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Sulfate Sources Required for Thermochemical Sulfate Reduction in Dolostone Reservoirs in the Upper Permian Changxing Formation, Yuanba Gas Field, Sichuan Basin, China: Insights from the Origin of Celestite

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Abstract: Thermochemical sulfate reduction (TSR) commonly occurred in the dolostone reservoirs of the Upper Permian Changxing Formation (P3c) in the Yuanba (YB) gas field, Sichuan Basin, yet controversy remains regarding the source of sulfate required for TSR. To trace the source of the sulfate, sulfur and strontium isotopic compositions were measured for three diagenetic celestite (SrSO4) samples found in the P3c dolostone reservoirs in the YB gas field. In addition, the sulfur isotopic compositions of carbonate-associated sulfates (CAS) from the P3c carbonates and spheroidal pyrites in dolomicrites from the P/T boundary (PTB) in the YB gas field were measured for comparative studies. The results show that the sulfur isotopic compositions of celestites are significantly heavier than those of the contemporaneous seawater, and these celestites have strontium isotopic values consistent with those of the host dolostones and contemporaneous seawater. The −33.68‰ fractionation in average δ34S values between pyrites and celestites indicated that their formation was likely to be related to bacterial sulfate reduction (BSR). During the P/T extinction event that accompanied the end-Permian regression, the reflux of brine directly precipitated 34S-rich celestites in the fractures and vugs of the dolostone reservoirs due to the BSR and the evaporation of seawater. These 34S-rich celestites and associated pore fluids provide a new explanation for the source of sulfate required for the late TSR.

Keywords: sulfate source; celestite; sulfur isotopes; dolomitization; bacterial sulfate reduction; thermochemical sulfate reduction

1. Introduction

Thermochemical sulfate reduction (TSR) by organic–inorganic interactions in carbonate hydrocarbon reservoirs, particularly those associated with dolostone reservoirs, is one of the common diagenetic interactions and is widely studied due to its highly corrosive nature to production equipment, its toxicity to life, its impact on reservoirs, and its indicative significance in hydrocarbon source and evolution studies [1–7]. In most reported TSR geologic cases, liquid hydrocarbons and natural gases are the explicit primary reducing agents, whereas there are different sources of the oxidizer sulfate, with possible sources including sedimentary anhydrites [8,9], anhydrite cements [10], dissolved sulfates [11–13], dolomitizing fluids [14–16], and carbonate-associated sulfates (CAS) [17–19]. During TSR, inorganic sulfur from oxidant sulfate is incorporated into solid bitumen, H2S, and some metal sulfides (e.g., pyrite), leading to the enrichment of 34S in these sulfur-bearing species and thus approximating the sulfate isotopic composition of sulfate [1,20–22]. Solid bitumen formed by TSR, for example, typically has sulfur isotopic fractionation values in the range of −15‰ to 0‰ with respect to sulfate [21,23,24]. Therefore, the source of the sulfate
required for TSR can be determined from the sulfur isotopic fractionation values between the sulfur-bearing species formed by TSR and the potential sulfates.

Intense TSR has occurred in the dolostone reservoirs in the Lower Triassic Feixianguan Formation (T1f4), Puguang (PG) gas field, northeast Sichuan Basin, with hydrogen sulfide contents ranging from 5.1% to 62.2% (average 18.4%) [4,5], which is proposed to be related to the evaporative depositional environment of the reservoir rocks [13,25]. However, in the absence of evaporite deposition in the Changxing Formation (P3c) in the YB gas field, significant TSR still occurred in the large-scale dolostone reservoirs, with hydrogen sulfide contents ranging from 1.2% to 25.7% (average 7.0%) [15]. Regarding the source of sulfates required for the TSR in the P3c in the YB gas field, Li et al. [26] concluded that the sulfates mainly originated from the fourth member of the Feixianguan Formation (T1f4) by comparing the sulfur isotopic compositions of the reservoir solid bitumens in the P3c with those of the anhydrites in the T1f4. In contrast, Tian et al. [27] believed that evaporative fluids from the T1f4 and the Jialingjiang Formation (T1j) were not likely to penetrate the thick and tight limestones at the bottom of the T1f into the P3c reef and shoal carbonates. Li et al. [16] argued that the seepage reflux of evaporative seawater in the back-reef lagoons formed dolostone reservoirs during the Late Permian in the YB gas field, and the dolomitization process enriched porewater sulfates, which provided a sulfate source for the later TSR. Therefore, the source of sulfates required for the TSR in the P3c of the YB gas field remains controversial. This article is based on the study of the origin of three celestite (SrSO4) cements found in the P3c dolostone reservoirs of the YB gas field to elucidate the source of sulfate required for TSR.

2. Geological Setting

Sichuan Basin is a diamond-shaped basin in southwest China (Figure 1A), which was formed on the basement of the Presinian. The formation of the basin mainly went through two stages [28]. Before the early Indosinian movement, Sichuan Basin was mainly dominated by extensional setting and marine carbonate deposition. After the early Indosinian movement, the tectonic setting turned to compression, and the overall uplift of the Sichuan Basin resulted in the development of terrigenous clastic sediments, which were eventually shaped by folding and uplift during the Yanshanian and Himalayan movements [28].

During the Late Permian, the Sichuan Basin was rifted inside the stable platform of the Early Permian under the influence of the Emei taphrogeny [29]. In the northeast of the Sichuan Basin, a NW-SE continental shelf was formed, and an isolated carbonate platform was formed in the east, while a large platform developed in the west, which is in transition with the ancient land in the southwest (Figure 1A). Surrounding the shelf, several large gas fields have been discovered on the platform on both sides, such as the YB and PG gas fields. During the Late Permian and Early Triassic, the Wujaping (P3w) and Changxing (P3c) formations and the Feixianguan (T1f) and Jialingjiang (T1j) formations were deposited in the Sichuan Basin from bottom to top, respectively (Figure 1B). The mudstone hydrocarbon source rocks of the P3w were deposited inside the shelf due to rifting activities during the early phase of the Late Permian. By the end of the Permian, the reef and bioclastic shoal reservoirs of the P3c were deposited on the platform on both sides of the shelf. The P3c can be divided into the first (P3c1) and second (P3c2) members, which form a third-order shallowing-upward sequence. At the end of the Late Permian, the top of the P3c was short exposed due to the global sea-level fall [30,31]. During the early Early Triassic, the platform margins were dominated by the deposition of the T1f oolitic shoals. As the depositional environment varied, anhydrites were deposited within the isolated platform on the east side of the shelf, while no anhydrites were deposited on the open platform on the west side of the shelf (Figures 1 and 2). By the end of the deposition of the T1f, the entire northeast Sichuan Basin was in a restricted evaporative depositional environment due to further sea-level fall, where several layers of thin anhydrites were deposited. The T1f can be divided into four members from bottom through top: the first (T1f1), second (T1f2), third (T1f3) and fourth (T1f4) members, of which the T1f1 and T1f2
and T1f3 and T1f4 form a third-order shallowing-upward sequence, respectively. By the late phase of the Early Triassic, more restricted evaporative environments were widely developed, resulting in the deposition of the T1j thick evaporates. The T1j can be divided into five members, and evaporates are mainly developed in the second to fifth members (T1j2–5).

Figure 1. (A) Location map showing the Yuanba (YB) gas filed in the Sichuan Basin and sedimentary facies during the deposition of the P3c (Modified from Du et al. [32]). PG, Puguang gas field. (B) Generalized stratigraphy of the Upper Permian and Lower Triassic in the northeast Sichuan Basin. The lithology legends are shown in Figure 2. Fm., Formation.

Figure 2. Lithologic variations in the P3c and T1f in the Sichuan Basin from southwest to northeast. The well locations are shown in Figure 1A.
The YB gas field, discovered in 2007, is located in the northeast Sichuan Basin in a gentle tectonic zone with weak deformation and a lack of faults [33,34]. The main gas-producing reservoirs are the reef and bioclastic shoal dolostone reservoirs of the P3c, which commonly contain hydrogen sulfide and sulfur-bearing bitumen [26]. Gases from P3c in the YB gas field have been proven to be mainly derived from sapropel source rocks of the P3w [35,36]. Based on reconstructions of burial and thermal histories, the P3c and T1f in the northeast Sichuan Basin experienced a maximum burial depth of more than 6000 m and a maximum temperature of more than 180 °C before being uplifted to present-day depths [4,36,37].

3. Materials and Methods

After detailed core observation of the P3c in the YB gas field, only three celestite samples were obtained from a few wells. To study the origin of these celestites and their petroleum geological significance, several matrix carbonate samples near these celestites from the P3c as well as pyrite-bearing carbonates at the top of the P3c were also collected. Petrological and isotopic geochemical analyses were conducted for these samples.

Ten thin sections were prepared for detailed observation on a Nikon Eclipse E600 petrographic microscope. Three polished, platinum-coated thin sections were examined by FEI Quanta 200F scanning electron microscopy (SEM) operating at 10 KeV and 20 nA. The Raman analysis of the fluid inclusions in celestite minerals was conducted on the inVia Reflex micro-Raman instrument developed by Renishaw in the United Kingdom. The solid laser with a laser wavelength of 532 nm and a power of 50 mW was selected.

The sulfur isotopic compositions of three celestite samples, eight extracted carbonate-associated sulfate (CAS) samples, and six extracted pyrite sulfurs from P3c carbonate rocks were determined. The methods for CAS and pyrite extraction from carbonate rocks are referred to in Li et al. [38] and Jin et al. [39], respectively. The element analyzer (EA, Flash 2000, Thermo Fisher Scientific, Waltham, MA, USA) and isotope mass spectrometer (IRMS, Delta VPlus, Thermo Finnigan LLC, San Jose, CA, USA) were used to determine the sulfur isotopic compositions. Sulfur isotopic compositions are expressed in standard δ-notation as permil (‰) deviation from the V-CDT international standard. The mean standard deviation of the three international standard substances was 0.14‰. The strontium isotopic compositions of three celestite samples, one strontianite sample, and three host dolostone samples were determined on a Triton Ti mass spectrometer (Thermo Finnigan LLC, San Jose, CA, USA) in static mode. Full details of the treatment are referred to in Gao et al. [40] and Xu et al. [41]. The measurements of standard NBS-987 gave ⁸⁷Sr/⁸⁶Sr = 0.710228 ± 0.000007 (2σ).

4. Results

4.1. Petrography

Core observations reveal that the celestites are fully filling the dissolution fractures and vugs of the dolostones as cements (Figure 3), with the rims replaced by strontianites (Figure 3A,B). Microscopic and SEM observations also show the replacement of celestites by strontianites (Figures 4A–E and 5). A paragenesis of celestites, strontianites, bitumens, and pyrite was found in the P3c in the YB gas field. It appears that the presence of bitumens led to the alteration of celestites to strontianites, while the pyrites were precipitated in the nearby area (Figure 4E,F). Secondary inclusions distributed along fractures and joints are widely developed in the celestite minerals (Figure 6A), some of which were detected by laser Raman analysis as solid monatomic sulfur and gaseous H₂S (Figure 6B–D), indicating that these celestite minerals have been subjected to TSR alteration. Microscopic and SEM observations showed that spherical pyrites were common in the dolomicroites (about 3 m thick) at the top of the P3c in the well YB2 from the YB gas field (Figure 7A–F). In addition, terrigenous clay minerals and rounded quartz grains were observed in the microprores of the dolomicroites (Figure 7G).
Figure 3. Photographs of drilling cores showing the occurrence of celestites and strontianites in the YB gas field. (A) Celestite and strontianite minerals in the fracture of dolostone, 6640.15 m, P3c, YB29. (B) Celestite particles (blue arrow) and strontianite in the dissolution fracture of dolostone, 6461.73 m, P3c, YB205. (C) Celestite mineral completely filled in the dissolution vugs of dolostone, 6583.10 m, P3c, YB2.

Figure 4. Thin-section photomicrographs showing the occurrence of celestites and strontianites in the YB gas field. (A,B) Celestite and strontianite minerals in the fracture of dolostone, 6640.15 m, P3c, YB29. Note the development of solid bitumens (white arrow) in the intercrystalline pores (P) of dolomite. (A), under plane-polarized light (PPL); (B), under Cross-polarized light (CPL). (C,D) Celestite and strontianite minerals in the dissolution fracture and pore of dolostone, 6461.73 m, P3c, YB205. Note the development of solid bitumens (white arrow) in the intercrystalline pores (P) of dolostone. (C), under PPL; (D), under CPL. (E,F) Celestites, strontianites (red arrow), solid bitumens (white arrow), and pyrites (Py) in the dolostone dissolution pore, 6583.10 m, P3c, YB2. (E), under CPL; (F), under reflected light.
Figure 5. Back scattered electron images (A) and qualitative analysis of minerals of three points (B–D) in (A) using energy-dispersive spectrometry, 6640.15 m, P3c, YB29.

Figure 6. (A) Thin-section photomicrograph showing the fluid inclusions in celestite minerals of secondary origin, 6583.10 m, P3c, YB2. (B–D) Microscopic laser Raman spectra analysis of fluid inclusions in celestite minerals, 6640.15 m, P3c, YB29.
Figure 7. Thin-section and SEM photomicrographs showing pyrites and terrigenous materials near the Permian and Triassic boundary (PTB) in the well YB2. (A, B) Pyrites in dolomicrite, 6549.05 m, P3c. (A), under PPL; (B), under reflected light. (C, D) Pyrites in dolomicrite, 6549.83 m, P3c. (C), under PPL; (D), under reflect light. (E) Altered spheroidal pyrite, 6549.05 m, P3c. (F) Spheroidal pyrite, 6549.83 m, P3c. (G) Terrigenous clast and clay in dolomicrite, 6549.83 m, P3c.

4.2. Sulfur and Strontium Isotopic Compositions

Three celestite samples show very heavy sulfur isotopic compositions ranging from 35.53‰ to 39.78‰, with an average of 38.05‰ (Table 1). The sulfur isotopic compositions of CAS from five dolostone samples ranged from 18.96‰ to 27.53‰, with an average of 23.61‰ (Table 2). Three limestone samples have similar CAS sulfur isotopic compositions as the dolostone samples, ranging from 19.10‰ to 26.51‰, with an average of 22.86‰. The pyrites in six dolomicrite samples from the top of the P3c in the well YB2 showed light sulfur isotopic compositions, ranging from 1.09‰ to 10.79‰ (Table 2), with an average of 4.37‰.

Table 1. $\delta^{34}$S and $^{87}$Sr/$^{86}$Sr values for the celestite and strontianite minerals and the host rock dolostones in the P3c in the YB gas field.

| Well    | Depth (m) | Sample   | Occurrence | $\delta^{34}$S (VCDT, ‰) | $^{87}$Sr/$^{86}$Sr |
|---------|-----------|----------|------------|--------------------------|---------------------|
| YB2     | 6583.10   | Celestite| Vug-filling| 35.53                    | 0.707168            |
| YB205   | 6461.73   | Celestite| Vein-filling| 38.83                    | 0.707411            |
| YB29    | 6640.15   | Celestite| Vein-filling| 39.78                    | 0.707415            |
| YB29    | 6640.15   | Strontianite| Vein-filling| /                        | 0.707471            |
| YB29    | 6640.15   | Dolostone| Matrix     | /                        | 0.707399            |
| YB205   | 6461.73   | Dolostone| Matrix     | /                        | 0.707396            |
| YB2     | 6583.10   | Dolostone| Matrix     | /                        | 0.707232            |

/: no data.
### Table 2. $\delta^{34}$S values for carbonate-associated sulfates (CAS) and pyrites extracted from P$_3$c carbonates in the YB gas field.

| Well   | Depth (m) | Sample                  | $\delta^{34}$S (V-CDT, ‰) |
|--------|-----------|-------------------------|-----------------------------|
| YB123  | 6872.7    | CAS in limestone        | 22.97                       |
| YB123  | 6951.9    | CAS in limestone        | 19.10                       |
| YB224  | 6621.8    | CAS in limestone        | 26.51                       |
| YB224  | 6640.9    | CAS in dolostone        | 27.53                       |
| YB2    | 6556.6    | CAS in dolostone        | 18.96                       |
| YB2    | 6535.2    | CAS in dolostone        | 25.72                       |
| YB2    | 6580.6    | CAS in dolostone        | 23.29                       |
| YB2    | 6584.9    | CAS in dolostone        | 22.56                       |
| YB2    | 6549.1    | Pyrite in dolomicrite   | 1.09                        |
| YB2    | 6549.4    | Pyrite in dolomicrite   | 4.53                        |
| YB2    | 6549.7    | Pyrite in dolomicrite   | 4.93                        |
| YB2    | 6549.9    | Pyrite in dolomicrite   | 1.93                        |
| YB2    | 6550.0    | Pyrite in dolomicrite   | 10.79                       |
| YB2    | 6550.4    | Pyrite in dolomicrite   | 2.92                        |

The $^{87}$Sr/$^{86}$Sr ratios of the three celestite samples ranged from 0.707168 to 0.707471 (Table 1), with a wide range of variation and an average of 0.707331. The strontianite, an alteration product of celestite, has a relatively high $^{87}$Sr/$^{86}$Sr ratio of 0.707471, indicating the incorporation of radioactive strontium during the alteration process. The $^{87}$Sr/$^{86}$Sr ratios of the host rock dolostones range from 0.707232 to 0.707399, with an average of 0.707342. The $^{87}$Sr/$^{86}$Sr ratios of the celestite samples are close to those of the host rock dolostones.

### 5. Discussion

#### 5.1. Origin of Celestite

Celestite, a common but relatively minor diagenetic component of many marine carbonate platforms and reef sediments, has been extensively studied for its indicative role in depositional environments and diagenetic fluid properties. The major formation mechanisms that have been reported include: (1) Celestites precipitated in open pores by reactions between $\text{SO}_4^{2-}$ provided by anhydrite dissolution and $\text{Sr}^{2+}$ released during the conversion of aragonite to calcite and dolomite [42], or with $\text{Sr}^{2+}$ provided by the dissolution of anhydrites and carbonate rocks [43]; (2) Celestites formed by replacing carbonates and evaporites [44,45]; (3) Celestites formation as a byproduct of dolomitization [44,46,47]; (4) Hydrothermal origin [48,49].

Anhydrite deposits are not developed in the P$_3$c and adjacent formations (P$_3$w and T$_1$f$_1$–3) in the YB gas field (Figures 1B and 2). It is therefore unlikely that the celestites in the dolostone reservoirs of the P$_3$c in the YB gas field were formed through the dissolution and reprecipitation of anhydrite or by the replacement of anhydrite. The YB gas field is located in the gentle tectonic zone of the northern Sichuan Basin, with weak tectonic deformation and no fault development [33,34], thus excluding hydrothermal origin. The dolomitization process can form small amounts of sulfates [50,51]. Li et al. [47] suggested that the dolomitization process and aragonite-calcite conversion in the P$_3$c of the YB gas field enriched in $\text{Sr}^{2+}$ promoted the precipitation of a small number of celestites. In the following sections, the sources of $\text{Sr}^{2+}$ and $\text{SO}_4^{2-}$ ions of celestites in the P$_3$c of the YB gas field will be constrained based on the strontium and sulfur isotopic compositions.

#### 5.1.1. Source of $\text{Sr}^{2+}$ Ions

The $^{87}$Sr/$^{86}$Sr values of celestites in the P$_3$c in the YB gas field are close to those of the host dolostones (Table 1; Figure 8A), indicating that the $\text{Sr}^{2+}$ in the celestites are likely related to dolostones; in other words, the dolomitization provided $\text{Sr}^{2+}$ for the precipitation of the celestites. There are two existing possibilities: (1) The dolomitization fluids provided the $\text{Sr}^{2+}$ sources directly, or (2) Aragonite and calcite released large amounts of $\text{Sr}^{2+}$ during dolomitization [47,52], which in turn provided $\text{Sr}^{2+}$ for the precipitation of the celestites.
Regarding the former, the dolomitization fluids can be either contemporaneous or late exotic fluids. Previous studies have suggested that the Early Triassic evaporative brines provided dolomitization fluids for the P₃c carbonates [53,54]. In contrast, Tian et al. [27] argued that the evaporative brines hardly penetrated the thick and tight limestones at the bottom of the T₁f into the P₃c, and the dolomitization fluids of the P₃c mainly derived from the contemporaneous seawater. The dolomitized T₁f oolitic shoals, which are spatially closer to the evaporate layer in the YB gas field (Figure 2), were small-scale, with thicknesses below 10 m. Most of the areas have not experienced dolomitization (Figure 9A). In contrast, large-scale dolomitization occurred in the reefs and the bioclastic shoals of the P₃c, which are far from the brine sources (Figure 9B), suggesting that the dolomitization fluids of the P₃c probably did not come from the Early Triassic evaporative brines. The CAS δ³⁴S values of dolostones (18.96~27.53‰) in the P₃c from the YB gas field are close to those of the contemporaneous limestones (19.10~26.51‰) (Figure 10) and the contemporaneous seawater (16.57~26.52‰) [55], indicating that the dolomitization fluids originated from the contemporaneous seawater.

![Figure 8. Comparison of ⁸⁷Sr/⁸⁶Sr values for celestites, strontianites, and host dolostones from P₃c in the YB gas field (A) and contemporaneous seawater (B). The δ³⁴S values of celestites are also shown in A. The ⁸⁷Sr/⁸⁶Sr values of Late Permian and Early Triassic seawater are referred to in Martin and Macdougall [56] and Song et al. [57].](image)

![Figure 9. Distribution area and thickness of dolostones from T₁f (A) and P₃c (B) in the YB gas field. Note that the celestite samples are distributed in the northwest of the YB gas field.](image)
Figure 9. Distribution area and thickness of dolostones from T1f (A) and P3c (B) in the YB gas field. Note that the celestite samples are distributed in the northwest of the YB gas field.

Figure 10. Comparison of $\delta^{34}S$ values for reservoir celestites, pyrites [8,58], and bitumens [26] in the P3c and T1f. Pyrites in PTB, CAS in the P3c carbonates in the YB gas field, the Lower Triassic anhydrites in the Sichuan Basin [8,26,58–61], and the Late Permian and Early Triassic seawater [55,62]. The approximate correspondence between stratigraphy and geologic age is referred to Xu et al. [63]. Cs., Chronostratigraphy; Fm., Formation; Wuchia., Wuchiapingian; Gries., Griesbachian; Dien., Dienerian.

The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the P3c celestites, strontianites, and host dolostones (0.707168–0.707471) in the YB gas field are all in the range of the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the contemporaneous seawater (0.70694–0.70758) [56,57] and are significantly different from the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Early Triassic seawater (Figure 8), indicating that the Sr$^{2+}$ in celestites are mainly derived from the contemporaneous seawater. The positive correlation between the strontium and sulfur isotopic compositions of these celestites indicates similar sources of the Sr$^{2+}$ and SO$_4^{2-}$. Whether the Sr$^{2+}$ in celestites were directly derived from contemporaneous seawater or released from aragonite and calcite during the contemporaneous seawater dolomitization needs to be determined from the sulfur isotope data.

5.1.2. Source of SO$_4^{2-}$ Ions

The $\delta^{34}S$ values of the celestites in the P3c dolostones in the YB gas field are significantly heavier than those of the contemporaneous seawater and the CAS $\delta^{34}S$ values of carbonate rocks at the same formation (Figure 10). Simply compared with the $\delta^{34}S$ values of T1f$^4$ anhydrites, it appears that the SO$_4^{2-}$ in the celestites originated from the evaporated brines at the late Induan or the early Olenekian. However, as mentioned earlier, this is difficult to interpret from a geologic perspective. Here, we propose an alternative possible explanation considering the special paleoenvironmental context of the end-Permian mass extinction event.

A large number of pyrite grains were found in the dolomicroites at the top of the P3c in the well YB2 (Figure 7). The $\delta^{34}S$ values of these pyrites range from 1.09‰ to 10.79‰ (average 4.37‰), which were significantly lower than those of the contemporaneous seawater and the CAS of the P3c carbonate rocks and were also significantly different from the reported high $\delta^{34}S$ values of the TSR-induced pyrites in the T1f in the PG gas field (Figure 10). We propose that these pyrites distributed in the dolomicroites at the top of the P3c in the YB gas field are of BSR origin. Previous studies have shown that BSR preferentially metabolizes light sulfur ($^{32}S$), causing the enrichment of heavy sulfur ($^{34}S$) in
the remaining sulfate \[64,65\]. This explains the high $\delta^{34}S$ values of the celestites in the $P_3c$ dolostone reservoirs in the YB gas field. The $-33.68\%o$ fractionations in the average $\delta^{34}S$ value between the pyrites and celestites in the $P_3c$ dolostones (Figure 10) are within the range of the fractionation values during BSR ($-15\%o$ to $-65\%o$) \[21\], indicating the BSR origin of these celestites.

The occurrence of the celestites filling in dissolution veins and vugs in $P_3c$ dolostone reservoirs suggests that the celestites formed during or after dolomitization. Assuming that the $SO_4^{2-}$ originated from the dolomitization process, the celestites should have similar $\delta^{34}S$ values as those of the CAS of the $P_3c$ dolostones. In fact, the $\delta^{34}S$ values of the celestites are significantly higher than those of the CAS of the $P_3c$ dolostones (Figure 10), suggesting that the $SO_4^{2-}$ did not derive from the dolomitization process (Figure 11A). We infer that the $SO_4^{2-}$ originated from the evaporated lagoonal seawater in the back-reef and the intershoal during the global sea-level fall at the end-Permian, which refluxed into the dissolution pores of dolostones under the combination of BSR and evaporative modifications and precipitated $^{34}S$-rich celestites after mixing with Sr-rich pore water from early dolomitization (Figure 11B). The positive correlation between the $^{87}Sr/^{86}Sr$ and $\delta^{34}S$ values of the celestites suggests that these evaporative brines provided part of Sr$^{2+}$ for the precipitation of the celestites.

Figure 11. A schematic model for the formation of celestites, as well as the sources and evolution of sulfates. (A) Reflux dolomitization during Late Permian. (B) BSR during the P/T extinction event. (C) TSR during petroleum accumulation. See text for details. T., Temperature.
5.2. Insights into the Sulfate Required for TSR

The diagenetic effect should be considered before using the sulfur isotopic composition of celestite to decipher the source of sulfate required for TSR in the P3c in the YB gas field. However, there is no evidence for significant diagenetic alteration of the celestite since its formation to TSR alteration, including hydrothermal alteration that can significantly affect the sulfur isotopic composition [24,66]. Thus, the sulfur isotopic composition of celestite can be used to decipher the source of sulfate required for TSR in the P3c in the YB gas field.

The early precipitated celestites and associated fluids in the P3c dolostone reservoirs of the YB gas field provide a sufficient source of sulfate for the intensive TSR that occurred in the late stage. The reservoir bitumens in the P3c and T1f of the northeast Sichuan Basin have been subjected to TSR alteration, in which the sulfur components are mainly of TSR origin [4,26], showing a heavy sulfur isotopic composition close to that of the reservoir sulfates (Figure 10). For example, in the T1f of the PG gas field, the fractionation value of the average sulfur isotopic composition between reservoir bitumen and sulfate is 10.01‰, which is consistent with the TSR during high temperatures [21]. The fractionation value of the average sulfur isotopic composition between reservoir bitumen and celestite in the P3c of the YB gas field is 10.14‰, which is also consistent with the TSR during high temperatures, suggesting that the celestites and related fluids provided a sulfate source for the late TSR (Figure 11B,C). Further indications of the involvement of celestite in TSR are the replacement of celestite rims by strontianite (Figures 3A, 4A–E and 5), the paragenesis of celestites with bitumens and pyrite (Figure 4E,F), and the detection of hydrogen sulfide and monatomic sulfur in the inclusions of celestite (Figure 6). It is precisely because of the alteration of celestite by TSR that the celestites are not common in the P3c in the YB gas field. The residual celestites are only distributed in the present-day gas reservoirs in the high tectonic part of the northwest part of the YB gas field [36], where the lack of pore water prevented the occurrence of TSR [3,15], thus protecting the small number of celestites from alteration.

The formation and evolution of the celestites in the P3c dolostone reservoirs of the YB gas field can be organized into the following three stages: (1) During the deposition of P3c, the multistage eustatic regressions promoted the evaporation of back-reef lagoon seawater, which in turn led to reflux dolomitization in reefs and bioclastic shoals, allowing for pore water enrichment of Sr2+ (Figure 11A); (2) By the end of the Permian, further evaporative reflux of back-reef lagoon seawater occurred as a result of the large-scale global sea-level fall, while, at the same time, the flourishing BSR that occurred in the context of the P/T extinction event led to the enrichment of 34S in evaporated seawater, which precipitated 34S-rich celestites by mixing with previously Sr2+-rich pore fluids (Figure 11B); (3) These 34S-rich celestites and the related fluids provided a sufficient source of sulfate for the occurrence of TSR during late hydrocarbon accumulation, resulting in the heavier sulfur isotopic compositions of the present-day P3c reservoir bitumen in the YB gas field (Figure 11C).

6. Conclusions

The celestites in the dolostone reservoirs of the Upper Permian Changxing Formation in the Yuanba gas field were not a byproduct formed during dolomitization but by direct precipitation of concentrated lagoonal brine due to the evaporation brine refluxing into the open pores of the dolostones during the end Permian regression. The heavy sulfur isotopic compositions of the celestites are the result of the bacterial sulfate reduction that occurred in the lagoonal sedimentary environment under the context of the P/T extinction event. These 34S-rich celestites with associated pore fluids provide a new explanation for the source of sulfate required for the late TSR. However, it still cannot be ruled out that some evaporated brines entered the P3c dolostone reservoirs through fractures to provide a sulfate source for the late TSR during the deposition of the T1f under shallow burial environment conditions.
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