

Article

Localized CO₂-Induced Alteration at a Sandstone–Mudstone Interface and Its Implications for a Potential Self-Sealing Mechanism in the Lishui Sag, East China Sea Basin

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Abstract

Mudstone caprocks are important sealing formations for geological CO₂ storage, but the extent and mineralogical response of CO₂-induced alteration within mudstone caprocks remain poorly constrained. This study examines a Paleocene mudstone caprock from the Mingyuefeng Formation in the Lishui Sag, East China Sea Basin, where natural CO₂ charging has occurred. Mineralogical and geochemical analyses, including X-ray diffraction (XRD), rare earth elements (REE), and carbon–oxygen isotopes, were used to characterize CO₂–water–rock interaction at the reservoir–caprock transition. The studied caprock is dominated by quartz and clay minerals, with mineralogical characteristics favorable for caprock sealing. REE signatures indicate a felsic source and limited vertical REE redistribution within the studied interval. Carbonate minerals display distinct vertical variations across the sandstone–mudstone interface, with localized carbonate redistribution near the transition and carbonate depletion accompanied by clay–mineral alteration above it. Most samples retain $\delta^{13}\text{C}$ values close to background levels, whereas a decimeter-scale interval adjacent to the interface exhibits depleted $\delta^{13}\text{C}$ values accompanied by localized $\delta^{18}\text{O}$ variations, consistent with the localized influence of CO₂-bearing fluids. The altered zone is restricted to a decimeter-scale interval above the reservoir–caprock transition, suggesting that CO₂-related alteration was spatially restricted within the studied interval. Carbonate redistribution and clay–mineral transformation may have contributed to geochemical buffering during CO₂–water–rock interaction, although their quantitative effects on pore structure and sealing performance require further petrophysical investigation. These results provide a natural analogue for understanding localized CO₂-induced alteration and potential geochemical self-sealing processes at reservoir–caprock interfaces.

Academic Editor: Luca Aldega

Received: 18 July 2026

Revised: 13 August 2026

Accepted: 24 August 2026

Published: 26 August 2026

Keywords: mudstone caprock; CO₂-water-rock interaction; CO₂-induced alteration; geochemical buffering; diagenesis

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1. Introduction

Mudstone caprocks play an essential role in both hydrocarbon preservation and the long-term security of geological CO₂ storage [1–5]. Their sealing capacity is commonly attributed to low permeability, high capillary entry pressure, and sufficient thickness.

However, pore structure, clay mineral composition, and wettability also exert important controls by influencing fluid–rock interactions and capillary sealing behavior [1,3,6–8].

When caprocks are subjected to CO₂-rich fluid charging from different geological sources, fluid–rock interaction may significantly modify their properties. Dissolution of primary minerals, precipitation of secondary carbonates, and alteration of pore networks can either weaken or enhance sealing performance, depending on the evolution of fluid chemistry and reaction pathways [9–13]. These processes introduce considerable uncertainty in evaluating caprock integrity under CO₂-rich conditions.

Previous studies from natural CO₂ reservoirs and experimental systems indicate that CO₂-related alteration may extend from decimeter scale to several meters, and in some cases exceed ten meters. Natural CO₂ analogue studies have also demonstrated that mineral dissolution and secondary mineral precipitation may modify fluid pathways and contribute to localized geochemical buffering processes [14,15]. For example, isotopic and mineralogical evidence from the North Sea suggests that CO₂-bearing fluids can penetrate up to ~10–12 m into overlying caprocks [16,17]. Such variability highlights the strong dependence of CO₂ migration and reaction fronts on geological conditions.

Despite these advances, the vertical extent of CO₂-related alteration and its impact on sealing behavior remain insufficiently constrained, particularly in lacustrine mudstone systems. In addition, the coupling between geochemical reactions, mineral transformation, and pore structure evolution is still not well resolved at small spatial scales. Whether CO₂-induced alteration can remain restricted to sub-meter intervals remains an open question.

This study focuses on the Paleocene mudstone caprock of the Mingyuefeng Formation in the Lishui Sag, East China Sea Basin, where natural CO₂ charging has occurred. Integrated mineralogical and geochemical analyses, including X-ray diffraction (XRD), rare earth elements (REE), and carbon–oxygen isotopes, are used to (1) constrain the vertical extent of CO₂-related alteration, (2) characterize fluid–rock interaction processes at the reservoir–caprock interface, and (3) evaluate the implications of mineralogical alteration for caprock response to CO₂-bearing fluids. The results show that recognizable CO₂-related alteration is restricted to a decimeter-scale interval and suggest a potential geochemical self-sealing process associated with localized carbonate redistribution and clay-mineral alteration, providing new constraints on localized CO₂–water–rock interaction at reservoir–caprock interfaces.

2. Geological Setting

The Lishui Sag, located in the southwestern part of the East China Sea Shelf Basin, is a Cenozoic fault-controlled depression developed along the southeastern continental margin of China. Structurally, it exhibits a typical asymmetric half-graben geometry, with major boundary faults on the western side and relatively gentle overlap toward the east. The basin experienced multi-stage tectonic evolution, characterized by Paleocene-Eocene rifting followed by subsequent thermal subsidence, which together controlled sedimentary architecture and fluid migration pathways [18,19] (Figure 1).

The Paleocene Mingyuefeng Formation represents one of the key sedimentary intervals in the sag and is dominated by lacustrine depositional systems. Sandstone bodies are commonly interbedded with thick mudstone successions, forming a typical reservoir–seal assemblage. The mudstones are laterally continuous and widely distributed, with thicknesses generally ranging from several tens to over one hundred meters, providing effective sealing conditions for hydrocarbon accumulation [20,21].

Geochemical and isotopic investigations have demonstrated that gases in the Lishui Sag include a significant proportion of CO₂, derived from both organic and deep inorganic sources. Previous regional studies have reported mantle-derived CO₂ in several structures of the Lishui Sag and interpreted its migration to be associated with fault systems [20,22].

The accumulation of CO₂-rich fluids beneath mudstone caprocks makes this area a representative natural system for studying caprock behavior during interaction with CO₂-bearing fluids.

Overall, the Lishui Sag provides a suitable natural geological analogue for examining CO₂–water–rock interaction in lacustrine mudstone caprocks, particularly the spatial extent of CO₂-related alteration and associated mineralogical responses.

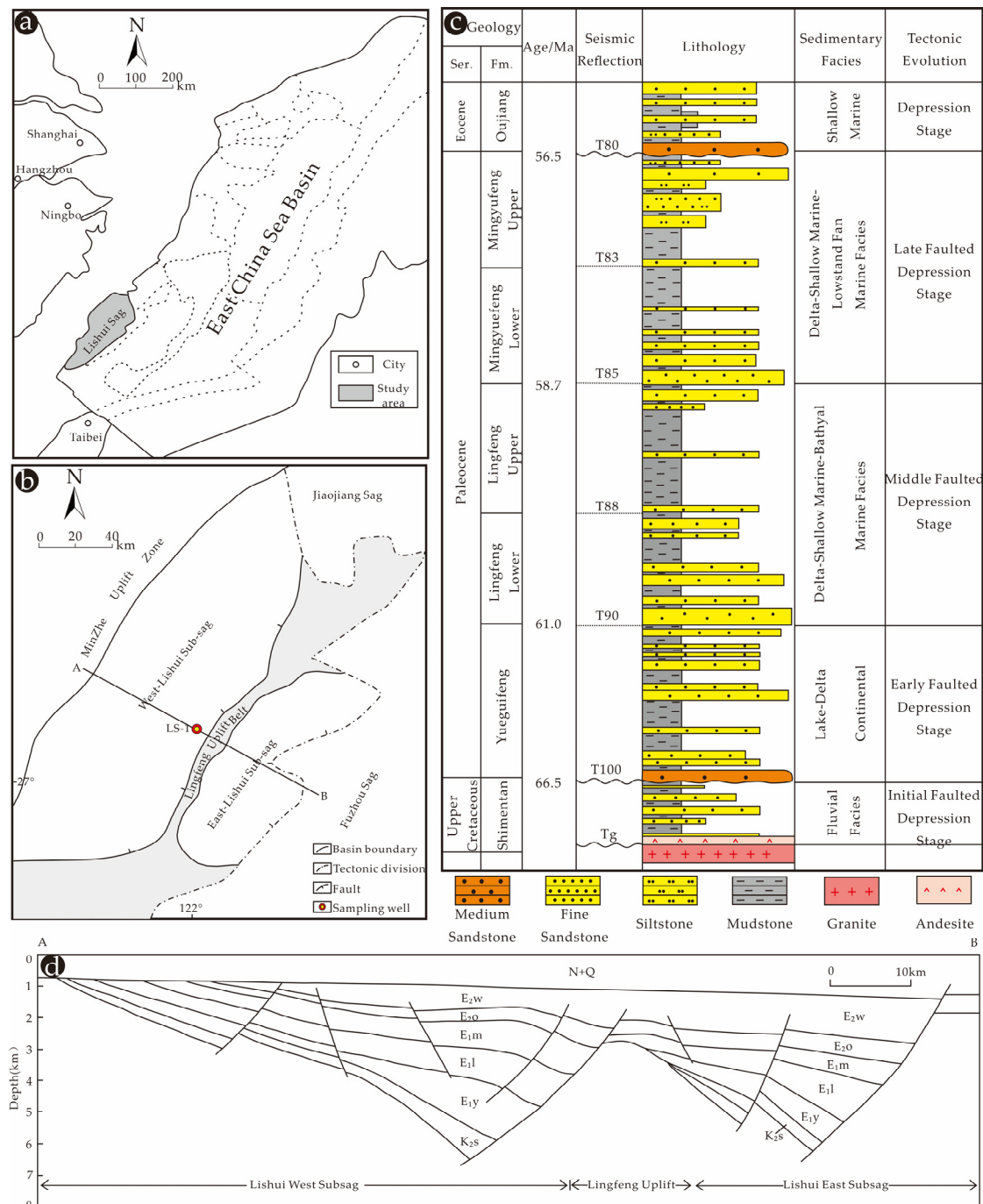


Figure 1. Tectonic setting and stratigraphic framework of the study area. (a) Tectonic division of the East China Sea Basin and location of the Lishui Sag (modified from Wu et al., 2023 [23]); (b) tectonic location of the study area within the Lishui Sag (modified from Zhao et al., 2018 [21]); (c) stratigraphic column of the Paleogene in the Lishui Sag (modified from Liu et al., 2022 [24]); and (d) geological cross-section of the Lishui Sag (modified from Lei et al., 2024 [25]).

3. Samples and Methods

Core samples were collected from the Paleocene Mingyuefeng Formation in the Lishui Sag, East China Sea Basin. The sampled interval covers the sandstone–mudstone transition zone, which represents the key interface for upward CO₂ migration and caprock sealing.

A total of 18 samples were analyzed, including 13 mudstone samples from the caprock and 5 sandstone samples from the underlying reservoir. The mudstone samples were obtained from a narrow interval immediately above the reservoir–caprock interface, spanning less than 2 m in thickness. Sampling was conducted at closely spaced depth intervals (generally <0.3 m, locally <0.1 m), providing a decimeter- to sub-decimeter-scale resolution of mineralogical and geochemical variations. In contrast, sandstone samples were collected from the adjacent reservoir interval below the interface.

Mineral compositions of both mudstone and sandstone samples were determined by X-ray diffraction (XRD) using PANalytical X'Pert PRO MPD (PANalytical B.V., Almelo, The Netherlands). Bulk-rock mineral assemblages were analyzed from powdered samples, and clay minerals were identified from separated clay fractions using oriented mounts following conventional procedures. Sandstone samples were further prepared as thin sections for petrographic observations under polarized light microscopy to identify CO₂-related mineralization features.

Rare earth elements (REE) were analyzed for the mudstone samples using inductively coupled plasma mass spectrometry (ICP-MS, ELEMENT XR, Thermo Fisher Scientific, Bremen, Germany). These data were used to characterize provenance-related geochemical signatures and evaluate the extent of REE redistribution within the studied interval. Analytical precision was generally better than ±5%.

Carbon and oxygen isotope analyses were performed on bulk-rock powders from both mudstone and sandstone samples. The powdered samples were reacted with phosphoric acid, and CO₂ released at different reaction stages was collected to determine the carbon and oxygen isotopic compositions of calcite and ankerite, respectively. Isotopic compositions were measured using a stable isotope ratio mass spectrometer and are reported in standard δ notation relative to VPDB, with analytical precision better than ±0.1‰ for $\delta^{13}\text{C}$ and ±0.2‰ for $\delta^{18}\text{O}$.

4. Results

4.1. Mineral Composition of the Mudstone Caprock

Whole-rock XRD analyses show that the mudstone caprock is dominated by quartz and clay minerals (Table 1; Figure 2). Quartz contents range from 38% to 52%, with an average of approximately 44%. Clay minerals are mainly composed of illite-smectite mixed layers (averaging ~20%) and kaolinite (averaging ~18%).

Table 1. Mineral composition of caprock mudstones from LS-1.

Sample	Depth (m)	Lith	Quartz	K-Feldspar	Plagioclase	Calcite	Ankerite	Siderite	Illite/Smectite	Kaolinite	Illite	Dawsonite
Y-1	2233	Mudstone	44	6	4	4	3	2	22	15	0	0
Y-2	2233.08	Mudstone	44	5	6	4	2	1	23	15	0	0
Y-3	2233.19	Mudstone	43	4	6	3	3	1	23	17	0	0
Y-4	2233.28	Mudstone	38	4	6	5	5	2	20	20	0	0
Y-5	2233.5	Mudstone	40	4	4	4	3	1	22	22	0	0
Y-6	2233.61	Mudstone	52	3	4	2	4	1	18	16	0	0
Y-7	2233.76	Mudstone	43	4	5	2	4	1	21	20	0	0
Y-8	2234	Mudstone	43	5	4	2	4	1	21	20	0	0
Y-9	2234.05	Mudstone	46	3	4	1	4	2	20	20	0	0
Y-10	2234.24	Mudstone	44	4	5	2	3	1	21	20	0	0
Y-11	2234.55	Mudstone	43	5	4	0	0	0	23	25	0	0
Y-12	2234.71	Mudstone	51	6	7	0	0	0	19	17	0	0

Y-13	2234.86	Mudstone	52	8	7	0	15	0	11	7	0	0
Y-14	2234.97	Sandstone	51	6	12	0	4	0	4	14	9	0
Y-15	2235.15	Sandstone	49	7	5	0	11	0	3	15	9	1
Y-16	2235.57	Sandstone	49	5	6	0	7	0	4	19	8	2
Y-17	2235.97	Sandstone	47	9	7	0	0	0	2	20	11	4
Y-18	2236.19	Sandstone	54	6	3	0	10	0	6	12	7	2

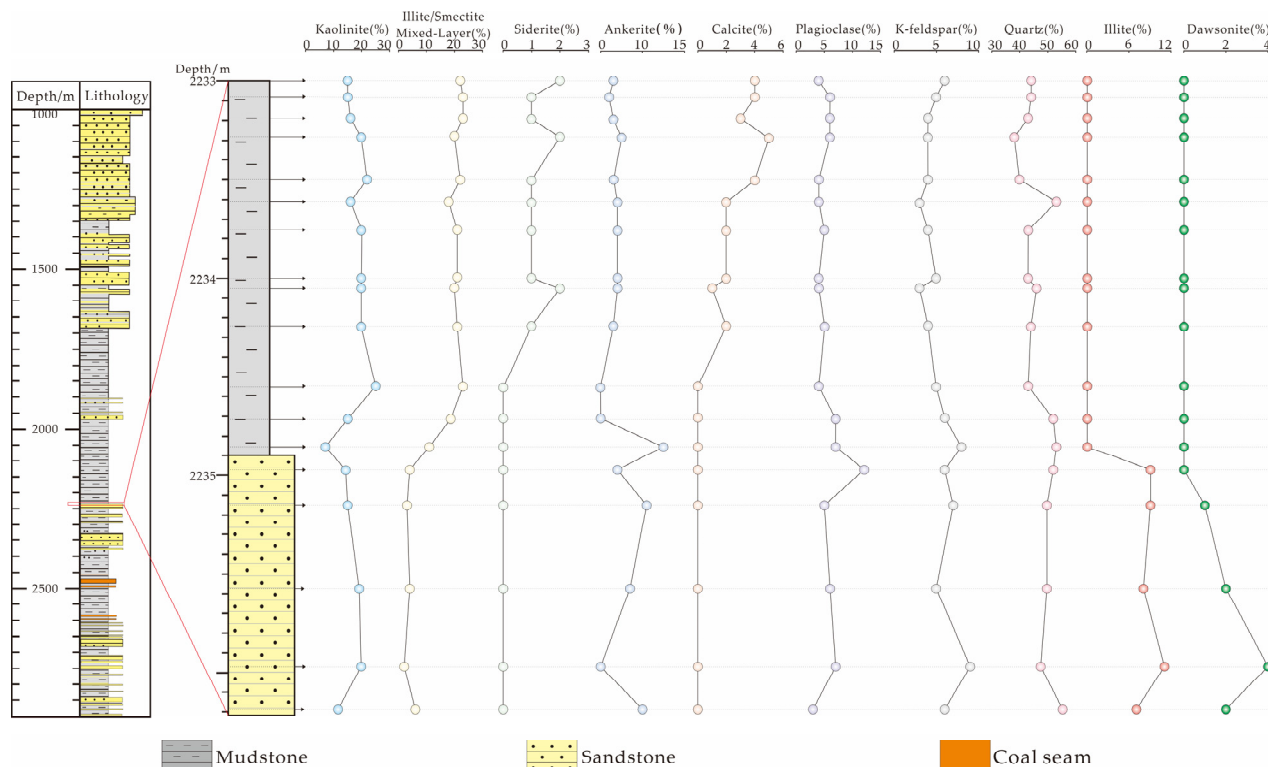


Figure 2. Vertical variations in mineral contents of the mudstone samples from Well LS-1.

Feldspar minerals are present in minor amounts, including K-feldspar (~4.7%) and plagioclase (~5.08%). Carbonate minerals are generally present in low abundances in most mudstone samples; however, localized carbonate enrichment occurs near the sandstone–mudstone transition, with ankerite reaching 15% in sample Y-13.

Vertically, the mineral composition remains relatively stable across most of the studied interval. However, localized mineralogical variations occur near the sandstone–mudstone transition. In particular, the mudstone sample closest to the reservoir–caprock boundary (Y-13, 2234.86 m) exhibits elevated ankerite content (15%), showing localized carbonate enrichment adjacent to the transition. In contrast, relatively elevated kaolinite contents occur in the overlying mudstone samples Y-11 (25%) and Y-12 (17%), whereas Y-13 immediately above the interface contains only 7% kaolinite.

4.2. Rare Earth Element Geochemistry

The total rare earth element content (ΣREE) of the mudstone samples ranges from 82.23 to 182.04 ppm, with an average value of 154.64 ppm (Table 2). Chondrite-normalized REE patterns display consistent enrichment of light rare earth elements (LREE) relative to heavy rare earth elements (HREE), with LREE/HREE ratios between 7.27 and 10.01 (Figure 3).

Table 2. Rare earth element geochemical parameters of LS-1.

Sample	ΣREE	LREE	HREE	LREE/HREE	LaN/YbN	δEu	δCe
Y-1	160.31	144.32	15.99	9.03	9.77	0.77	1.01
Y-2	160.6	144.62	15.98	9.05	10.26	0.63	0.96

Y-3	137.28	123.64	13.64	9.06	10.13	0.7	0.96
Y-4	82.23	72.29	9.94	7.27	10.7	0.74	0.99
Y-5	167.16	151.82	15.34	9.9	12.59	0.72	0.96
Y-6	161.66	146.32	15.34	9.54	10.16	0.68	1.03
Y-7	158.2	142.61	15.59	9.15	9.89	0.64	1
Y-8	153.93	138.39	15.54	8.91	10.32	0.6	0.93
Y-9	140.06	127.29	12.77	9.97	11.44	0.7	0.97
Y-10	180.37	163.03	17.34	9.4	9.66	0.57	0.97
Y-11	171.91	156.3	15.61	10.01	11.38	0.62	1.03
Y-12	182.04	164.87	17.17	9.6	10.89	0.61	0.94

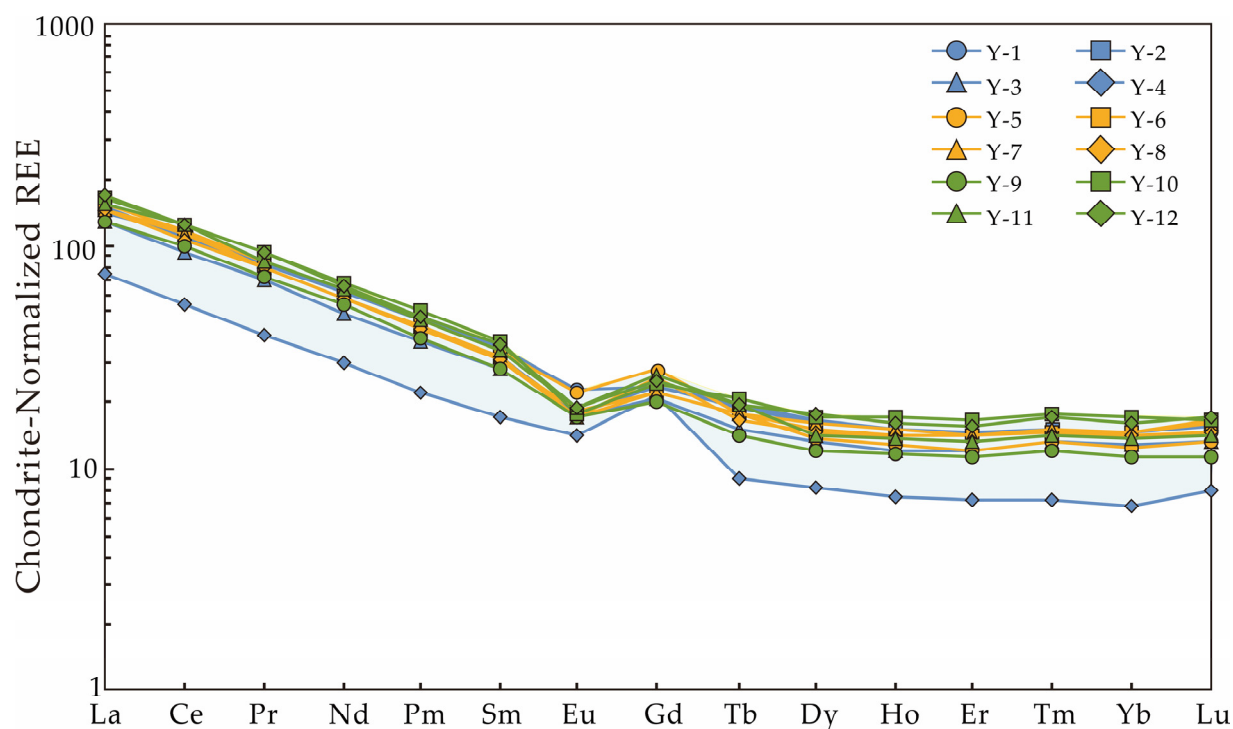


Figure 3. Chondrite-normalized REE patterns of the studied mudstone samples. The shaded area represents the min-max range of samples Y-1~Y-12. Y-4 is shown separately because of its relatively low REE abundance.

The La_n/Yb_n ratios range from 9.66 to 12.59, indicating pronounced fractionation between LREE and HREE, which likely reflects inherited provenance characteristics. All samples show weak negative Eu anomalies ($\delta\text{Eu} = 0.57\text{--}0.77$), whereas Ce anomalies are generally absent or very weak ($\delta\text{Ce} \approx 0.9\text{--}1.03$). The overall REE patterns are consistent across the studied interval, with no significant vertical variation.

4.3. Carbon–Oxygen Isotope Characteristics

Carbon and oxygen isotope compositions of carbonate minerals show distinct differences between mudstone and sandstone samples, as well as among different mineral phases within the sandstone (Table 3; Figure 4).

Table 3. Carbon–oxygen isotope data of LS-1.

Sample	Depth (m)	Lithology	Mineral	$\delta^{13}\text{C}_{\text{V-PDB}} (\text{‰})$	$\delta^{18}\text{O}_{\text{V-PDB}} (\text{‰})$	$\delta^{18}\text{O}_{\text{V-SMOW}} (\text{‰})$
Y-1	2233	Mudstone	Bulk carbonate	0.3	−9.6	21
Y-2	2233.08	Mudstone	Bulk carbonate	−0.2	−8.9	21.7
Y-3	2233.19	Mudstone	Bulk carbonate	0.8	−9.9	20.7

Y-4	2233.28	Mudstone	Bulk carbonate	0.7	−9.6	21
Y-5	2233.5	Mudstone	Bulk carbonate	0.5	−9.2	21.4
Y-6	2233.61	Mudstone	Bulk carbonate	1.7	−10	20.6
Y-7	2233.76	Mudstone	Bulk carbonate	1.1	−11.9	18.6
Y-8	2234	Mudstone	Bulk carbonate	0.7	−12	18.5
Y-9	2234.05	Mudstone	Bulk carbonate	1	−12	18.5
Y-10	2234.24	Mudstone	Bulk carbonate	0.2	−12.4	18.1
Y-11	2234.55	Mudstone	Bulk carbonate	−4.8	−14.3	16.2
Y-12	2234.71	Mudstone	Bulk carbonate	−14.2	−4.8	26
Y-13	2234.86	Mudstone	Bulk carbonate	3.5	−10.5	20
Y-15	2235.15	Sandstone	Dawsonite	−2.4	−9.8	20.8
Y-15	2235.15	Sandstone	Ankerite	−0.4	−9.4	21.2
Y-16	2235.57	Sandstone	Dawsonite	−1.2	−10.3	20.2
Y-16	2235.57	Sandstone	Ankerite	−0.9	−9.7	20.9
Y-17	2235.97	Sandstone	Dawsonite	−2.4	−11.2	19.4
Y-18	2236.19	Sandstone	Dawsonite	−1.3	−10.8	19.8

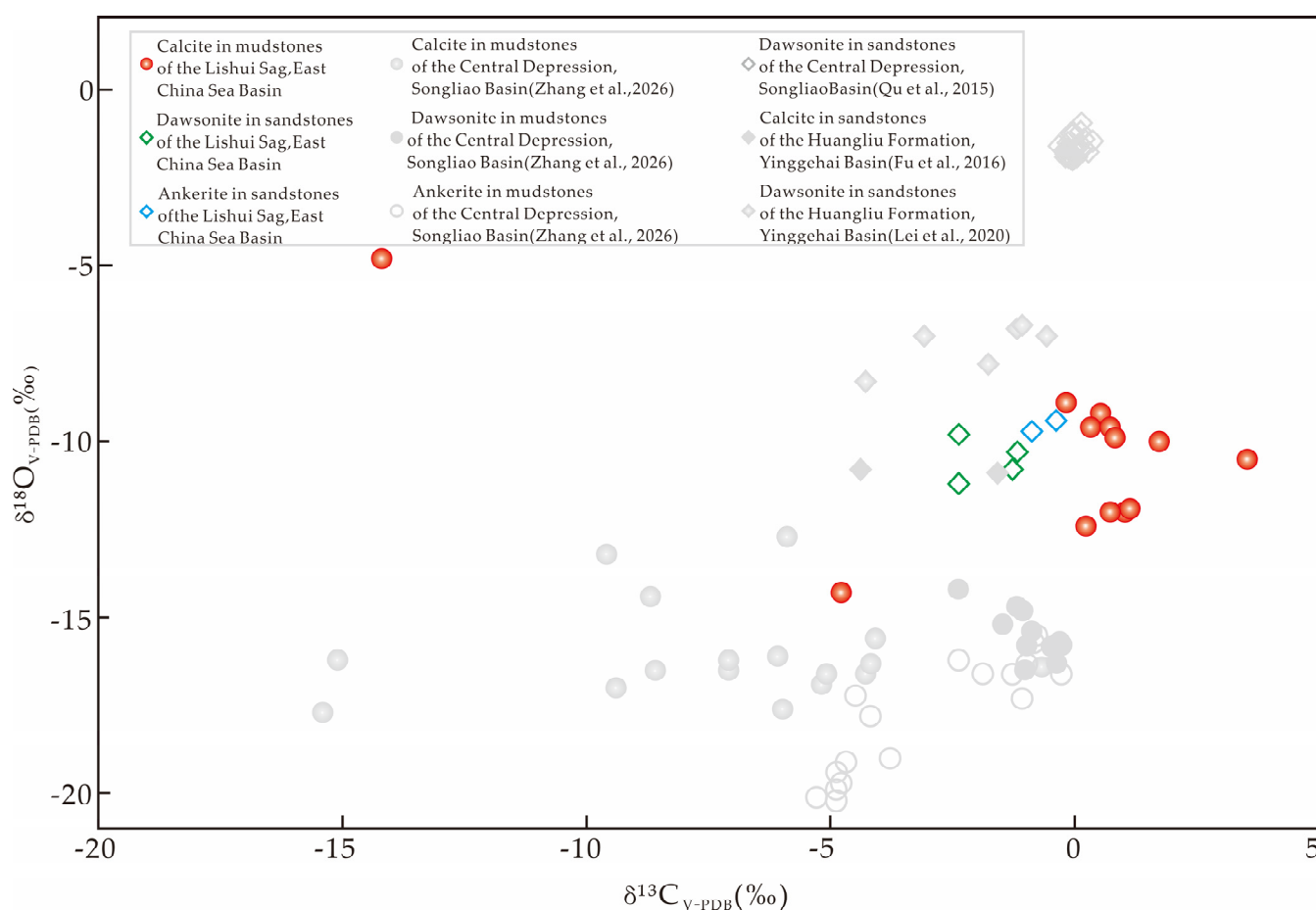


Figure 4. Carbon and oxygen isotopic compositions of carbonate minerals in LS-1 and comparison with published natural CO₂-bearing systems. Published comparison data include calcite, dawsonite, and ankerite from mudstones in the Central Depression, Songliao Basin (Zhang et al., 2026 [26]); dawsonite from sandstones in the Central Depression, Songliao Basin (Qu et al., 2015 [27]); dawsonite from the Huangliu Formation, Yinggehai Basin (Lei et al., 2020 [28]); and calcite from the Huangliu Formation, Yinggehai Basin (Fu et al., 2016 [29]).

In the mudstone samples, $\delta^{13}\text{C}$ values range from −14.2‰ to 3.5‰. Most values are concentrated between 0‰ and 3.5‰, whereas one of the samples displays markedly

lower $\delta^{13}\text{C}$ values down to -14.2‰ . The $\delta^{18}\text{O}$ values vary from -14.3‰ to -8.9‰ , with a relatively narrow distribution compared to $\delta^{13}\text{C}$.

In the sandstone samples, dawsonite shows $\delta^{13}\text{C}$ values of -12‰ to -8‰ , distinctly lower than ferroan dolomite (-2‰ to 2‰). The oxygen isotope values of these minerals also vary, with dawsonite tending toward lower $\delta^{18}\text{O}$ values compared to ankerite.

Overall, the isotopic data reveal a heterogeneous distribution of carbon and oxygen isotopes across the sandstone–mudstone interface, with the most pronounced variability occurring near the boundary interval.

5. Discussion

5.1. Characteristics of Mudstone Caprock and Depositional Implications

The mudstone caprock of the Paleocene Mingyuefeng Formation is characterized by a quartz-rich and clay-dominated mineral assemblage, with minor carbonate minerals such as calcite and ankerite. This composition reflects a fine-grained and relatively homogeneous lithology. Sedimentological features suggest that the mudstone was deposited in a low-energy lacustrine environment, where quiet water conditions favored the accumulation of fine particles and the development of laterally continuous mudstone layers.

Chondrite-normalized REE patterns show consistent enrichment of light rare earth elements (LREE) relative to heavy rare earth elements (HREE), with relatively high La_n/Yb_n ratios and weak negative Eu anomalies. These characteristics are typical of sediments derived from felsic continental crust [30,31] (Figure 5). Petrographic observations further indicate that lithic fragments are mainly derived from intermediate-felsic igneous rocks, consistent with previous studies in the Lishui Sag [20].

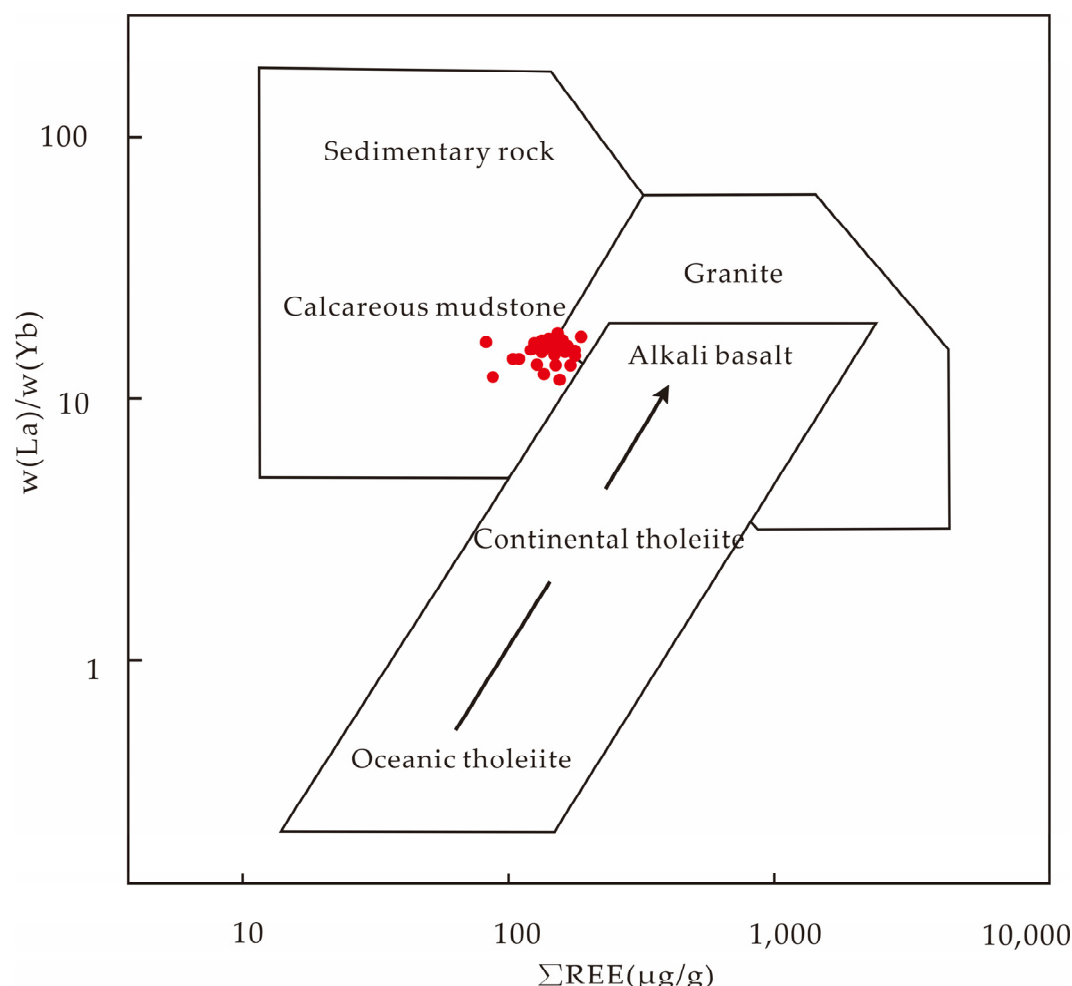


Figure 5. Relationship between ΣREE and La/Yb ratios of the studied mudstones.

The studied interval corresponds to the A-stage of middle diagenesis. This is supported by the transformation of clay minerals, with smectite contents in illite-smectite mixed layers ranging from 20% to 35%, reflecting progressive illitization during burial [32–34]. In addition, vitrinite reflectance (R_o) values of approximately 0.5% are consistent with this diagenetic stage [35–37] (Figure 6). The transition from early diagenesis B-stage to middle diagenesis A-stage occurs at approximately 2230 m, close to the sampling interval.

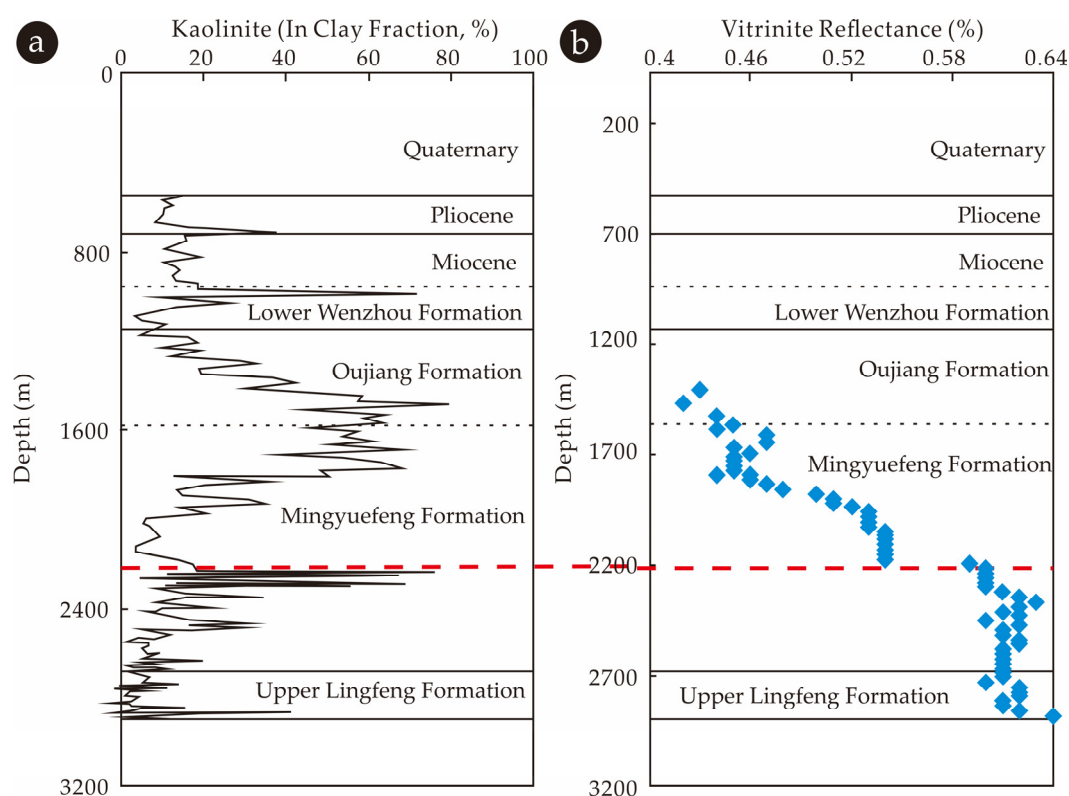


Figure 6. Variation in kaolinite content (a) (modified from Zhao et al., 2013 [38]) and vitrinite reflectance (R_o) (b) with burial depth in LS-1.

Under normal burial diagenesis, increasing temperature and depth typically promote the transformation of kaolinite into illite or chlorite, resulting in a gradual decrease in kaolinite content [39]. However, within the studied interval, locally elevated kaolinite contents occur in a narrow mudstone interval above the reservoir–caprock interface rather than showing a simple progressive decrease with burial depth. This localized variation is difficult to explain solely by progressive burial-driven diagenetic evolution.

The geothermal regime of the Lishui Sag provides an additional constraint. The basin is characterized by a relatively high geothermal gradient (~ 4.0 – 4.5 °C/100 m) [40,41], and the burial temperature at the sampling depth (~ 2233 – 2235 m) is estimated to be close to 90 °C. At such burial temperatures, progressive kaolinite transformation would generally be expected during diagenesis [39,42]. Therefore, the locally elevated kaolinite contents are difficult to explain by burial-related thermal evolution alone.

5.2. Localized Clay Mineral Transformation Associated with CO_2 -Bearing Fluid Activity

The vertical mineralogical variations across the sandstone–mudstone transition indicate a heterogeneous response to CO_2 -bearing fluid–rock interaction. Relatively elevated kaolinite contents occur within the altered mudstone interval above the

reservoir–caprock interface, whereas the immediate interface is characterized by localized carbonate redistribution. In particular, carbonate minerals were not detected by bulk XRD in Y-11 and Y-12, where kaolinite contents are relatively high, while Y-13 immediately above the sandstone–mudstone interface contains locally abundant ankerite. This spatial differentiation indicates a vertically heterogeneous mineralogical response rather than uniform alteration across the reservoir–caprock transition.

The occurrence of dawsonite in the underlying sandstone provides mineralogical evidence for CO₂-bearing fluid–rock interaction (Figure 7), although its formation also depends on suitable geochemical conditions, including Na availability and fluid chemistry [21,43]. Experimental and thermodynamic studies indicate that dawsonite formation requires specific geochemical conditions involving sufficient Na and Al availability and elevated CO₂ activity, while its formation and stability are also strongly influenced by fluid composition and competing mineral reactions [44,45]. Together with the localized mineralogical and isotopic anomalies near the interface, these features suggest that CO₂-bearing fluids migrated upward from the reservoir and interacted with the overlying mudstone caprock, consistent with previous studies documenting CO₂ charging and migration in the Lishui Sag [20,46].

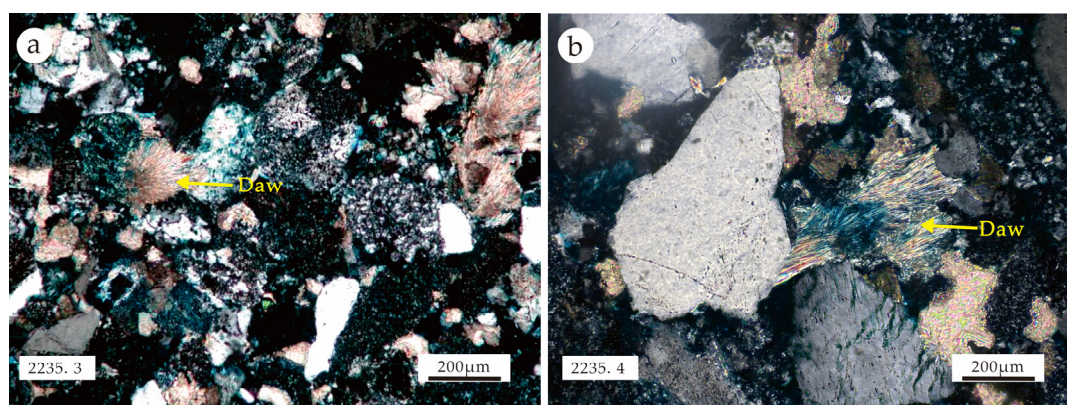
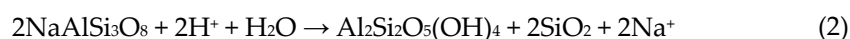
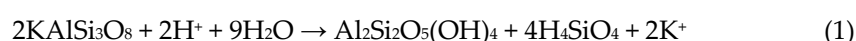


Figure 7. Radial aggregates of dawsonite in sandstone. (a) Well LS-1, 2235.3 m; (b) Well LS-1, 2235.4 m. Thin-section micrograph, crossed polars.

Kaolinite formation can be promoted by acidic conditions generated by dissolved CO₂ in formation water. The dissolution of CO₂ can decrease fluid pH and promote the alteration of aluminosilicate minerals, including feldspar. For example, K-feldspar and albite can be altered to kaolinite through reactions such as:



These reactions represent possible mineral transformation pathways during CO₂-bearing fluid–rock interaction [42,47,48]. However, the relative contribution of individual reactions cannot be quantitatively constrained by the present mineralogical dataset.

Under normal burial diagenesis, kaolinite generally decreases with increasing temperature due to transformation into illite or chlorite [39]. In the studied interval, relatively elevated kaolinite contents occur within a narrow mudstone interval above the reservoir–caprock interface rather than increasing continuously toward the sandstone contact. This distribution differs from a simple burial-related clay mineral trend and suggests that localized fluid–rock interaction may have contributed to kaolinite preservation or formation during burial diagenesis.

Kaolinite can also originate from surface weathering or meteoric-water alteration, which generally produces broader distribution patterns and is commonly associated with unconformities or exposure surfaces [49]. In contrast, the kaolinite variation observed here occurs within a deeply buried mudstone interval and is spatially associated with other evidence of fluid–rock interaction, including dawsonite in the underlying sandstone and localized carbon–oxygen isotopic anomalies. Therefore, although alternative origins cannot be completely excluded, the observed kaolinite distribution is consistent with a contribution from CO₂-bearing fluid–rock interaction.

The mineralogical characteristics therefore record a vertically heterogeneous alteration pattern across the reservoir–caprock transition. The interval immediately above the interface is characterized by localized carbonate redistribution, whereas the overlying mudstone records carbonate depletion accompanied by clay-mineral alteration. These spatially differentiated mineralogical responses indicate that CO₂-related alteration was localized rather than pervasive throughout the studied caprock interval.

5.3. Mineralogical Evidence for a Potential Geochemical Self-Sealing Mechanism

The reservoir–caprock transition in Well LS-1 occurs at approximately 2234.9 m, between the last mudstone sample Y-13 (2234.86 m) and the first sandstone sample Y-14 (2234.97 m). Carbonate minerals show distinct vertical variations across this transition. Y-13, immediately above the interface, contains relatively abundant ankerite (15%), whereas carbonate minerals were not detected by bulk XRD in the overlying Y-11 and Y-12 samples. This distribution indicates localized carbonate redistribution near the reservoir–caprock transition. Although the ankerite enrichment in Y-13 may reflect secondary carbonate precipitation during fluid–rock interaction, pre-existing diagenetic heterogeneity cannot be excluded based on the present data.

Under elevated PCO₂ conditions, dissolved CO₂ in formation water can generate acidic fluids that promote carbonate dissolution and release Ca²⁺ and dissolved inorganic carbon. During subsequent fluid evolution, changes in CO₂ activity and pH may favor secondary carbonate precipitation. Such dissolution–precipitation processes provide a possible mechanism for the localized carbonate redistribution observed near the reservoir–caprock interface and may contribute to geochemical buffering between CO₂-bearing reservoir fluids and the overlying caprock [26,50].

Carbon and oxygen isotopic compositions provide additional constraints on the spatial extent of fluid–rock interaction. Most mudstone samples exhibit bulk-carbonate $\delta^{13}\text{C}$ values close to background lacustrine inorganic carbon values, indicating that much of the studied mudstone interval retained its original carbon isotopic signature [31]. In contrast, samples within the altered interval above the sandstone–mudstone interface show strongly depleted $\delta^{13}\text{C}$ values, accompanied by localized $\delta^{18}\text{O}$ variations (Figure 8). Such negative carbon isotope shifts are consistent with carbon isotopic modification during later fluid–rock interaction [21]. The localized $\delta^{18}\text{O}$ variations may further reflect isotopic re-equilibration associated with changes in fluid composition and temperature conditions.

The mineralogical and isotopic anomalies are concentrated within a decimeter-scale interval near the reservoir–caprock transition, whereas the overlying mudstone retains relatively stable characteristics. This vertical pattern suggests that CO₂-related alteration was spatially restricted rather than pervasive throughout the studied caprock interval. Together, the carbonate depletion, clay-mineral alteration, and localized carbonate redistribution define a vertically heterogeneous alteration pattern across the reservoir–caprock transition (Figure 8).

These coupled mineralogical and isotopic responses suggest that fluid–rock reactions may have contributed to geochemical buffering during CO₂ migration. Carbonate

redistribution and clay-mineral alteration could potentially modify pore structure and fluid pathways, providing a possible geochemical self-sealing mechanism. However, their effects on pore connectivity, permeability, and sealing performance cannot be directly evaluated from the present dataset. Therefore, the proposed self-sealing mechanism should be regarded as a mineralogical and geochemical inference rather than a directly measured improvement in caprock sealing capacity.

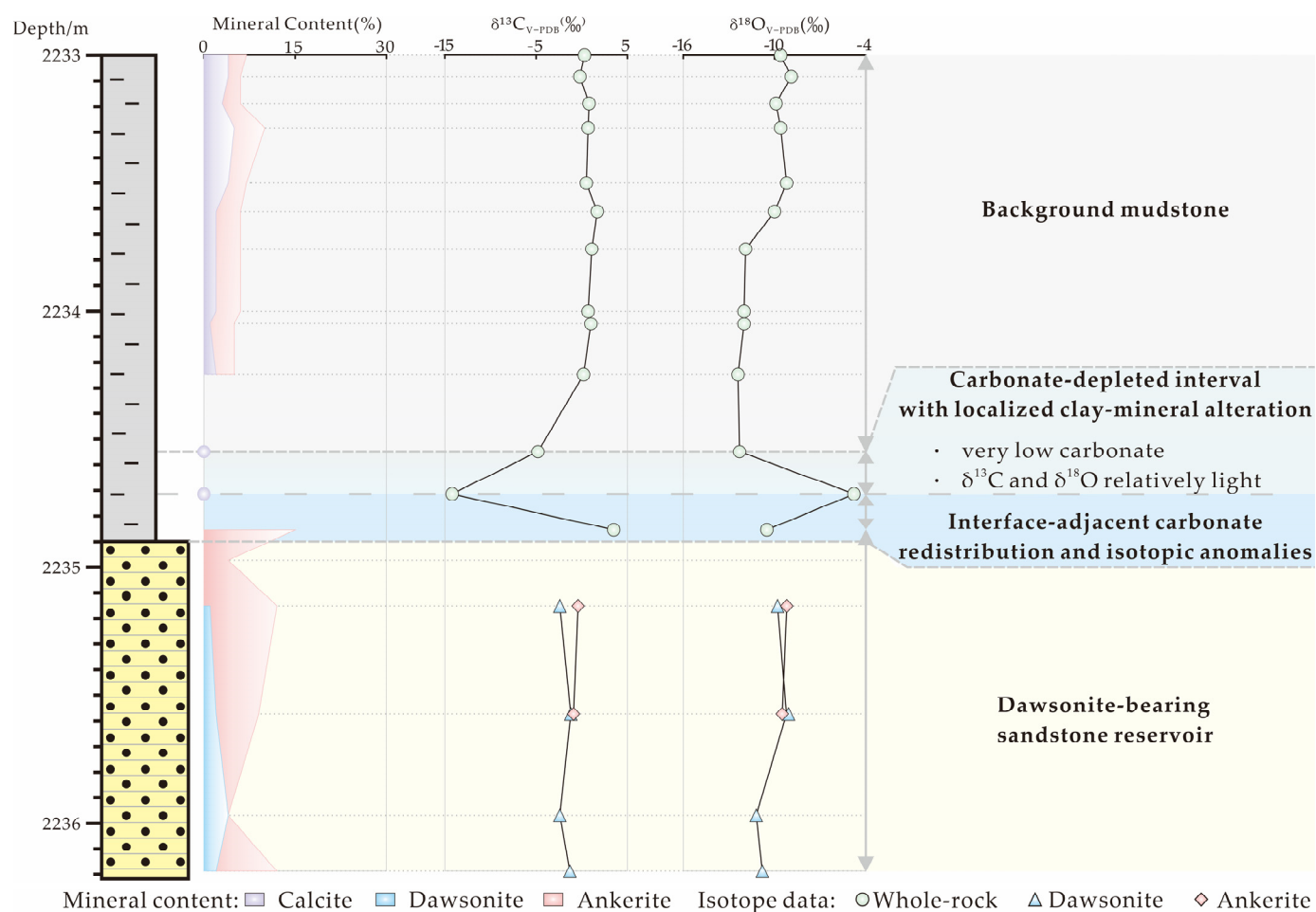


Figure 8. Vertical mineralogical and isotopic variations and interpreted alteration pattern across the reservoir–caprock transition in Well LS-1. The reservoir–caprock transition occurs at approximately 2234.9 m. A narrow interval within the overlying mudstone shows carbonate depletion and localized clay-mineral alteration, whereas localized carbonate redistribution occurs immediately adjacent to the transition. Carbon and oxygen isotope anomalies are concentrated near the transition, and dawsonite occurs in the underlying sandstone reservoir. Boundaries between the interpreted alteration intervals are approximate due to the sampling resolution.

5.4. Implications for CO₂-Induced Alteration and Potential Geochemical Self-Sealing

The combined mineralogical and isotopic evidence from the LS-1 reservoir–caprock transition provides a natural analogue for understanding the spatial extent of CO₂-induced alteration and its implications for mudstone caprock response during geological CO₂ storage. As this study focuses on a single reservoir–caprock transition, the observed alteration pattern represents a localized example of CO₂–water–rock interaction rather than a general representation of all caprock systems.

Within the studied interval, localized carbonate redistribution near the reservoir–caprock transition, carbonate depletion accompanied by clay-mineral alteration in the overlying mudstone, and associated isotopic deviations indicate that the effects of CO₂–

water–rock interaction were concentrated within a decimeter-scale interval. Above this interval, the mudstone retains relatively stable mineralogical and isotopic characteristics. This vertical pattern is consistent with a decreasing influence of CO₂-bearing fluids away from the reservoir–caprock transition.

Carbonate dissolution and redistribution near the transition, together with localized clay-mineral alteration, may have contributed to geochemical buffering during fluid–rock interaction. However, their quantitative effects on pore structure, permeability, and hydraulic properties cannot be evaluated from the present dataset and require further petrophysical investigation.

Compared with other natural CO₂ systems, where alteration zones may extend over several meters (e.g., approximately 10–12 m in some North Sea analogues [16,17]), the alteration observed in LS-1 is confined to a decimeter-scale interval. This difference highlights the influence of geological conditions, fluid pathways, and host-rock properties on the spatial extent of CO₂-induced alteration. Unlike our previous study of CO₂-related alteration in mudstone caprocks from the southern Songliao Basin [26], the present study focuses on the decimeter-scale mineralogical and isotopic response across a sandstone–mudstone reservoir–caprock transition in the Lishui Sag.

The localized mineralogical and isotopic responses suggest a potential geochemical self-sealing mechanism, in which mineral reactions may contribute to buffering CO₂ migration at the reservoir–caprock transition. The limited vertical variation of REE patterns further suggests that widespread REE redistribution did not occur within the studied mudstone interval. Nevertheless, the proposed self-sealing mechanism remains a mineralogical and geochemical inference, and direct evaluation of sealing performance requires integration of petrophysical measurements and reactive transport modelling in future studies.

6. Conclusions

(1) The mudstone caprock is characterized by high quartz and clay mineral contents, representing a fine-grained lithology with mineralogical characteristics favorable for caprock sealing.

(2) CO₂-bearing fluids migrated upward from the reservoir and interacted with the reservoir–caprock transition zone. The recognizable mineralogical and isotopic alteration was restricted to a decimeter-scale interval adjacent to the transition, indicating limited vertical propagation of CO₂-related alteration within the studied interval.

(3) CO₂–water–rock interaction was associated with a vertically heterogeneous alteration pattern, characterized by localized carbonate redistribution near the reservoir–caprock interface and carbonate depletion accompanied by clay-mineral alteration in the overlying mudstone. These mineralogical responses suggest a potential geochemical buffering mechanism.

(4) The localized mineralogical and isotopic responses observed at the reservoir–caprock transition provide a natural analogue for understanding CO₂-induced alteration and its potential implications for caprock sealing in geological CO₂ storage systems.

Author Contributions: J.X. contributed to methodology, investigation, data curation, and writing of the original draft. N.L. supervised the research, contributed to conceptualization, and revised the manuscript. S.Z. (Songxu Zhang) performed formal analysis and visualization. S.Z. (Shuang Zhao) contributed to data curation and investigation. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the National Natural Science Foundation of China, (No.42272146, No.41202073).

Data Availability Statement: The data presented in this study are available within the article.

Acknowledgments: We are grateful to the administrators and geological staff of the offshore exploration license area for their assistance with core sampling and access to geological data. We also thank the Editor and anonymous reviewers for their constructive comments and suggestions, which helped improve the manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

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