difficult to disentangle the relative effect of OSR and SD-AOM on framboid formation based on $\delta^{34}\text{S}_{\text{py}}$ values alone. Indeed, OSR probably took place in the ancient seep environments and contributed to framboid formation, but the contribution from OSR was probably minor because seep carbonates form where methane flux is high and SD-AOM is prominent; such an environment will therefore be characterized by a stronger impact of SD-AOM than OSR on framboid formation compared to settings with diffusive transport of methane.

Framboids enclosed in the Whiskey Creek limestones display a large variability of $\delta^{34}\text{S}_{\text{py}}$ values (from -40.7‰ to 9.9‰ ; Fig. 5 and 6). Interestingly, the lowest $\delta^{34}\text{S}_{\text{py}}$ values of framboids from both Phanerozoic seep deposits are quite similar (-40.1‰ , Beauvoisin and -40.7‰ , Whiskey Creek), suggesting similar degrees of sulfur isotope fractionation during the formation of framboids during SD-AOM under conditions of high sulfate replenishment (seawater sulfate $\delta^{34}\text{S}$ value of 21‰ in the late Eocene; Kampschulte and Strauss, 2004). In contrast, the ^{34}S enriched framboidal pyrite can be attributed to lower sulfate replenishment of dissolved sulfate, resulting in higher $\delta^{34}\text{S}$ values in a deeper SMTZ. Framboids forming in sediments with pore water typified by ^{34}S enriched dissolved sulfate show high $\delta^{34}\text{S}$ values (Hu et al., 2020). Therefore, the large variation of $\delta^{34}\text{S}_{\text{py}}$ values of many of the framboids in the Whiskey Creek seep deposit reveals that pyrite formation was a successive process that relied on (1) the continuous supply of sulfide, primarily produced by SD-AOM, and (2) the presence of sufficient reactive iron during long-lasting methane seep activity (cf. Goedert et al., 2003). This interpretation agrees with the higher CRS contents of the Whiskey Creek deposit (0.0 wt.% to 2.0 wt.%) compared to the Beauvoisin seep limestones (0.0 wt.% to 0.5 wt.%). Although the framboids of the Whiskey Creek deposit show larger variability of $\delta^{34}\text{S}_{\text{py}}$ values, the bulk $\delta^{34}\text{S}_{\text{CRS}}$ values (-10.8‰ and 2.9‰) fall into a narrower range compared to the values of the Beauvoisin framboids (-23.0‰ to 1.8‰). Given that all $\delta^{34}\text{S}_{\text{CRS}}$ values fall into the range of values obtained by SIMS analysis, such variation observed for the bulk samples probably reflects the changing proportions of ^{34}S depleted framboids and ^{34}S enriched euhedral crystals. This observation highlights the importance and effectiveness of the application of SIMS to resolve processes within the sulfur cycle from the sulfur isotope variation of sulfide minerals.

The higher $\delta^{34}\text{S}_{\text{py}}$ values of euhedral pyrite of the Beauvoisin and Whiskey Creek seep deposits reflect later stage formation of hydrogen sulfide. The euhedral pyrite enclosed in the Beauvoisin limestones apparently formed later than the framboids because the former is most common in the periphery of framboid-rich carbonate nodules, sometimes forming rims around carbonate nodules (Fig. 4). In contrast, it is difficult to establish a sequence for the formation of framboids and euhedral pyrite for the Whiskey Creek limestone based on structural relationships, given the scattered distribution of the different types of pyrite. Applying conventional sulfur

isotope analysis of pyrite, Peckmann et al. (2003) found small scale variability of $\delta^{34}\text{S}_{\text{CRS}}$ values for the Whiskey Creek seep limestones and argued that microbial sulfate reduction occurred in different microenvironments and utilized small, residual pools of seawater sulfate.

The $\delta^{34}\text{S}_{\text{py}}$ data of different types of pyrite from various seepage-affected sediments and seep limestones are compiled in Table 1 and Figure 6. Like the pattern observed in this study, $\delta^{34}\text{S}_{\text{py}}$ values generally tend to increase from framboids to overgrowth layers of pyrite and finally euhedral pyrite for both ancient and modern settings. This trend is most probably caused by a progressive enrichment of ^{34}S in residual pools of dissolved sulfate in the pore water. Interestingly, the $\delta^{34}\text{S}_{\text{py}}$ values determined for the ancient seep limestones show lower and narrower ranges of values than values for pyrite from modern seepage-affected sediments, for which $\delta^{34}\text{S}_{\text{py}}$ values higher than 100‰ have been documented (Fig. 6). Seep carbonates tend to form at a shallow SMTZ – from a few millimeters to several meters below the seafloor – where sulfate exchange between seawater and pore water is higher than at greater depth (e.g., Haas et al., 2010). At shallow depth, high sulfate replenishment impedes the establishment of an extremely ^{34}S enriched sulfate pool during continuous sulfate reduction, preventing the development of high $\delta^{34}\text{S}_{\text{py}}$ values (cf. Morelli, 2019; Chen et al., 2021). Because carbonate authigenesis at seeps is a vigorous process (e.g., Bayon et al., 2013), the engulfment of pyrite by authigenic carbonate will terminate the local pyritization process. Such engulfment of pyrite will therefore prevent the development of any later stages of pyrite at greater depth from residual, sulfate depleted pore water pools. Incorporation of authigenic pyrite by seep carbonate therefore necessarily cuts short the diagenetic history of pyrite formation in methane-rich environments. We put forward the hypothesis that extremely high $\delta^{34}\text{S}_{\text{py}}$ values like those observed for pyrite extracted from modern seepage-affected sediments will not be found for authigenic pyrite enclosed in seep limestones. To sum up, (1) preferential formation at shallow depth in pore water typified by high sulfate replenishment in association with carbonate authigenesis and (2) and engulfment of pyrite aggregates in authigenic carbonate during early diagenesis prevent the development of the complete sequence of pyritization in methane-rich environments as it has been observed for seep environments without significant carbonate authigenesis.

Table 1. Sample locations and studied materials.

Sample	Location	Material	Reference
Beauvoisin	Southeastern France	Ancient seep carbonate	This study
Whiskey Creek	Western Washington State	Ancient seep carbonate	This study
TVG-11	South China Sea	Modern seep carbonate	Chen et al., 2021
GB-382	Gulf of Mexico	Modern seep carbonate	Morelli, 2019
GC-272	Gulf of Mexico	Modern seep carbonate	Morelli, 2019
GC-140	Gulf of Mexico	Modern seep carbonate	Morelli, 2019
HD109	South China Sea	Modern seepage-affected sediment	Lin et al., 2017a
DH-CL11	South China Sea	Modern seepage-affected sediment	Lin et al., 2017a
HS148	South China Sea	Modern seepage-affected sediment	Lin Z. et al., 2016
HS217	South China Sea	Modern seepage-affected sediment	Lin Z. et al., 2016

Finally, conditions typically vary significantly within seepage-affected sediments, with variability commonly caused by various factors including the intensity of methane flux, the depth of the SMTZ, the dominance of advection vs. diffusion, and the nature of the local pore space in seep environments. Such changing conditions lead to different types of pyrite with variable sulfur isotope composition. For example, in sedimentary environments typified by sluggish diffusion of methane, pyrite can reveal particularly high $\delta^{34}\text{S}$ values in deep SMTZs (Lin et al., 2016b; Lin et al., 2016a; Wang et al., 2017). In contrast, pyrite tends to show low $\delta^{34}\text{S}$ values when methane flux is high (Lin et al., 2017b). However, such processes cannot be identified easily by the analysis of bulk pyrite. By applying in-situ sulfur isotope measurements, the combined information of (1) the paragenetic sequence of pyrite crystal of different habit and (2) the small-scale variability of $\delta^{34}\text{S}_{\text{py}}$ values provides useful constraints on past sulfur cycling in sedimentary environments during early and later stages of diagenesis (Fig. 7).

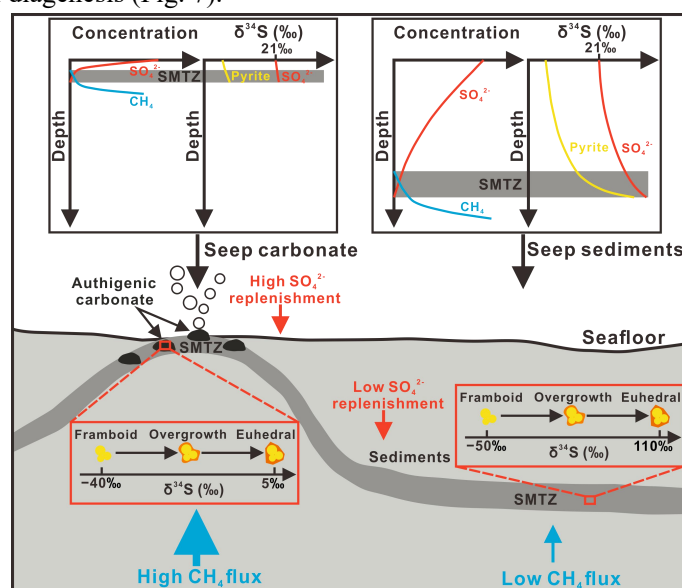


Fig. 7. Model diagram of bulk and in-situ sulfur isotope patterns of pyrite in seep carbonate or sediments. The certain $\delta^{34}\text{S}$ values shown in in-situ sulfur isotope patterns (red boxes) are referred from Fig. 6.

5. Conclusions

Determination of the sulfur isotopic composition of pyrite with in-situ microscale analysis (e.g., SIMS) is useful for the reconstruction of sedimentary environments and local sulfur cycling. Such an approach is potent for any sedimentary environment with a prominent sulfur cycle and high enough amounts of reactive iron, but it proves to be particularly useful for seep environments with their high production of dissolved sulfide by sulfate-driven anaerobic oxidation of methane (SD-AOM). In this study, in-situ SIMS analysis of various types of pyrite is implemented for two Phanerozoic seep deposits. Pyrite framboids enclosed in the Jurassic seep limestones of Beauvoisin have low $\delta^{34}\text{S}_{\text{py}}$ values from -40.1‰ to -23.9‰ , whereas framboids of the Whiskey Creek deposit reveal a wider range of values from -40.7‰ to 9.9‰ . Most of the euhedral pyrite crystals from both sites display higher $\delta^{34}\text{S}_{\text{py}}$ values (mainly from 4.4‰ to 5.7‰ for Beauvoisin; mainly from 0.4‰ to 3.6‰ for Whiskey Creek). The variability of $\delta^{34}\text{S}_{\text{py}}$ values of different formation stages of pyrite (early framboids vs. later euhedral crystals) observed for the studied ancient seep deposits is consistent with patterns recognized for modern seep environments,

controlled by factors like the rate of sulfate reduction and sulfate replenishment in the seep sediments. The lack of $\delta^{34}\text{S}_{\text{py}}$ values of higher than 100‰, as observed for pyrite from modern seepage-affected sediments, in the studied Phanerozoic seep limestones is partially ascribed to the engulfment of pyrite in authigenic carbonate, impeding the formation of later stages of ^{34}S enriched pyrite after engulfment. Our study on the sulfur isotopic composition of authigenic pyrite enclosed in two Phanerozoic seep deposits confirms that systematic studies on the paragenetic sequence of pyrite aggregates, combined with the analysis of the sulfur isotope composition of the successive stages of pyrite, can help to better understand sulfur cycling during diagenesis and the marine sulfur cycle.

Acknowledgments

This research was funded jointly by the Natural Science Foundation of China (No. 41806049) and the National Key Research and Development Program of China (2018YFC0310004). Qinyi Zhang acknowledges funding provided by a China Scholarship Council fellowship (file No. 202304910070). Comments of two anonymous reviewers helped to improve the manuscript.

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Chapter 4 Sulfur isotope and trace element variations in pyrite from corroded seep carbonates: records of redox condition changes and episodic methane seepage

Manuscript in preparation

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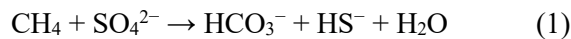
Abstract: Authigenic carbonate in ancient strata serves as a key indicator of fluctuant seepage activity. However, corrosion events resulting from the reaction between CH₄ or H₂S and O₂ are commonly observed in such carbonates, reflecting dynamic changes in redox conditions during carbonate precipitation and corrosion. Pyrite preserved in seep carbonates is a critical proxy for reconstructing seep environments. In particular, sulfur isotopic and trace element signatures archived in pyrite advance our understanding of sulfur biogeochemical processes and associated elemental cycles at seeps. However, pyrite formation coexisting with corroded seep carbonates is rarely analyzed, limiting our understanding to interpret pyrite's role in recording episodic seepage events. In this study, two types of pyrite (framboids and euhedral pyrite crystals), which precipitated before and after the corrosion event, were identified from ancient seep carbonates from the Willapa Bay area. In-situ sulfur isotopic and trace element analyses were conducted on these pyrite generations to reveal their growth histories and ambient environments. Framboids exhibit a large range of $\delta^{34}\text{S}$ values (from -36.13‰ to 18.40‰) and significantly higher contents of trace elements associated with organic matter and ferromanganese oxide dissolution compared to the pattern of euhedral crystals. These features suggest initially substantial replenishment of sulfate from seawater and subsequent engulfment and enhanced input and degradation of substrates during framboid formation before corrosion event. In contrast, euhedral crystals after corrosion event show narrower range of $\delta^{34}\text{S}$ values (from -11.02‰ to -6.43‰) and lower trace element contents, indicating a consistently open system with reduced input and decomposition of organic matter and ferromanganese oxides. Collectively, the coupled sulfur isotope and trace element signatures of pyrite sensitively record variations in fluid sources and redox conditions during authigenic carbonate formation in seep environments.

Key words: Ancient seep carbonate; Authigenic pyrite; Corrosion event; Sulfur stable isotopes; Trace elements

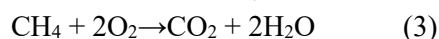
1. Introduction

Seepage activity is widespread along continental margins and plays a key role in linking the carbon cycle from the geosphere to the hydrosphere, and even to the atmosphere through massive methane emissions (Judd and Hovland, 2007; Ni et al., 2025). Chemosynthesis-based communities, which thrive in seep environments, have utilized hydrocarbons (primarily methane) from seep fluids since at least the Silurian period, leaving behind abundant fossil markers such as fecal pellets and shells (MacDonald et al., 1990; Gaillard et al., 1992; Xu et

al., 2020; Jakubowicz et al., 2022). The dominant biogeochemical process of methane consumption in seep environments is sulfate-driven anaerobic oxidation of methane (SD-AOM), mediated by a consortium of methanotrophic archaea and sulfate-reducing bacteria (Eq. (1); Boetius et al., 2000). In addition to SD-AOM, organoclastic sulfate reduction (OSR), which utilizes organic matter as a substrate, leads to pyrite formation in normal marine sediments (Eq. (2); Berner, 1984; Canfield, 1991).



Authigenic carbonate commonly precipitates in methane-seep environments due to locally elevated alkalinity, which leads to supersaturation with respect to CaCO_3 (Suess, 2020; Kravchishina et al., 2021; Jakubowicz et al., 2025). However, seep carbonates typically record multiple stages of formation with distinct mineral phases (e.g., aragonite, Mg-calcite, and dolomite) in response to dynamically changing pore-water conditions (Li et al., 2018; Tseng et al., 2023; Smrzka et al., 2025). In addition, corrosion textures are pervasively observed in seep carbonates and are attributed to aerobic oxidation of CH_4 or H_2S (Eqs. (3) and (4), respectively; e.g., Crémière et al., 2012; Leprich et al., 2021; Cordova-Gonzalez et al., 2023). Thus, better constraints on the extent and impact of corrosion are required to accurately assess the amount of methane-derived carbon permanently sequestered in seep carbonates (Cai et al., 2006; Himmler et al., 2011).



Unlike authigenic carbonates, which commonly form through multiple phases, the composition of pyrite (FeS_2) is relatively fixed. Framboids represent the most common morphology of pyrite in seep sediments and carbonates, forming under conditions supersaturated with respect to pyrite; in contrast, the formation of euhedral crystals is considerably slower, typically due to limited replenishment of iron or sulfur (Merinero et al., 2008; Rickard, 2012a, 2021; Farquhar et al., 2013). Recently, coupled analyses of sulfur isotopes and trace elements in pyrite have been increasingly employed to investigate material cycling and redox fluctuations in seep environments (Lin et al., 2022; Chen et al., 2023; Song et al., 2026).

In seep settings, variations in $\delta^{34}\text{S}$ values between framboidal and euhedral pyrite are commonly interpreted to reflect the degree of system openness during pyrite formation, given that the primary sulfur source is sustained by seawater sulfate (Magnall et al., 2016; Guo et al., 2022). Early-formed framboids typically exhibit lower $\delta^{34}\text{S}$ values because ^{32}S is preferentially utilized from porewater sulfate, leaving a ^{34}S -enriched sulfate pool for the subsequent precipitation of euhedral crystals (Lin et al., 2016, 2017; Grema et al., 2022).

Trace elements associated with pyrite are primarily considered to have been initially adsorbed onto or complexed by organic matter and ferromanganese oxides, and subsequently released upon decomposition under reduced, sulfidic conditions, which are prevalent in seep environments (Gregory et al., 2015; Chen et al., 2024; Smrzka et al., 2024; Yu et al., 2025). Chen et al. (2024) suggested that weakly positive correlations among Co, Ni, and As, but poor correlations among Cu, Zn, and As in pyrite, indicate the occurrence of microbial methanogenesis rather than anaerobic oxidation of methane. This interpretation is based on the fact that Co and Ni are essential for enzyme synthesis in both methanogenic and anaerobic

methanotrophic archaea, whereas Cu is absent and Zn is less required (Glass and Orphan, 2012), in contrast to their abundance in organic matter (Berner et al., 2012; Smrzka et al., 2019). Furthermore, variable contents of redox-sensitive elements such as Mo, As, and Sb in pyrite from seep sediments reflect dynamically changing inputs and dissolution of ferromanganese oxides under reduced conditions (Lin et al., 2022; Miao et al., 2022; Gong et al., 2025). Overall, the coupled interpretation of sulfur isotope and trace element patterns is advantageous for constraining the sources, transport, and immobilization pathways of trace elements under varying degrees of system openness during seep activity.

Although significant progress has been made in studying the evolution of trace elements in pyrite from marine sediments, investigations that integrate pyrite sulfur isotopes to decipher trace element cycling in ancient seep carbonates remain exceptionally rare. This scarcity largely stems from the predominant use of modern seep-impacted sediments as sample materials (Lin et al., 2022; Miao et al., 2022; Wang et al., 2022; Chen et al., 2023; Ruban et al., 2025; Yu et al., 2025). Furthermore, as corrosion textures are ubiquitously observed in seep carbonates, elucidating how redox conditions fluctuate and how pyrite sulfur isotopes and trace element compositions vary within these corroded seep carbonates can substantially advance our understanding of the dynamic evolution of seep activity. To address this knowledge gap, representative ancient seep carbonates were collected from the Willapa Bay area. In situ analyses of sulfur isotopes and trace element contents were performed on pyrite preserved in these carbonates. Distinctly different pyrite formation stages identified within the seep carbonates, along with their corresponding sulfur isotopic and trace element signatures, offer meaningful insights into redox condition changes and the transport and immobilization of trace elements in this extreme environment.

2. Geological background

The study area, Willapa Bay, is located in the state of Washington, northwestern USA, and its tectonic setting is governed by the interaction between the Juan de Fuca Plate and the North American Plate (Fig. 1). Subduction of the Juan de Fuca Plate beneath the North American Plate generated compressive forces during the Eocene in southwestern Washington (Kiel, 2010). An extensive accretionary wedge has developed within the subduction zone in this region and has since undergone continuous exhumation and erosion (Snively, 1987; Kiel, 2010). In the Willapa Bay area, the sedimentary succession predominantly consists of thick Tertiary strata (e.g., Eocene and Miocene), which are locally overlain by unconsolidated to semi-consolidated Quaternary deposits (Wells, 1989). Deep-seated faults and abundant fractures dissect the accretionary wedge into numerous structural units and serve as fluid conduits from deeper sedimentary sequences (Wells, 1989; Goedert and Squires, 1990). Ancient methane seeps have been widely identified in Willapa Bay and adjacent areas, as evidenced by distinctive fossilized chemosynthetic biotic communities and authigenic carbonates (Goedert and Squires, 1990; Squires and Goedert, 1991; Kiel, 2010; Nesbitt et al., 2013). However, the carbon isotope values of authigenic carbonates in these areas exhibit considerable variability (Nesbitt et al., 2013; Taylor et al., 2023). Some isotopic results, particularly those with $\delta^{13}\text{C}$ values higher than -30‰ , are insufficient to unambiguously demonstrate methane oxidation during carbonate precipitation (Smrzka et al., 2013, 2015). This discrepancy suggests variations in the composition of hydrocarbon-bearing fluids or diagenetic alteration during authigenic carbonate

formation.

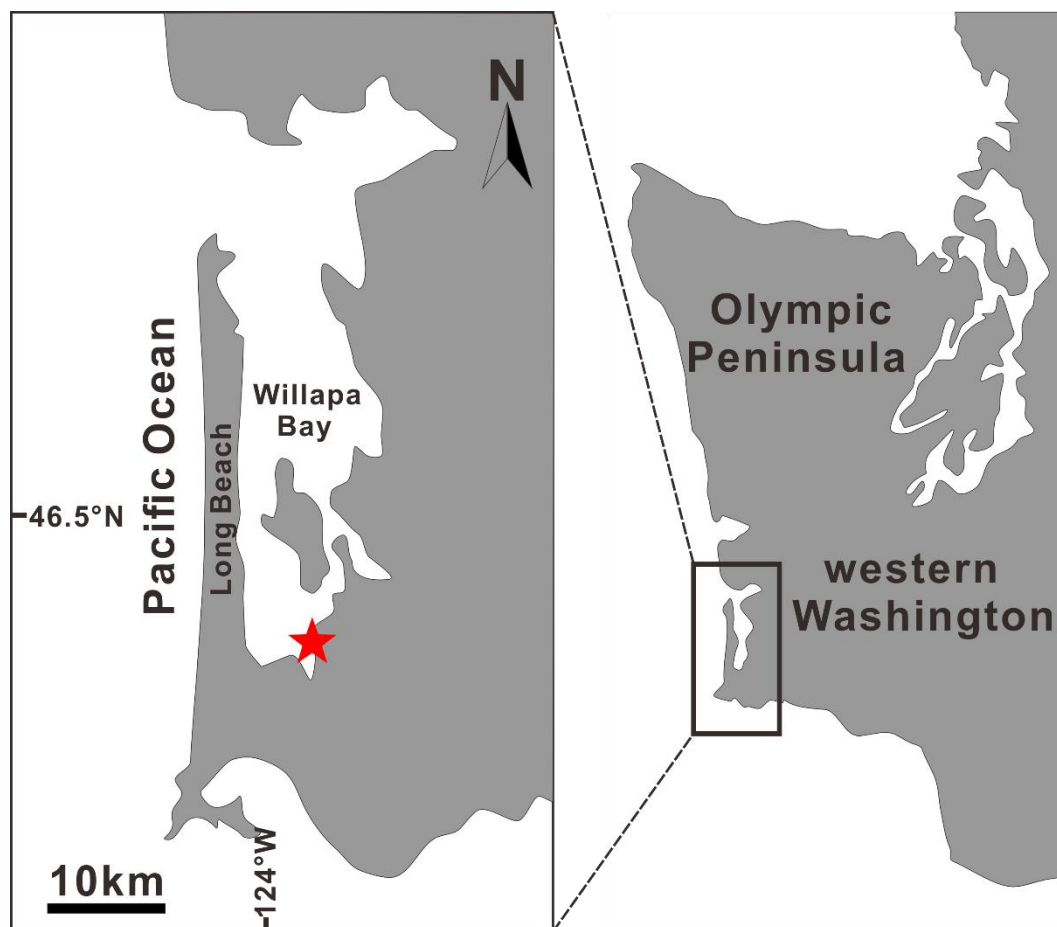


Fig. 1. Sampling location of this study in Willapa bay (marked in red star).

3. Sample and methods

3.1 Sampling

Ancient authigenic carbonates were collected from an outcrop adjacent to Highway 101 during low tide. The host sedimentary strata containing the authigenic carbonates consist of dark-grey, thin-bedded siltstone of Middle to Late Eocene age. Bulk carbonate rocks were cut to expose fresh surfaces. Carbonate pieces showing abundant pyrite visible to the naked eye were selected for thin-section preparation (thickness $>50\ \mu\text{m}$) for subsequent observation and analysis (Fig. 2).

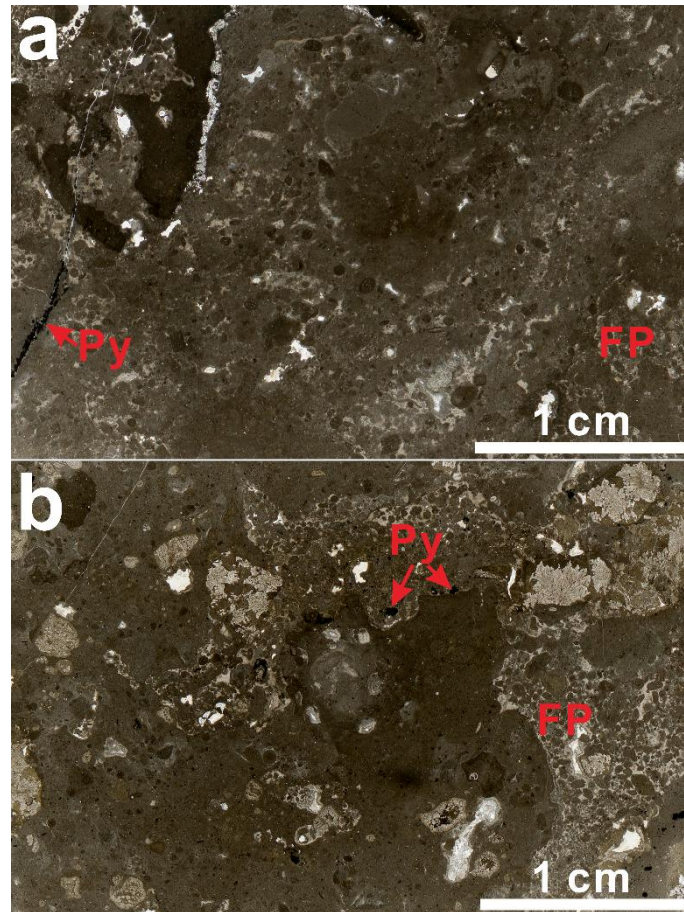


Fig. 2. Scanning thin sections of the collected seep carbonate. Two distinct pyrite textures are linear (Fig. a; sample 301D) and porphyritic aggregates (Fig. b; sample WB-SSB-1), both occurring as opaque black phases. Abundant, well-preserved fecal pellets attributed to the ichnogenus *Palaxius* are observed throughout the thin sections. FP: fecal pellets. Py: pyrite.

3.2 Optical and Scanning Electron Microscope (SEM) observation

Optical microscopy and scanning electron microscopy (SEM) were conducted at the Fachbereich Erdsystemwissenschaften – Geologie, Universität Hamburg. Pyrite spots for sulfur isotope and trace element analyses were selected under reflected light using a ZEISS Axioscope 5 microscope. SEM imaging was performed using a TM4000 microscope operated in backscattered electron (BSE) mode.

3.3 Determination of sulfur isotope

In this study, in-situ sulfur isotope analyses of mineral micro-areas were conducted at the State Key Laboratory of Continental Dynamics, Northwest University. Isotopic measurements were performed using laser ablation–multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS). The laser fluence for sulfur isotope analysis was set to 3.6 J/cm², with a repetition rate of 3 Hz and an ablation spot size ranging from 25 to 37 μm. A single-point ablation mode was employed. High-purity helium (280 mL/min) served as the carrier gas, while argon (approximately 0.86 L/min) was used as the make-up gas. Sulfur isotope analysis was carried out using a Nu Plasma 1700 MC-ICP-MS. Data were acquired in TRA mode, with an integration time of 0.2 s, a background acquisition time of 30 s, a sample

integration time of 50 s, and a purge time of 75 s. Sulfur isotopic compositions are expressed as δ values relative to a standard: $\delta^x\text{S} = [({}^x\text{S}/{}^{32}\text{S})_{\text{sample}} / ({}^x\text{S}/{}^{32}\text{S})_{\text{standard}} - 1] \times 1000$, where x denotes 34 or 33. The historical international standard is VCDT (Vienna Canyon Diablo Troilite), which has long been exhausted. Currently, IAEA-S-1 (Ag_2S , with a known $\delta^{34}\text{SV-CDT}$ value of -0.3‰) is routinely used as a reference material, and measured values are converted to $\delta^{34}\text{SV-CDT}$. The laboratory internal standards for sulfur isotopes were calibrated by gas-source stable isotope mass spectrometry or solution-nebulization MC-ICP-MS. The reference materials used for calibration include IAEA-S-1, IAEA-S-2, and IAEA-S-3 (Ag_2S powders). Data correction followed a “standard-sample-standard” (SSB) bracketing protocol, wherein a standard was measured immediately before and after each unknown sample. The ${}^{34}\text{S}/{}^{32}\text{S}$ ratio of the standard was taken as the average of the two bracketing standard measurements. Given the significant matrix effect inherent in LA-MC-ICP-MS sulfur isotope analysis, a matrix-matched standard (pyrite Py-4, $\delta^{34}\text{SV-CDT} = 1.7 \pm 0.3\text{‰}$) was employed. To monitor data accuracy, a pair of pyrite internal standards (Py-4 and PTST-2, $\delta^{34}\text{SV-CDT} = 32.5 \pm 0.3\text{‰}$) was inserted after every eight samples. The analytical precision was better than 0.3‰ .

3.4 Analysis of trace element contents

Trace elements in pyrites were analyzed on thin section by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Faculty of Geosciences at University of Bremen, Germany, using an ESL Artifact193 laser and a Thermo Scientific iCAP MTX-900 triple quadrupole ICP-MS. The laser was connected to the plasma torch via a 20 mL Twinnabar™ cyclonic spray chamber for signal smoothing. Analytical conditions included a plasma power of 1100 W, 0.8 L/min He as sample gas through the ablation cell, 0.44 L/min Ar added behind the cell, 0.8 L/min Ar as plasma gas, and iCAP operation in single-quad no-gas mode. Measured isotopes were ${}^{25}\text{Mg}$, ${}^{34}\text{S}$, ${}^{44}\text{Ca}$, ${}^{51}\text{V}$, ${}^{55}\text{Mn}$, ${}^{57}\text{Fe}$, ${}^{59}\text{Co}$, ${}^{60}\text{Ni}$, ${}^{63}\text{Cu}$, ${}^{66}\text{Zn}$, ${}^{75}\text{As}$, ${}^{95}\text{Mo}$, ${}^{111}\text{Cd}$, ${}^{114}\text{Cd}$, ${}^{121}\text{Sb}$, ${}^{182}\text{W}$, ${}^{208}\text{Pb}$ and ${}^{238}\text{U}$ with a dwell time of 50 ms. The laser operated with 4 J/cm^2 fluence at 5 Hz for standards and 10 Hz for samples. We used a circular beam of 25 μm diameter circles for standards and euhedral pyrite and only 10 μm for framboids, with dwell times of 50 s for standards and up to 30 s for samples.

Data reduction was carried out using Iolite (Paton et al., 2011) with the trace element scheme and ${}^{57}\text{Fe}$ as internal standard. For external calibration we applied USGS sulfide standard MASS-1 (Wilson et al., 2002) for V, Co, Ni, Mo, Sb and Pb, and blended ore standard OREAS-624-NP (nanopellet from myStandards GmbH, Kiel, Germany) for all other elements. Compromises had to be made because OREAS-624 nanopellet exhibited spikes in the ablation signals due to heterogeneities on the μm -scale. Also, for Mg, Cu and Zn the standards' contents are in the wt% range and are far above those in the pyrite samples. As secondary standards for monitoring analytical accuracy we used USGS basalt glasses BCR-2G and BHVO-2G (Jochum et al., 2005), noting that recovery is principally limited by the strong difference in matrix composition and element contents as compared to the calibration materials. We also used MASS-1 and OREAS-624-NP, but only for those elements that have not been calibrated on the respective standard. The standard data are shown in Table S1.

For the pyrite samples we initially assumed a stoichiometric Fe content of 46.67 wt%. After quantification we corrected this content to account for some carbonate that was inevitably ablated together with the pyrites. For this we assumed pyrite as $(\text{Fe,Mn})\text{S}_2$ and carbonate as

(Ca,Mg)CO₃, calculated the sum, and then normalized Fe to a sum of 100 wt%. The trace element contents were then corrected to the new Fe values. Under these assumptions we could see that the proportion of carbonate in the ablated volumes was <1 wt% in most cases, and <11 wt% in general (Table S1). In addition to pyrites some calcites were analyzed to assess their trace element impact on mixed analyses; for these ⁴⁴Ca served as internal standard (Table S1).

4. Results

4.1 Distributive and morphological features of two generations of pyrite

The distribution patterns of pyrite within authigenic carbonate are highly variable, ranging from linear arrangements, particularly along the corrosion surfaces of gray micrite (Fig. 2a, 3a–c, 4a, b; Smrzka, 2013), to porphyritic aggregates (Fig. 2b, 4d, e). The morphologies of pyrite include: (a) framboids—spherical or elliptical microcrystal aggregates, sometimes encased by a thin overgrowth layer, representing the most commonly reported pyrite type in modern methane seep environments (Fig. 4g–i; Lin et al., 2016, 2022; Wang et al., 2022; Tang et al., 2024); (b) a small number of evolved framboids, where microcrystals have been overgrown by euhedral crystals (Fig. 4j, k); and (c) massive euhedral crystals of variable sizes (Fig. 4c, f, i).

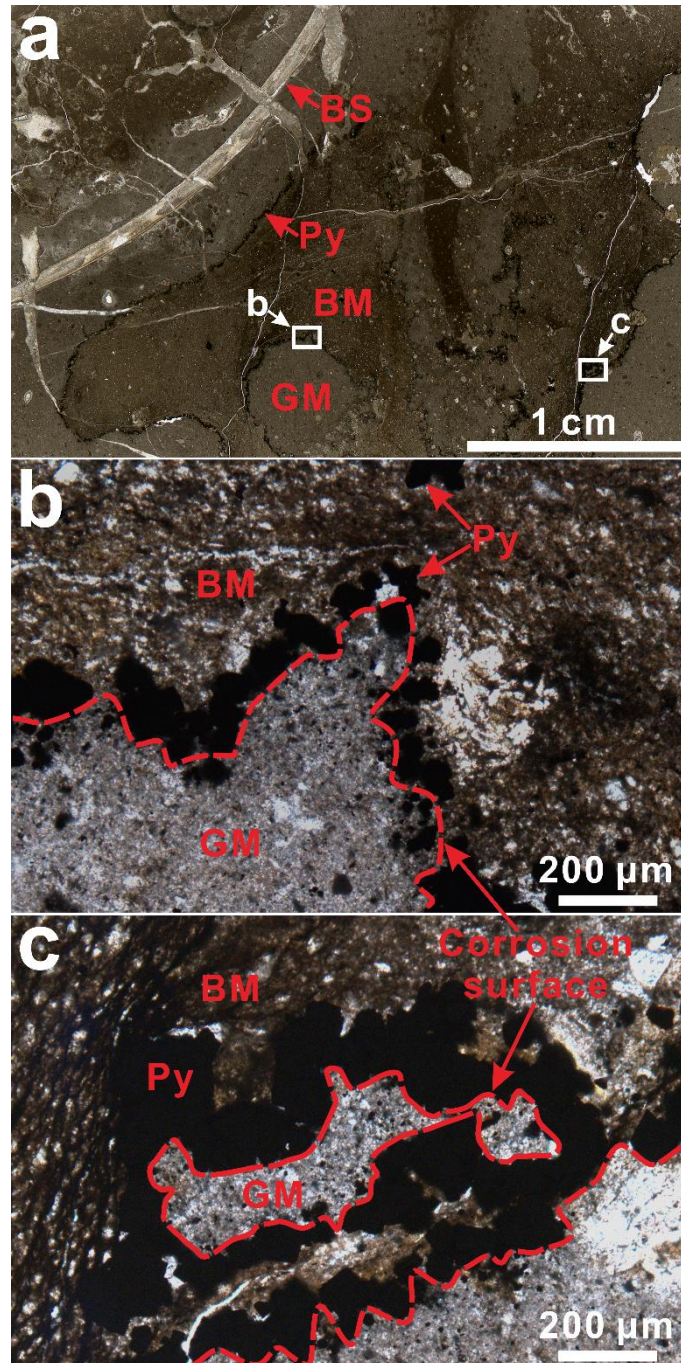


Fig. 3. Evidence of a corrosion event within gray micrite is recorded during the formation of seep carbonate, characterized by two clearly discernible generations of micrite (Fig. a; sample WB-SSB-6). The corrosion surface is distinctly irregular, and abundant massive pyrite crystals typically precipitate from this surface (Figs. b, c). The white-boxed regions in (a) are shown at higher magnification in (b) and (c), respectively. Py: pyrite. BS: bivalve shell. GM: gray micrite. BM: brown micrite.

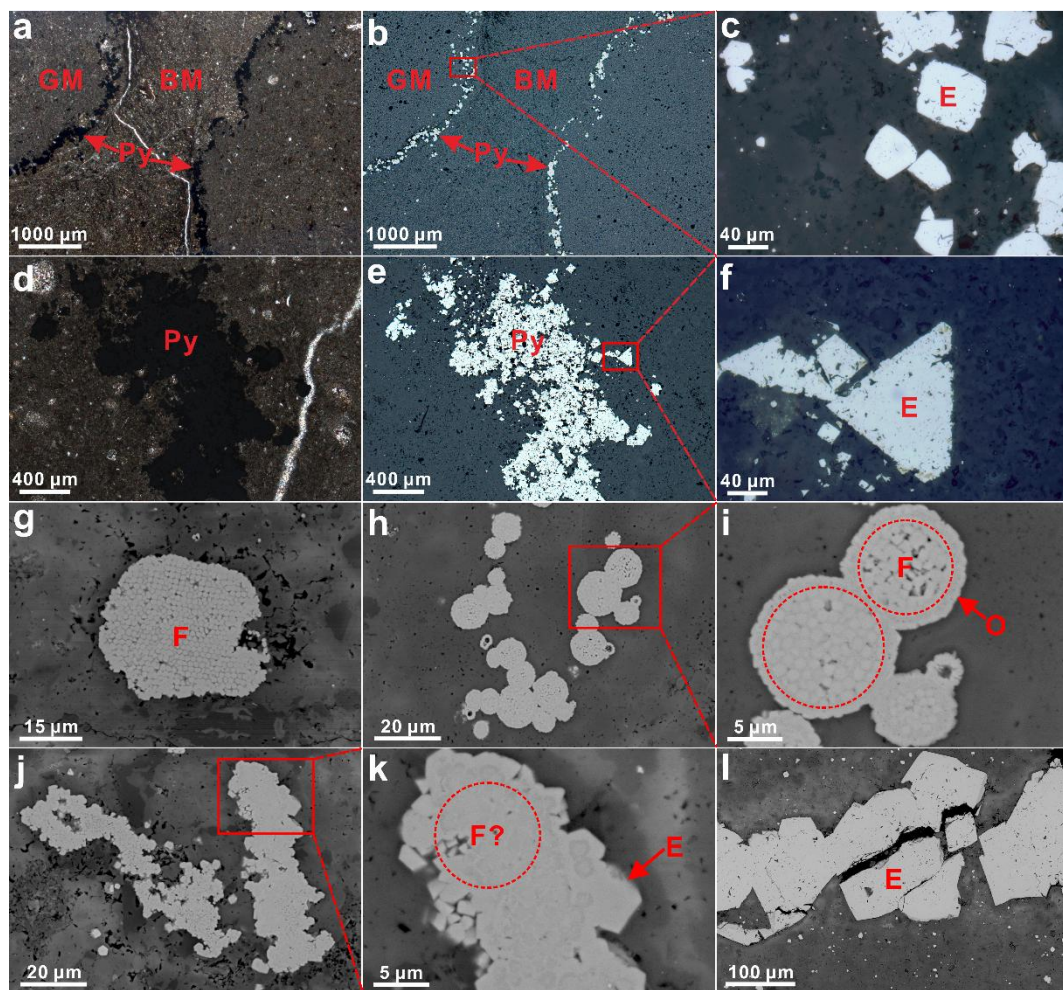


Fig. 4. Distribution and morphology of pyrite in seep carbonate from Willapa Bay. Linear (a–c) and porphyritic (d–f) pyrite aggregates observed under plane-polarized transmitted light and reflected light (samples WB-SSB-6 and WB-SSB-9, respectively). BSE images show: isolated large framboid (g; sample WB-SSB-6); framboid aggregates with a thin overgrowth layer (h, i; sample WB-SSB-1); evolved framboids (j, k; sample WB-SSB-1); and massive euhedral crystals (l; sample 301D). Py: pyrite. GM: gray micrite. BM: brown micrite. F: framboids. O: overgrowth. E: euhedral crystals.

4.2 Sulfur isotope values of pyrite

Due to the laser beam size exceeding 25 μm , only framboidal and euhedral pyrite grains larger than this threshold were analyzed. Framboidal pyrite, including its evolved forms, exhibits highly variable $\delta^{34}\text{S}$ values, ranging from -36.13‰ to 18.40‰ ($n = 30$; Fig. 5). In contrast, euhedral pyrite yields consistently negative $\delta^{34}\text{S}$ values with a narrower range, from -11.02‰ to -6.43‰ ($n = 50$; Fig. 5).

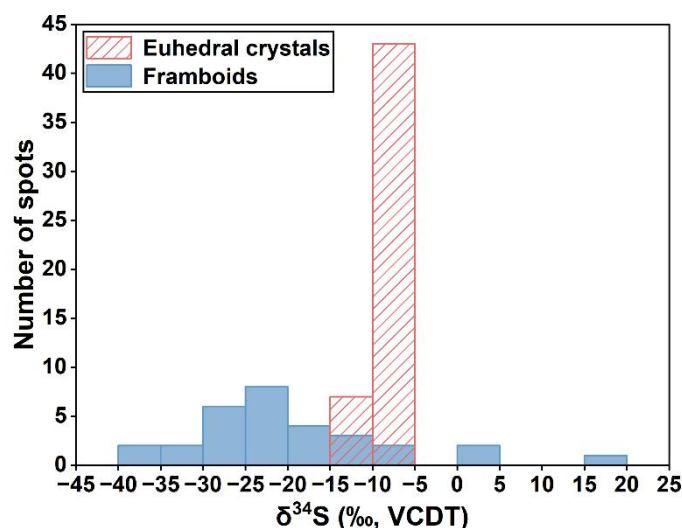


Fig. 5. Number of laser ablation spots of $\delta^{34}\text{S}$ values for framboids and euhedral crystals.

4.3 Trace element contents of pyrite

The trace element contents of pyrite exhibit considerable variation not only among different elements but also between euhedral crystals and framboids (Fig. 6). Most trace elements, including As, Mn, Pb, Ni, Co, Mo, Cu, Zn, Sb, Cd, and W, are generally present at lower contents in euhedral crystals and higher contents in framboids. In contrast, V shows comparably consistent contents in both pyrite types, whereas U displays slightly higher contents in euhedral crystals relative to framboids. The mean trace element contents in euhedral crystals are as follows (Table S1; $n=29$): As (514.22 ppm) > Pb (39.14 ppm) > Mn (27.37 ppm) > Cu (19.01 ppm) > Sb (11.56 ppm) > Ni (10.21 ppm) > Co (5.71 ppm) > Mo (5.57 ppm) > Zn (4.30 ppm) > V (2.93 ppm) > U (1.43 ppm) > Cd (0.47 ppm) > W (0.18 ppm). For framboids, the average contents are (Table S1; $n=21$): As (1749.37 ppm) > Mn (1039.54 ppm) > Pb (432.44 ppm) > Ni (287.64 ppm) > Co (179.99 ppm) > Mo (162.75 ppm) > Cu (143.98 ppm) > Zn (56.80 ppm) > Sb (53.44 ppm) > V (3.27 ppm) > Cd (2.35 ppm) > U (0.37 ppm) > W (0.26 ppm).

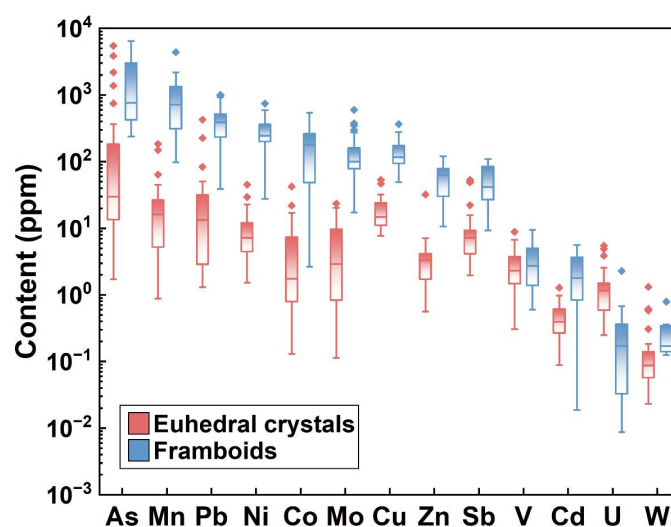


Fig. 6. Box plot of trace elements contents in declining orders of framboids and euhedral

crystals.

5. Discussion

5.1 Corrosion event during ancient seep carbonate formation

The ancient seep carbonate exhibits an apparently corroded surface, which is the most conspicuous texture observed at the study site (Fig. 3; Fig. 4a–c; Smrzka, 2013). It is generally suggested that recurrent methane (hydrocarbon) pulses (Campbell et al., 2002; Jean-Philippe et al., 2017) or biotic benthic activity—evidenced by numerous fecal pellets in this case (Fig. 2; Kuechler et al., 2011; Crémière et al., 2012; Pierre et al., 2014)—lead to abundant O₂ from the water column reacting with CH₄ or H₂S (Hanson and Hanson, 1996; Natalicchio et al., 2015; Leprich et al., 2021; Cordova-Gonzalez et al., 2023). The massive H⁺ released during these processes induces extensive dissolution of seep carbonate, leaving an irregular corrosion surface, as likely observed in Fig. 3 (Beauchamp et al., 1989; Machel, 1989; Himmler et al., 2011). Moreover, redox conditions display a reduced–oxic–reduced shift due to the complete consumption of O₂, thus indicating the migration of the redox front within the seep carbonate (Beauchamp and Savard, 1992; Campbell et al., 2002; Cai et al., 2006). Lastly, massive cavities left by the dissolution of early micrite—gray micrite in this case (Fig. 3; Fig. 4a–c)—together with thorough winnowing and ventilation, provide sustained space for the formation of later minerals (Matsumoto, 1990; Esteban and Taberner, 2003). However, given the limited evidence in this study, it is not possible to distinguish which process (e.g., methane pulses vs. bioturbated activity) predominates, nor which reaction substrate (CH₄ vs. H₂S) plays the key role in O₂ consumption. Further work addressing these questions likely requires high-resolution determination of biomarkers or fluid inclusions in seep carbonate (e.g., Esteban and Taberner, 2003; Natalicchio et al., 2015; Cordova-Gonzalez et al., 2023).

5.2 Disparate pyrite authigenesis in ancient seep carbonate

During periods of bottom-water oxygen ingress into seep carbonates due to corrosion events, the formation and growth of early pyrite (e.g., framboids) are interrupted. Subsequent pyrite (e.g., euhedral crystals) initiates when conditions return to anoxic. Framboids are randomly distributed within the seep carbonate (Fig. 4g–k), suggesting they are syndimentary with gray micrite and later engulfed. In contrast, euhedral crystals exhibit linear and porphyritic textures (Fig. 2, 3, and 4a–f, i), indicating that their formation is clearly linked to the internal carbonate structure.

The $\delta^{34}\text{S}$ values of framboids range from -36.13‰ to 18.40‰ (Fig. 5), reflecting progressive ^{34}S enrichment in the sulfate pool (Seal, 2006), consistent with observations from modern seep carbonates (Gong et al., 2018; Crémière et al., 2020). This “engulfment effect” results from isolation of the local sulfate pool during seep carbonate cementation, which restricts replenishment by seawater sulfate (Paiste et al., 2024). The significant $\delta^{34}\text{S}$ fractionation ($\sim 58\text{‰}$) relative to coeval seawater ($\sim 22\text{‰}$ VCDT; Kampschulte and Strauss, 2004) falls within the fractionation ranges of both SD-AOM ($20\text{--}60\text{‰}$; Deusner et al., 2014) and OSR (up to 66‰ ; Canfield, 2001; Sim et al., 2011). Although OSR likely occurred in ancient seep environments and contributed to framboid formation, its role was minor because seep carbonates form under high methane flux where SD-AOM dominates, leading to a stronger impact of SD-AOM on framboid formation compared to settings characterized by diffusive

methane transport (Formolo and Lyons, 2013).

Compared to framboids, euhedral crystals show characteristically negative and narrowly ranging $\delta^{34}\text{S}$ values (Fig. 5; from -11.02‰ to -6.43‰), indicating a homogeneous sulfur signal distinctly different from the more positive $\delta^{34}\text{S}$ values reported from sulfate-restricted environments (Lin et al., 2016; Wang et al., 2021; Grema et al., 2022; Karamova et al., 2025). These distinctive $\delta^{34}\text{S}$ values point to the existence of a ^{32}S -enriched sulfate pool, potentially sustained by seawater sulfate ingress, especially given that early framboids already show positive values (up to 18.40‰). Negative and narrow $\delta^{34}\text{S}$ values in euhedral crystals have also been reported from sedimentary environments (Passier et al., 1997; Lin et al., 2017; Chen et al., 2021), attributed to variable degrees of sulfate replenishment from overlying seawater during microbial sulfate reduction. Frequent exchange between seawater and porewater during and immediately after carbonate corrosion events makes the ingress of ^{32}S -enriched seawater from the upper water column into carbonate cavities plausible, thereby diminishing Rayleigh fractionation effects during euhedral crystal growth. Meanwhile, euhedral crystals are typically interpreted to grow under lower supersaturation due to limited availability of free Fe^{2+} or S^{2-} compared to framboids (Wilkin and Arthur, 2001; Rickard, 2012a). However, limited sulfur replenishment is contradicted by persistently negative $\delta^{34}\text{S}$ values, instead suggesting slow iron supply during euhedral crystal growth (Raiswell, 1982; Coleman and Raiswell, 1995; Passier et al., 1997). Iron was possibly released from dissolution of early gray micrite, which contains minor Fe (Table S1; $<4\%$) or iron-bearing silicates (e.g., Commeau et al., 1987; Raiswell and Canfield, 2012). This hypothesis requires further confirmation.

The Co/Ni ratios of both framboids and euhedral crystals are mostly <1 , indicating a sedimentary origin for the pyrite (Fig. 7; Large et al., 2014; Gregory et al., 2015; Lin et al., 2022). High contents of most trace elements in framboids (Fig. 6; except V and U) are comparable to values reported from settings influenced by intense particulate shuttle effects during crystallization, with direct diffusion from seawater being secondary (Tribovillard et al., 2013; Hu et al., 2014; Gregory et al., 2015; Smrzka et al., 2019). The lower trace element contents in euhedral crystals (Fig. 6) relative to framboids indicate limited trace element incorporation. This phenomenon is widely documented in studies analyzing thousands of pyrite grains (Rickard, 2012b; Large et al., 2014, 2022; Gregory et al., 2015), explained by lower porewater trace element concentrations during euhedral crystal formation, as trace element carriers were significantly consumed by substantial H_2S generation via SD-AOM prior to the corrosion event. This is supported by the notably high Mn content (>4000 ppm) in framboids (Table S1 and Fig. 6; Shikazono et al., 1994; Lin et al., 2022; Gong et al., 2025; Yu et al., 2025). At higher degrees of pyritization ($>40\%$), reactive iron (amorphous and crystalline phases) becomes more resistant to reduction as amorphous phases are depleted, and sediments exhibit elevated dissolved sulfide and dissolved $\text{Mn}^{2+}/\text{Fe}^{2+}$ ratios (Morse and Luther, 1999). The carbonate also shows high Mn content (Table S1; >2000 ppm) and low Mg content (Table S1; $<2\%$; i.e., low-Mg calcite; Stanienda-Pilecki, 2023), indicating shallow-depth diagenesis, consistent with sulfur isotope patterns discussed above. On the other side, dilution effect of seawater on trace element contents of euhedral crystals under persistent open system is also probable (Dellwig et al., 2002). This environment must be sedimentary, excluding hydrothermal or metamorphic influences (e.g., Gadd et al., 2016; George et al., 2018; Rieger et al., 2023).

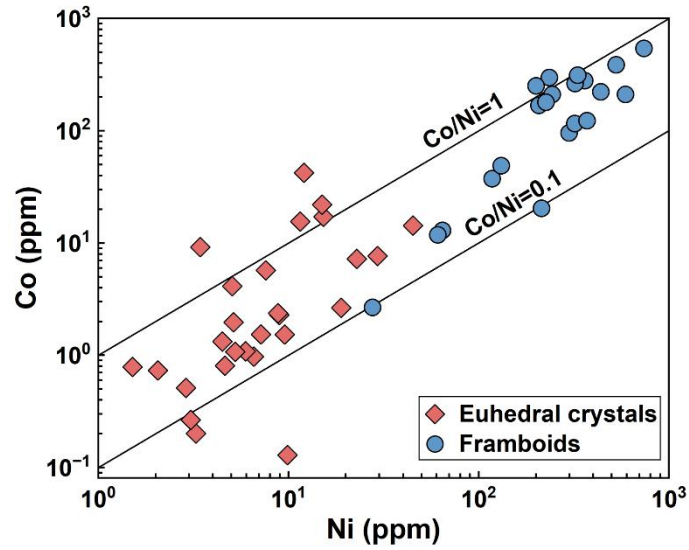


Fig. 7. Scatter plot of Co and Ni contents of framboids and euhedral crystals.

Co, Ni, Cu, Zn, and Cd are typically present in the organic matter fraction and/or ferromanganese oxide of sediments; Co and Ni generally substitute for Fe in pyrite, whereas the others are incorporated as independent sulfides (Algeo and Maynard, 2004; Scholz and Neumann, 2007; Berner et al., 2012; Rickard, 2012b; Smrzka et al., 2019). Thus, higher contents of these trace elements in framboids compared to euhedral crystals reveal more intense organic matter and/or ferromanganese oxide input and dissolution under reducing conditions (Fig. 8). The exception of V may be attributed to both organic and siliciclastic sources (Berner et al., 2012; Large et al., 2022).

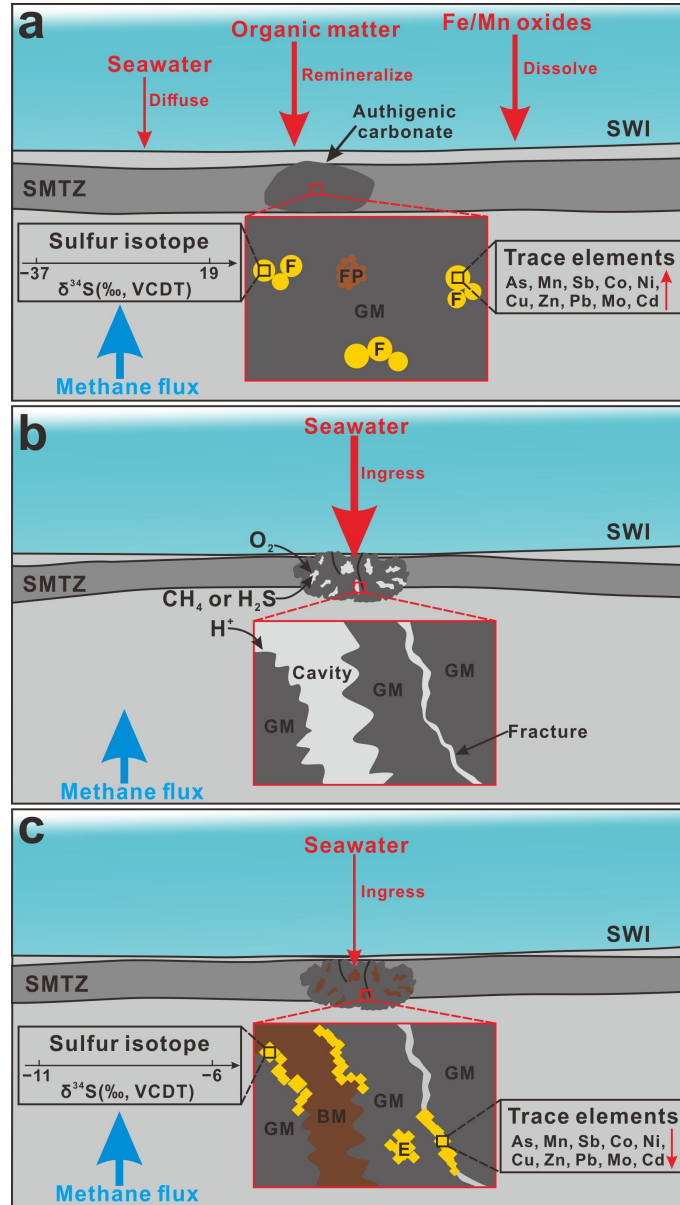


Fig. 8. Schematic illustration of sulfur isotope and trace element patterns during the formation of framboids (a; early-stage pyrite) and euhedral crystals (b, c; late-stage pyrite) in seep carbonate. The $\delta^{34}\text{S}$ values of pyrite are from this study. The red arrow in the black box in (a) indicates higher contents of selected trace elements in framboids relative to those in euhedral crystals, whereas the opposite trend is shown in (c). SWI: sediment water interface. SMTZ: sulfate-methane transition zone. GM: gray micrite. BM: brown micrite. FP: fecal pellets. F: framboids. E: euhedral crystals.

As representative redox-sensitive elements, the content patterns of As, Mo, Sb, U, and possibly Pb in framboids and euhedral crystals reflect contrasting redox conditions and sources. These elements exist as chemically conservative oxyanions in oxic seawater (e.g., AsO_4^{3-} , MoO_4^{2-} , $\text{Sb}(\text{OH})_6^-$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, PbCO_3^0), are effectively scavenged by ferromanganese oxide particles (As, Mo, Sb, Pb) or organic matter and seawater diffusion (U), and are readily immobilized in sediments upon reaction with hydrogen sulfide (Andreae and Froelich Jr, 1984; Filella et al., 2002; McManus et al., 2005; Smrzka et al., 2019; Tribovillard, 2020; Lin et al.,

2022; Gong et al., 2025). Therefore, significantly higher As, Mo, Sb, and Pb contents in framboids compared to euhedral crystals indicate stronger ferromanganese oxide input and dissolution (Fig. 8). However, slightly higher U and lower Mo contents in euhedral crystals show opposite trends to those in framboids (Fig. 6). Under less reducing conditions, U is enriched preferentially over Mo because U(VI) is reduced at the Fe(II)-Fe(III) redox boundary, whereas Mo enrichment requires significant sulfate reduction and sulfide accumulation (Algeo and Tribovillard, 2009; Ning et al., 2025). Thus, the reversed U contents between framboids and euhedral crystals reveal a shift from reducing/sulfidic to less reducing conditions, reasonably attributed to O₂ ingress and subsequent consumption during the corrosion event (Fig. 8). Although U can be adsorbed by organic matter and transported from the euphotic zone to the seafloor (McManus et al., 2006), other organic-matter-associated elements (e.g., Co, Ni, Cu, Zn, Cd) are markedly lower in euhedral crystals than in framboids, indicating that the main U source for euhedral crystals is seawater. Therefore, assessing the immigration (e.g., particulate shuttle and diffusion), immobilization pathways (e.g., SD-AOM and OSR), and trace element sources (e.g., organic matter, ferromanganese oxides, seawater) is essential when interpreting how pyrite trace elements reflect sources and redox changes in corrosion-event-impacted seep carbonates.

6. Conclusion

Pyrite serves as a faithful archive of substrate and redox condition changes associated with corrosion events in seep carbonates. In this study, in-situ sulfur isotope and trace element contents of both framboidal and large euhedral pyrite from ancient seep carbonates in the Willapa Bay area were analyzed to investigate sulfur sources and redox condition changes before and after the corrosion event, integrated with petrographic and mineralogical observations. The framboids exhibit a progressively positive trend in $\delta^{34}\text{S}$ values (from -36.13‰ to 18.40‰), reflecting the influence of Rayleigh fractionation. Their significantly higher contents of most trace elements (e.g., As, Mn, Pb, Ni, Co, Mo, Cu, Zn, Sb, and Cd) suggest enhanced input and dissolution of organic matter and ferromanganese oxides during framboid formation in the seep environment. In contrast, the euhedral crystals show consistently negative and narrowly ranged $\delta^{34}\text{S}$ values (from -11.02‰ to -6.43‰), indicating frequent replenishment of seawater-derived sulfur, which resulted in lower contents of most trace elements in euhedral pyrite, with the exception of uranium. The contrasting patterns of Mo and U contents between framboids and euhedral crystals thus sensitively record a redox condition shift induced by the corrosion event. Overall, this study provides a meaningful framework for deciphering changes in sulfur sources and redox conditions during the formation of ancient seep carbonates by integrating sulfur isotope and trace element data of pyrite.

Acknowledgement

Qinyi Zhang Acknowledges Funding Provided by a China Scholarship Council Fellowship (fileNo. 202304910070).

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Chapter 5 General discussion

Authigenic carbonate, including glendonite, and pyrite characteristically reveal multiple paragenetic phases. The formation of these paragenetic phases is strongly controlled by contemporaneous micro-environmental elemental concentrations and redox conditions in the surrounding porewater. Therefore, interpretations based on conventional bulk-sample extraction are insufficient to fully reconstruct the entire formation processes of these minerals during early diagenesis.

5.1 Calcite varieties record changing micro environment during glendonite formation

Glendonites for phases analysis were collected from ancient seepage-impacted strata in Siberia, Russia, which typically exhibit a stellate shape and reach several centimeters in size (Fig. 1a). Their morphology is analogous to those reported from both modern marine sediments and ancient strata (De Lurio and Frakes, 1999; Selleck et al., 2007; Vickers et al., 2018; Popov et al., 2019; Rogov et al., 2021). These glendonites display a mosaic texture composed of four calcite varieties, revealing distinct paragenetic sequences (Fig. 1b-e): replacive calcite, light calcite, fibrous calcite (including gerbil tail and botryoidal subtypes), and blocky calcite. Replacive calcite is characterized by abundant inclusions of organic matter and is interpreted as a product after the dehydration of ikaite (Teichert and Luppold, 2013; Vickers et al., 2018; Rogov et al., 2025). Light calcite constitutes the largest volume fraction of the glendonites and exhibits a close spatial relationship with replacive calcite. Fibrous calcite shows variable textures and typically grows from either replacive or light calcite. Blocky calcite displays complex textural characteristics and fills cavities left after the formation of earlier calcite phases. Additionally, pyrite is pervasively observed both within the glendonites and in the surrounding host rock (Fig. 1c, 2), suggesting that intense sulfate reduction may have influenced glendonite formation (Qu et al., 2017).

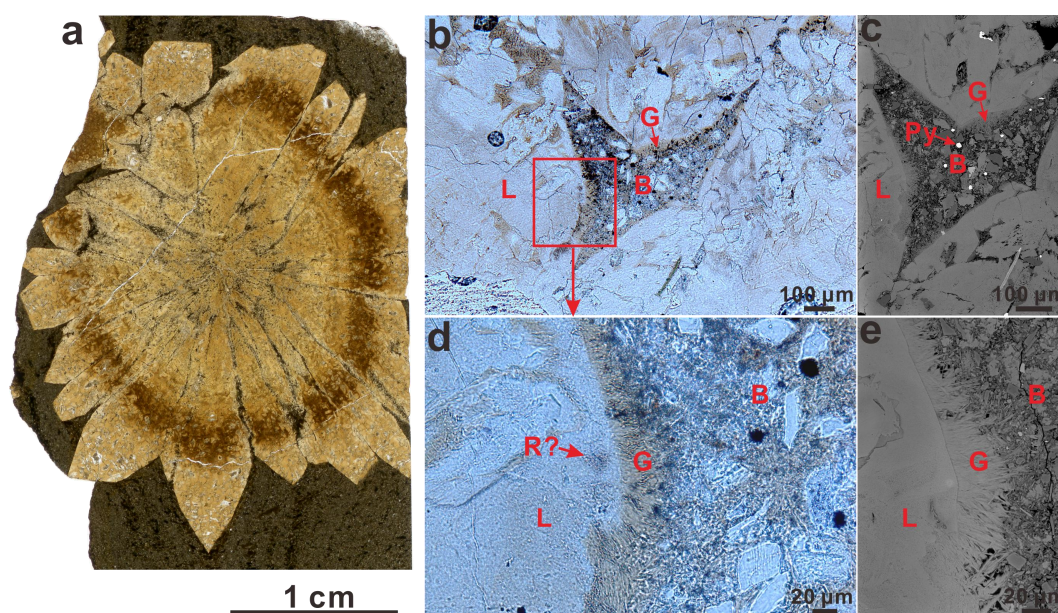


Fig. 1. Bulk glendonite and mineral phases from Siberia. a) Thin section image. b) Plane-

polarized light micrograph showing gerbil-tail calcite and blocky calcite infilling a cavity originally formed by early-stage light calcite. (c) Backscattered electron (BSE) image of the same area in (b), revealing that pyrite (bright phase) is distributed within both light calcite and blocky calcite. (d) Plane-polarized light micrograph of the area outlined by the red box in (b). (e) BSE image corresponding to (d), providing higher-resolution textural details. R: replacive calcite; L: light calcite; G: gerbil tail calcite; B: blocky calcite. Py: pyrite.

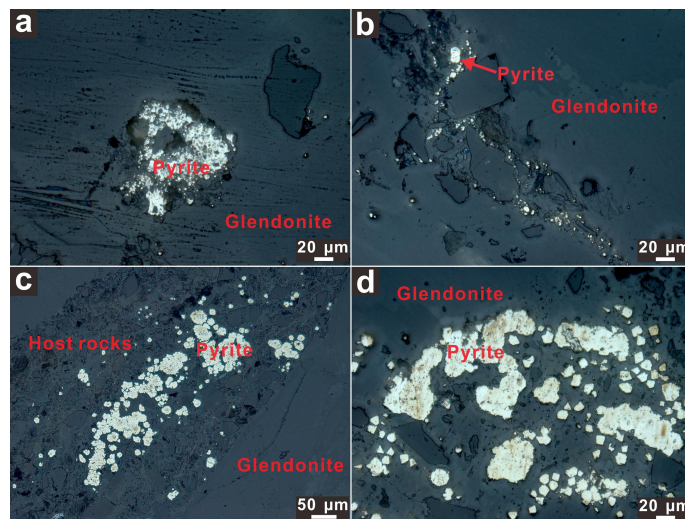


Fig. 2. Distributive modes of pyrite (reflected light). a) and b) Pyrite is enclosed by the glendonite minerals. c) and d) Pyrite distributes in the surrounding host rock of glendonite.

The electron microprobe (EMPA) results reveal that trace elements (e.g., Mg, Fe, and P; Fig. 3) were heterogeneously incorporated during the formation of each calcite variety, spanning from early to late diagenesis (Vickers et al., 2020, 2024), and likely reflecting different redox zones (e.g., from sulfidic to post-sulfidic, potentially methanogenic zone). Combined with trace element contents, FTIR spectra indicate varying degrees of Mg^{2+} and Fe^{2+} cationic substitution at the Ca^{2+} site during the formation of these calcite varieties. Given the smaller effective ionic radii (Ca^{2+} : 1.18 Å; Fe^{2+} : 0.78 Å; Mg^{2+} : 0.72 Å; Shannon, 1976), such substitution would be expected to increase both the ν_4 ($\sim 709\text{ cm}^{-1}$) and ν_2 ($\sim 876\text{ cm}^{-1}$) wavenumbers of carbonate in FTIR spectra (Purgstaller et al., 2016; Bishop et al., 2021). However, considering the low concentrations of both Mg (<2%) and Fe (<2%) in all calcite varieties, the observed shifts in ν_4 (2 cm^{-1}) and ν_2 (9 cm^{-1}) are insufficient to be attributed solely to cationic substitution. Notably, carbon ($^{13}\text{C}/^{12}\text{C}$) and oxygen ($^{18}\text{O}/^{16}\text{O}$) isotope effects have more recently been recognized as significant factors influencing carbonate FTIR spectra (Xu et al., 2018; King et al., 2023). Bulk glendonite $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$ values range from -44.5‰ to -0.4‰ and from -14.7‰ to -0.8‰ , respectively (Morales et al., 2017), indicating a potentially non-negligible influence on ν_4 and ν_2 wavenumber shifts. Nevertheless, carbon and oxygen isotope analyses on individual calcite varieties are lacking in this study due to the small crystal sizes and complex intergrowth of phases (Figs. 1, 3).

Above all, refined spectral interpretations combined with high-resolution geochemical analyses are essential to fully exploit the potential of FTIR in investigating paleoclimate information archived by diverse calcite varieties within glendonite. Collectively, the above

results imply that glendonite formation is considerably more complex than previously suggested, and investigating calcite varieties may help decipher dynamically changing pore-water conditions in sedimentary environments during early diagenesis (Fig. 3).

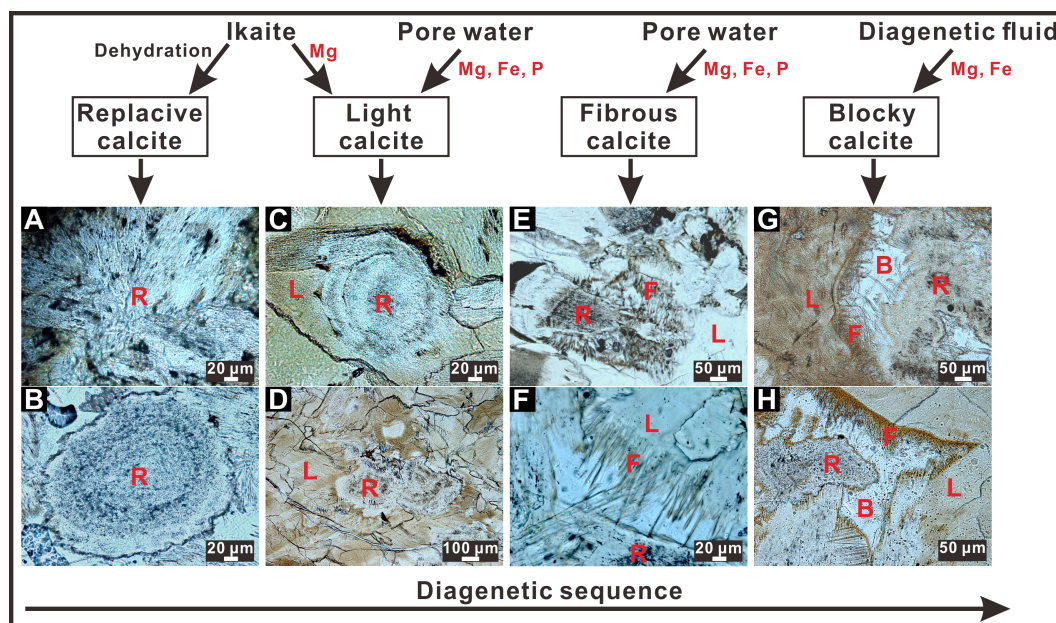


Fig. 3. Schematic illustration of glendonite formation during early diagenesis. R: replacive calcite; L: light calcite; F: fibrous calcite; B: blocky calcite.

5.2 Pyrite habits archive fluctuating open degree and elemental cycling in systems

Multiple generations of pyrite enclosed in the ancient seepage-impacted authigenic carbonate which were collected from Whiskey Creek (Eocene, USA), Beauvoisin (Jurassic, France), and Willapa Bay (Eocene, USA) (Fig. 3). These carbonates are characteristically composed of multiple minerals, including calcite, pyrite, and quartz (Peckmann et al., 1999, 2003; Louis-Schmid et al., 2007; Smrzka, 2013). Typically, framboids and euhedral crystals of pyrite habits were identified in these seep carbonates and analyzed (Fig. 4). The size of individual framboids is remarkably similar across all three sites, generally smaller than 50 μm (Fig. 4a, b), comparable to the size of euhedral crystals observed in the Whiskey Creek and Beauvoisin samples. In contrast, euhedral crystals from the Willapa Bay seep carbonate are distinctly larger (Fig. 4c, d; >100 μm). In the Whiskey Creek seep carbonate, framboids occur either within concretions or as rims at concretion margins. However, in the Beauvoisin seep carbonate, euhedral crystals are more abundant at the periphery of early micrite. Finally, pyrite distribution in the Willapa Bay seep carbonate exhibits a more complex pattern, with euhedral crystals forming rims on corroded surfaces of early micrite, occurring as porphyritic aggregates, or infiltrating tiny fractures. These differences in framboid and euhedral crystal occurrence among the authigenic carbonate from three sites suggest spatiotemporal variations in the availability of sulfur and iron during pyrite formation (Raiswell, 1982; Coleman and Raiswell, 1995; Peckmann et al., 2003; Raiswell and Canfield, 2012).

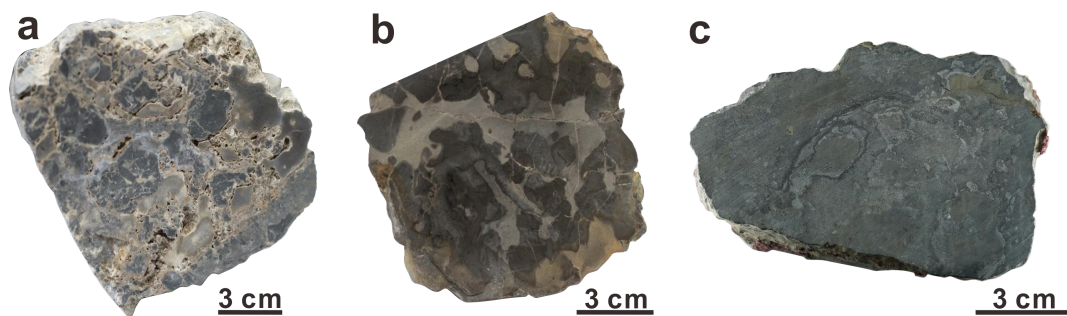


Fig. 3. Bulk seep carbonate from a) Whiskey Creek (USA), b) Beauvoisin (France), and c) Willapa bay (USA) aerias.

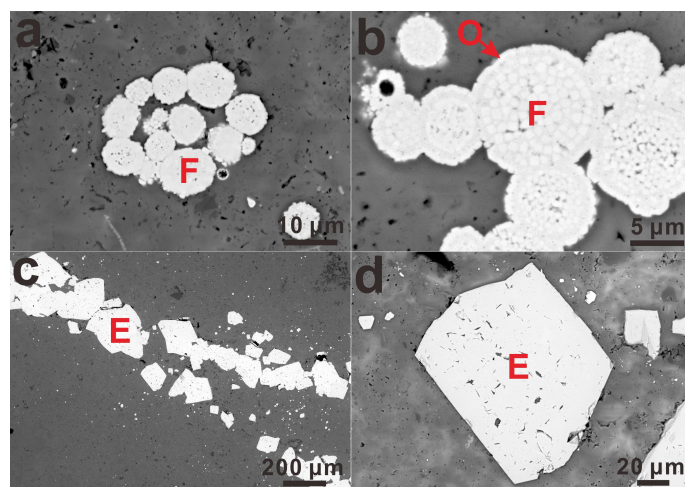


Fig. 4. Representative types of pyrite in seep carbonate (Willapa bay area). a) and b) Framboids. c) and d) Large euhedral crystals. F: framboids; O: overgrowth; E: euhedral crystals.

The $\delta^{34}\text{S}$ values of framboidal pyrite in seep carbonates from the three sites show comparable results, with values as low as -35‰ , indicating a pronounced sulfur isotope fractionation relative to contemporaneous seawater sulfate ($\sim 60\text{‰}$; Kampschulte and Strauss, 2004). Such a large fractionation clearly points to the influence of sulfate-driven anaerobic oxidation of methane (SD-AOM; $\sim 66\text{‰}$; Deusner et al., 2014) or organoclastic sulfate reduction (OSR; up to 70‰ ; Canfield and Teske, 1996; Sim et al., 2011). OSR may have occurred in ancient seep environments and contributed to framboid formation, its role was likely minor. The reason is seep carbonates form under high methane flux conditions where SD-AOM predominates, resulting in a stronger influence of SD-AOM on framboid formation compared to settings dominated by diffusive methane transport (Formolo and Lyons, 2013). In contrast, the $\delta^{34}\text{S}$ values of euhedral pyrite crystals are mostly $>0\text{‰}$ in seep carbonates from Beauvoisin and Whiskey Creek, but are distinctly negative and exhibit a narrow range in seep carbonates from Willapa Bay. The former pattern is attributed to the encapsulation of pyrite by authigenic carbonate, whereas the latter reflects a consistently open system during and immediately after the corrosion event. Thus, the $\delta^{34}\text{S}$ values record variably open system conditions during the formation of framboids and euhedral crystals during early diagenesis, respectively.

Two generations of pyrite are discovered in the corroded authigenic carbonate collected from Willapa bay area. Framboids and euhedral crystals formed before and after the corrosion event according to their distributive patterns, respectively. The significant content variations between framboids and euhedral crystals reveal distinct sources of trace elements and fluctuating redox conditions during early diagenesis. The notably high contents of Mn, As, Mo, Sb, and Pb in framboids suggest intense ferromanganese oxide dissolution under sulfidic conditions (Shikazono et al., 1994; Lin et al., 2022). One side, it's suggested manganese is preferentially incorporated into pyrite when porewater Mn^{2+}/Fe^{2+} ratios are high, particularly as reactive iron (amorphous and crystalline phases) becomes resistant to reduction (Morse and Luther, 1999). On the other side, dilution effect of seawater on trace element contents of euhedral crystals under persistent open system is also probable (Dellwig et al., 2002). These mechanisms explain the substantially lower contents of the same elements in euhedral crystals. Similarly, elevated contents of Ni, Co, Cu, Zn, and Cd in framboids point to enhanced input and dissolution of labile organic matter and/or ferromanganese oxide compared with the period of euhedral crystal formation. In contrast, U shows slightly higher contents in euhedral crystals than in framboids, implying less reduced conditions, likely due to O_2 ingress during the corrosion event. Consequently, the high Mo and low U contents in framboids, reversing to low Mo and high U in euhedral crystals, archives redox fluctuations during the formation of the corroded seep carbonate. Although U can also be adsorbed by organic matter (McManus et al., 2006; Smrzka et al., 2019), the absence of similar enrichments in Ni, Co, Cu, Zn, and Cd in euhedral crystals suggests that U was replenished primarily by seawater.

5.2 Conclusion and outlook

Authigenic minerals serve as crucial archives of sedimentary environment. Studies on authigenic minerals in sedimentary environments provide direct evidence for deciphering elemental cycling and shifts of redox conditions during early diagenesis. However, in many instances, their formation involves complex, multi-stage processes that are unavailable to be resolved through whole-rock analysis alone. To explore the role of variable phases to redox condition changing and elemental cycles during authigenic minerals formation, glendonite and pyrite enclosed in the authigenic carbonate are selected to conduct the phase-specific analysis.

Glendonite show multiple calcite varieties, growing from replacive to light, fibrous and blocky calcite. FTIR and EMPA are employed to interpret the effect of trace elements, especially Mg^{2+} and Fe^{2+} on the formation of each calcite variety. The Mg and Fe contents of distinct calcite varieties within glendonites from ancient strata in Siberia, Russia, also exhibit considerable variation, which is linked to pore-water redox conditions and the availability of dissolved Mg^{2+} and Fe^{2+} . Furthermore, FTIR spectra of these calcite varieties indicate that the influence of carbon and oxygen isotopes must be considered, as bulk glendonites from the same locations display wide ranges of both $\delta^{13}C$ and $\delta^{18}O$, as reported in previous studies.

Similarly, pyrite display habits of framboids and euhedral crystals in the authigenic carbonate. SIMS and LA-(MC)-ICP-MS are utilized to illuminate the evolution of sulfur isotope and trace elements during the formation of each habit of pyrite. In seep carbonates from Whiskey Creek, Beauvoisin, and Willapa Bay, the $\delta^{34}S$ values of framboidal pyrite are extremely low (as low as -35%), indicating a fairly open system, with variations reflecting

different degrees of pyrite entrainment. In contrast, euhedral pyrite crystals from the same carbonates at Whiskey Creek and Beauvoisin formed from sulfate pools that were more enriched in ^{34}S relative to those of framboids, yielding positive $\delta^{34}\text{S}$ values ($>0\text{‰}$). This pattern differs markedly from the $\delta^{34}\text{S}$ values of euhedral crystals (approximately -10‰) in the Willapa Bay seep carbonate, where a persistently open system prevailed. Additionally, trace element contents differ significantly between framboidal and euhedral pyrite in the Willapa Bay carbonate, suggesting higher availability of organic matter and ferromanganese oxides during early framboidal pyrite formation, and less reduced conditions during the later formation of euhedral crystals. These findings are significant for interpreting complex redox fluctuations and elemental cycling from the water column or deeper sources to shallow sediments during early diagenesis.

Notably, the framboids and euhedral crystals observed in seep carbonates from Whiskey Creek, Beauvoisin, and Willapa Bay are sometimes too small in size ($<10\text{ }\mu\text{m}$) to be analyzed for sulfur isotopes and trace elements. Consequently, the potential information recorded by these tiny crystals remains unavailable for interpreting pyrite formation. Furthermore, given that the formation of framboids and euhedral crystals is primarily controlled by the availability of sulfur and iron, iron isotope analysis offers a promising approach to elucidate the developmental mechanisms of iron during the formation of different pyrite habits. This may require high-resolution in-situ iron isotope analysis combined with chemical sequential extraction. In addition, future studies investigating pyrite formation (e.g., via sulfur and iron isotope as well as trace element analyses) in glendonites could provide valuable constraints on the crystallization processes of calcite varieties, as sulfate reduction significantly influences pore-water chemical conditions and elemental behavior during early diagenesis.

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Acknowledgement

I would like to express my heartfelt gratitude to my supervisors, Jörn and Zhiyong, for giving me the precious opportunity to complete my doctoral program under their guidance. Their exceptional expertise, unwavering support, and constructive suggestions have significantly shaped the topic of this dissertation.

Many thanks to my colleagues and friends in the working group, especially Huan and Siyu, for their kind help in both daily life and academic studies over the past three years. As a foreign student arriving in Germany for the first time, it would have been difficult to settle into life here without your assistance.

Special thanks go to the co-authors listed in the publications or manuscripts, who provided help with samples, discussions, or advice on the manuscripts.

I sincerely acknowledge the funding provided by the China Scholarship Council (CSC) fellowship, which supported my living expenses in Germany.

Last but not least, I am deeply grateful to my dear parents and my girlfriend. Your support and encouragement have accompanied me throughout this entire adventure.