Carbonate formation in salt dome cap rocks by microbial anaerobic oxidation of methane

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Major hydrocarbon accumulations occur in traps associated with salt domes. Whereas some of these hydrocarbons remain to be extracted for economic use, significant amounts have degraded in the subsurface, yielding mineral precipitates as byproducts. Salt domes of the Gulf of Mexico Basin typically exhibit extensive deposits of carbonate that form as cap rock atop salt structures. Despite previous efforts to model cap rock formation, the details of subsurface reactions (including the role of microorganisms) remain largely unknown. Here we show that cap rock mineral precipitation occurred via closed-system sulfate reduction, as indicated by new sulfur isotope data. ¹³C-depleted carbonate carbon isotope compositions and low clumped isotope-derived carbonate formation temperatures indicate that microbial, sulfate-dependent, anaerobic oxidation of methane (AOM) contributed to carbonate formation. These findings suggest that AOM serves as an unrecognized methane sink that reduces methane emissions in salt dome settings perhaps associated with an extensive, deep subsurface biosphere.

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Earth's climate is modulated by the concentration of atmospheric greenhouse gases. These gases (e.g., CO₂ and CH₄) are largely generated at depth and subsequently transported to surface environments. These gases may fail to reach the surface due to chemical reaction along the way, resulting in their degradation and the subsequent precipitation of mineral phases. The geochemical compositions of these diagenetic minerals can provide insight into the nature of degradation mechanisms, thus leading to a better understanding of the fate of subsurface gaseous and aqueous chemical species.

Evaporites, elemental sulfur, metal sulfides, and carbonate minerals can co-occur in unique diagenetic settings. Examples of this association include those observed in cap rocks formed atop Jurassic salt in the Gulf of Mexico Basin (GMB)¹, Permian salt of Germany and the North Sea Basin, and Triassic salt in northern Tunisia². Similar deposits occur in Permian, hydrocarbon-bearing evaporite successions of the Delaware Basin in western Texas and Miocene strata in Carpathian basins of Poland, Ukraine, and Iraq³. These systems have been studied extensively due to their association with economic hydrocarbon and mineral resources⁴. Such environments provide appropriate conditions for microbial communities to take advantage of mineral-, aqueous-, and hydrocarbon-mediated or high temperature (>100 °C)⁵ reactions coupled with microbial sulfate reduction reactions to form elemental sulfur or with divalent metals to produce sulfide minerals. These processes tend to produce a unique spatial relationship among cap rock phases, where older precipitates broadly occur stratigraphically above younger layers (termed inverted stratigraphy)⁶. Ultimately, this paragenetic description represents a generalized sequence of events.

Despite this longstanding model for cap rock formation, the carbonate mineral-forming reactions remain poorly characterized. Of particular importance is the identification of specific microbial reaction pathways, many of which are known to yield alkalinity and promote carbonate precipitation⁷. Early studies report carbonate δ¹³C values (δ¹³C_carb) that range from −54‰ to −2‰ VPDB (Vienna-Pee Dee Belemnite)⁸, indicating precipitation from a carbon source depleted in ¹³C relative to seawater⁹. It was first proposed that carbonate carbon was sourced solely from liquid hydrocarbon due to its direct association with salt domes¹⁰,¹¹. Indeed, liquid hydrocarbon can promote carbonate precipitation via alkalinity production through microbially mediated or high temperature (>100 °C)¹² reactions coupled with sulfate:

\[
2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S},
\]

where CH₂O represents simplified liquid hydrocarbon. However, the δ¹³C values of modern GMB oils are relatively narrow, ranging from −28.0 to −23.0‰¹³. In the GMB subsurface, methane represents the only carbon source that is sufficiently ¹³C-depleted to produce δ¹³C_carb below −28‰¹⁴,¹⁵. Methane can act as a reducing agent during microbial sulfate reduction
through sulfate-dependent anaerobic oxidation of methane (AOM)\textsuperscript{21,22}, in accordance with the following net reaction:

\[ \text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}. \] (2)

Microbial anaerobic oxidation of methane has been shown to promote extensive authigenic carbonate formation on the seafloor and in shallow marine sediments\textsuperscript{23-25}. A similar reaction occurs at relatively high temperatures in the absence of microorganisms\textsuperscript{18}.

Solid sulfur-bearing phases occur predominantly in GMB cap rock as sulfates, sulfides, and elemental sulfur\textsuperscript{8}. Previous studies indicate that cap rock sulfur isotope values vary significantly among these phases, ranging from \(-40\) to \(+78\)‰ VCDT (Vienna-Canyon Diablo Troilite)\textsuperscript{13}. In general, sulfides and elemental sulfur in northern GMB cap rock express \(^{34}\)S-depleted isotope compositions relative to the gypsum and anhydrite inclusions contained within the parent Louann Salt. In contrast, cap rock sulfate-bearing barite and celestine (SrSO\textsubscript{4}) commonly exhibit \(^{34}\)S-enriched values\textsuperscript{8}. This sulfur isotope variability typifies microbially dominated systems, as large isotope fractionations can result from microbial sulfate reduction and/or disproportionation\textsuperscript{26}. Despite evidence for microbial cycling in salt dome settings, relationships between carbonate mineral production and these biogeochemical reactions remain poorly understood.

Here, we explore GMB cap rock from six domes across Texas and Louisiana: Boling, Davis Hill, Damon Mound, Hockley, Main Pass, and Winnfield domes (Fig. 1). Petrographic and isotopic data from carbonate and sulfur phases have been collected to better constrain carbonate mineralization pathways. These new data along with data provided in the literature support a relatively low-temperature, microbial precipitation mechanism that includes sulfate- and hydrocarbon-based reactants, as discussed in detail below.

**Results and Discussion**

**Cap rock paragenesis.** Previously reported carbon and sulfur isotope data\textsuperscript{8,11,13,16,17,27} indicate potential for hydrocarbon oxidation-linked sulfate reduction as a cap rock mineral precipitation mechanism. However, these data derive from different proxy reservoirs (carbonate mineral \(^{\delta^{13}}\)C and sulfur mineral \(^{\delta^{34}}\)S), which may have formed during distinct (and perhaps unrelated) diagenetic events. In fact, it has been proposed that barite and celestine (sulfate minerals that exhibit \(^{34}\)S enrichments consistent with sulfate reduction under sulfate-limited conditions) formed during relatively late stages of cap rock development\textsuperscript{8}.

Of the six domes explored here, four exhibit cap rock with significant elemental sulfur and sulfide mineral accumulations: Boling, Davis Hill, Hockley, and Main Pass domes. These sulfur phases exhibit variable paragenetic relationships with carbonate (Fig. 4). Carbonate occurs mostly as micritic, microspar, and spar cements. Later-stage vein precipitates commonly cross-cut early micritic and microspar cements\textsuperscript{8} (Fig. 2b). In many instances, carbonate phases formed after anhydrite and gypsum, as indicated by pseudomorphic replacement. Petrographic examination reveals that carbonate cements formed before, contemporaneous with, and/or after elemental sulfur and sulfide phases depending on the locality. Elemental sulfur in Boling Dome cap rock mineralized before and after carbonate, as indicated by cross-cutting relationships (Fig. 4a, b). Radiating sulfide crystals mimic carbonate (likely aragonite given the fibrous habit), perhaps reflecting contemporaneous or subsequent sulfide precipitation (Fig. 4c). Sulfide minerals at Davis Hill Dome tend to fill veins and cross-cut carbonate microspar cement, indicating sulfide mineralization after carbonate (Fig. 4d).

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**Fig. 2** Photographs and photomicrographs of Gulf of Mexico Basin cap rock. Samples from Boling Dome (a, d), Winnfield Dome (b, e), and Main Pass Dome (c, f) are pictured. Gypsum (G), host carbonate (C), vein carbonate (Cv), yellow elemental sulfur (S) and black metal sulfide (Su) minerals are clearly visible in hand sample and thin section. Red stain in d-f indicates calcium carbonate.
Salt dissolution, enrichment of anhydrite consistent with previous reports\textsuperscript{11,16}. Most of these values fall below modern GMB petroleum (with a minimum $\delta^{13}$C of $-28\%$\textsubscript{o}), likely indicating a significant carbon contribution from the oxidation of methane. In some cases, microbial oxidation of organic matter is accompanied by an isotopic depletion in the produced dissolved inorganic carbon. In general, however, this isotopic fractionation is small, leading to $^{13}$C-depletions in DIC of $\sim 3\%$ or less\textsuperscript{28–30} (although acetate oxidation reactions can yield more severe fractionations\textsuperscript{31}). Therefore, carbonate $\delta^{13}$C values that are less than $\sim -28\%$\textsubscript{o} likely indicate a methane carbon source. Cap rock that is less depleted in $^{13}$C (heavier than $-28\%$\textsubscript{o}) may have received carbon from the oxidation of liquid hydrocarbon or from the dissolution of marine limestone, both of which are abundant in the GMB subsurface. However, $\delta^{13}$C\textsubscript{carb} values greater than the liquid hydrocarbon minimum do not preclude a contribution from methane-derived carbon but rather suggest that carbon was provided from multiple sources (as has been recognized in marine cold seep settings\textsuperscript{32}).

Information about contemporaneous sulfur cycling can be obtained through the isotope composition of carbonate-associated sulfate ($\delta^{34}$S\textsubscript{CAS}). Carbonate-associated sulfate (CAS), trace sulfate incorporated into the carbonate mineral lattice upon precipitation, has been shown to record the sulfur isotope composition of ambient aqueous sulfate\textsuperscript{33,34}, including that of diagenetic systems\textsuperscript{35,36}. Given that CAS is incorporated as sulfate, it provides a unique opportunity to explore the isotopic evolution of the most oxidized end-member of sulfur. As a carbonate-hosted proxy, $\delta^{34}$S\textsubscript{CAS} can be used in tandem with $\delta^{13}$C\textsubscript{carb} to elucidate coupled carbon–sulfur reaction pathways and relationships to carbonate mineral precipitation. $\delta^{34}$S\textsubscript{CAS} values from host and vein cap rock carbonates range from $+12.5$ to $+68.8\%$\textsubscript{o} (Fig. 5). Dominantly $^{34}$S-enriched values (compared to the source sulfate derived from the Louann Salt, with a $\delta^{34}$S value of $+16\%$) indicate microbial sulfate reduction under sulfate-limited conditions\textsuperscript{37}. As bacteria preferentially reduce $^{32}$SO$_4^{2-}$, the residual sulfate pool experiences progressive enrichment in $^{34}$S\textsuperscript{37} and consequently yields relatively high $\delta^{34}$S\textsubscript{CAS} values in contemporaneously precipitated carbonate. Preferential reduction of $^{32}$SO$_4^{2-}$ to sulfate can promote the

Sulfide minerals within cap rock of Hockley Dome display disseminated (Fig. 4e) and botryoidal crystal habits (Fig. 4f, g). The disseminated habit may reflect precipitation contemporaneous with carbonate formation. Where botryoids dominate, carbonate cement crosscuts (Fig. 4f) and/or nucleates on sulfide. Elemental sulfur within cap rock of Main Pass Dome often crosscuts carbonate cement (Fig. 4h). Sulfide occurs as void-filling precipitates, with carbonate crystal terminations extending into the sulfide (Fig. 4i). These relationships indicate that both elemental sulfur and sulfide formed after carbonate.

Although in some cases petrographic relationships indicate variable formation timing between cap rock carbonate and sulfur phases, it has been proposed that these phases can form within a relatively narrow time window\textsuperscript{27}. When considered as a whole, however, complex paragenetic relationships (and an overall lack of phases that conclusively formed contemporaneously with carbonate) can confound interpretations regarding carbonate mineralization pathways. Ultimately, carbon and sulfur isotope data hosted in the same carbonate minerals will provide insight into the sulfur–carbon reactions that led to carbonate mineralization.

**Cap rock carbonate mineralization mechanism.** Our new $\delta^{13}$C\textsubscript{carb} data vary widely, ranging from $-52.7$ to $-2.9\%$\textsubscript{o} (Fig. 5), consistent with previous reports\textsuperscript{11,16}. Most of these values fall below modern GMB petroleum (with a minimum $\delta^{13}$C of $-28\%$\textsubscript{o}), likely indicating a significant carbon contribution from the oxidation of methane. In some cases, microbial oxidation of organic matter is accompanied by an isotopic depletion in the produced dissolved inorganic carbon. In general, however, this isotopic fractionation is small, leading to $^{13}$C-depletions in DIC of $\sim 3\%$ or less\textsuperscript{28–30} (although acetate oxidation reactions can yield more severe fractionations\textsuperscript{31}). Therefore, carbonate $\delta^{13}$C values that are less than $\sim -28\%$\textsubscript{o} likely indicate a methane carbon source. Cap rock that is less depleted in $^{13}$C (heavier than $-28\%$\textsubscript{o}) may have received carbon from the oxidation of liquid hydrocarbon or from the dissolution of marine limestone, both of which are abundant in the GMB subsurface. However, $\delta^{13}$C\textsubscript{carb} values greater than the liquid hydrocarbon minimum do not preclude a contribution from methane-derived carbon but rather suggest that carbon was provided from multiple sources (as has been recognized in marine cold seep settings\textsuperscript{32}).

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**Fig. 3** Proposed paragenetic evolution of Gulf of Mexico Basin cap rock. The specific nature of degraded hydrocarbon is largely uncharacterized, as is the relationship between degradation pathway and carbonate authigenesis (see step 4).
production of 34S-depleted reduced sulfur mineral phases (Fig. 5b). With progressive sulfate depletion, however, these sulfides can also exhibit relative 34S enrichment as the parent sulfate pool evolves. The common occurrence of metal sulfide δ34S values near 0‰ may indicate mineralization after the development of sulfate-limited conditions 27. Ultimately, 13C-depleted carbonate carbon and 34S-enriched CAS suggests simultaneous oxidation of methane and reduction of sulfate and thus that sulfate-dependent AOM (Eq. 2) promoted cap rock carbonate precipitation.

In many instances it can be difficult to distinguish between microbial and thermochemical reaction pathways using traditional carbon and sulfur isotope data alone. Thermochemical sulfate reduction, however, is limited to high-temperature environments (above ~100 °C)18. Clumped isotope compositions (reported as Δ47, see below) have proven useful in distinguishing carbonate mineralization temperatures in both primary and diagenetic settings. The Δ47 values of GMB cap rock carbonates range from 0.585 and 0.720‰ (reported in the absolute reference frame (ARF)38), suggesting carbonate precipitation temperatures between ~26 and 83 °C39,40, depending on the calibration. These temperatures fall well below the lower limit for thermochemical sulfate reduction (Fig. 6), in agreement with the common occurrence of single-phase fluid inclusions within calcite at these and other localities41. Modern marine cold seep carbonates precipitated via AOM yield anomalously low Δ47 compositions (likely inherited through kinetic effects), corresponding to precipitation temperatures significantly above ambient conditions42. Since these kinetic effects consistently yield temperature estimates higher than ambient conditions, we can expect the same for GMB carbonates. Specifically, it is likely that our temperatures are also overestimates and thus are well below those required for thermochemical sulfate reduction. Barite fluid inclusion data from Hazlehurst Salt Dome also indicate relatively low formation temperatures (<55 °C)27. In addition, samples recording the maximum degree of 34S-depletion in elemental sulfur and sulfide minerals preserved in cap rocks of the GMB are difficult to explain through thermochemical reactions alone, which generally exhibit maximum isotope discriminations of ~20‰18. Thus, temperature proxy data derived from both carbonate and sulfur phases indicate temperatures that are too low to facilitate thermochemical sulfate

Fig. 4 Photomicrographs displaying paragenetic relationships between reduced sulfur phases (elemental sulfur and sulfide) and carbonate. a-c Boling Dome. d Davis Hill Dome, e–g Hockley Dome, and h, i Main Pass Dome. Labels correspond to Gypsum (G), host carbonate (C), vein carbonate (Cv), yellow elemental sulfur (S), and metal sulfide (Su) phases. Red stain indicates calcium carbonate.
Host compositions of cap rock carbonate. Early (host) and late (vein) phases are lower than –Louann Salt (vertical dashed line). Carbonate carbon isotope composition of carbonate (and) and decreasing carbonate into bicarbonate via oxidation, thereby increasing pore salt dome cap rock were most likely mediated by microorganisms. 

reactions identified by symbol. In both panels, symbols are larger than the error for each measurement.

red. These findings support the hypothesis that the AOM reactions identified through integrated geochemical analyses of salt dome cap rock were most likely mediated by microorganisms.

Microbial AOM reactions occur in modern seafloor environments experiencing methane seepage and lead to the formation of extensive authigenic carbonate and sulfide phases. During AOM, a consortium of methanotrophic and sulfate-reducing microbes consume methane and sulfate and produce DIC and dissolved sulfide. This process leads to conversion of methane carbon into bicarbonate via oxidation, thereby increasing pore water DIC and alkalinity (promoting the formation of authigenic carbonate) and decreasing fluid $\delta^{13}C$ values. Reactions involving the oxidation of petroleum may also be important sources of alkalinity, although the higher $\delta^{13}C_{carb}$ data reported here do not conclusively indicate petroleum oxidation, as some carbon may also be sourced from the dissolution of $^{12}C$-enriched marine limestone. In contrast, $^{13}C$-depletions below ~28‰ are indicative of methane oxidation (Fig. 5a). In salt dome environments, both methane and petroleum oxidation may foster the growth of carbonate cap rock, although in this case (as opposed to marine cold seeps, for example) both calcium and sulfate are derived from the dissolution of sulfate minerals (anhydrite and gypsum) rather than seawater. Ultimately, without the increase in alkalinity generated through sulfate-dependent AOM and petroleum oxidation, the production of carbonate in cap rock would be less likely.

Some salt domes lack carbonate cap rock. Several Permian Zechstein salt diapirs in Germany and Poland exhibit only gypsum cap rock and lack associated hydrocarbons, carbonate, and elemental sulfur. In these settings, $\delta^{34}S$ values of dissolved sulfate in local aquifers indicate closed-system sulfate reduction, perhaps coupled with organic matter oxidation rather than with the oxidation of petroleum or methane. Despite the occurrence of sulfate reduction, authigenic carbonates are absent. This relationship may indicate that methane- and/or petroleum-coupled sulfate reduction is necessary for extensive formation of cap rock carbonate in salt-related diagenetic environments.

The above discussion (and Eq. 2) treats AOM as a sulfate-driven chemical reaction. However, anaerobic methane oxidation has been shown to occur through reaction with nitrate, iron oxides, and manganese oxides and is thermodynamically possible through other reaction pathways as well. Whereas most AOM is restricted to marine environments due to the abundance of sulfate in seawater, terrestrial and fresh water systems can exhibit both sulfate- and non-sulfate-dependent AOM. In addition, it has been shown that some deep subsurface microbial ecosystems can facilitate AOM and promote the precipitation of authigenic carbonate, a process that may have occurred throughout the Phanerozoic. Here, we demonstrate that salt dome basins represent unique, non-marine, subsurface environments wherein sulfate-dependent AOM occurs and leads to the production of authigenic carbonate and other minerals. This AOM is promoted through complex hydrological interactions that yield aqueous sulfate through calcium sulfate mineral dissolution. Similar sulfate-dependent AOM may occur in other environments where sulfate-rich minerals experience dissolution in proximity to significant methane accumulations, such as those produced in some evaporite settings.
Methane consumption in the salt dome environment. Methane has played an important role in global climate throughout Earth history and remains a significant contributor to greenhouse forcing today. It has been estimated that AOM reduces the emission of methane derived from marine sediments by ~80%67,68. Without this oxidation mechanism, it is projected that atmospheric CH4 levels would be 10–60% higher69–71. Mediating methane escape is especially important in the GMB region, where natural methane and petroleum seeps are abundant62,63. Salt migration creates extensive fault networks that serve as conduits whereby methane and petroleum may escape into the atmosphere and ocean62. AOM occurring in the GMB in association with salt domes may reduce methane emissions from these natural seeps64,65, perhaps serving as an important and unrecognized methane sink.

Ultimately, it is difficult to accurately determine the degree to which subsurface oxidation limits methane escape from the GMB subsurface. Now, we will attempt to broadly constrain the quantity of methane derived from marine sediments by ~80%57,58.

It is even more difficult to constrain the rate of methane consumption associated with cap rock reactions. This challenge is largely the result of our inability to accurately determine cap rock ages and formation rates. Theoretically, cap rock formation may have initiated any time after Louann Salt deposition (~165 Ma).

The global net rate of methane growth in the atmosphere has been approximated at ~6 Tg CH4/year67. In order for salt dome-associated methane oxidation to decrease this growth rate by ~1% requires formation of all onshore GMB cap rock carbonate over ~2.3 Myr (see Supplementary Figure 1, also includes sensitivity to methane carbon contributions). This estimate does not take into account the likelihood that some of the AOM-produced DIC may not have precipitated as carbonate or the possibility of carbonate dissolution. Indeed, the potentially very old (up to ~165 million years) age of cap rock provides ample opportunity to change the subsurface chemical environment to conditions that favor carbonate dissolution. Furthermore, many additional salt domes are present in offshore settings relative to onshore or nearshore continental shelves of the GMB (Fig. 1). The presence of carbonate cap rock in these offshore locales has been documented68, but the extent to which cap rock is developed is not well constrained. Ultimately, the AOM rate may not be (or have been) globally significant; however, the amount of carbonate produced as a result of this process has led to widespread mineral accumulation. These accumulations are so extensive that they have been commercially mined for economic use62.

The data of this study reveal that cap rocks in the GMB formed at relatively low temperatures as a product of substantial microbial methane oxidation. The results further suggest that such processes may mitigate against methane release to the atmosphere, although the global impact (as compared to modern methane growth rates) might be minimal. Cap rock carbonate represents a potentially unique biosignature recording extensive microbial activity within the deep subsurface.

Methods

Carbon isotope analyses. Samples were acquired from six salt domes across Texas, Louisiana, and offshore Gulf of Mexico (Fig. 1). Samples were prepared and analyzed for δ13C at California State University, Fullerton. Then, 5 mg of powdered sample was weighed out and placed into borosilicate glass Exetainer® vials. Atmosphere was evacuated by vacuum and 3 mL of 10% phosphoric acid was added to each vial to acidify carbonate and release CO2(g). The samples were allowed to react overnight. Produced CO2 was passed via ultra-high purity nitrogen carrier gas into a G2121-i Picarro Inc. Cavity Ringdown Spectrometer (CRDS) isotope analyzer through an Automated © Carbonate Prep Device. Carbonate isotope data are reported in permil (%o) using the standard δ-notations relative to the VPDB standard. Reproducibility is better than 0.3‰ (2 s.d.).

Sulfur. Extraction of cap rock CAS was performed following standard methods33,36. Samples were first cut into billets and then ground to a powder. Approximately 15 to 50 g of powdered samples were rinsed in 1 L of 10% NaCl solution in order to remove soluble sulfur species (gypsum and anhydrite). The mixture was allowed to sit for ~8 h, and the supernatant fluid was pipetted from the flask and discarded. The NaCl wash was then repeated. After two NaCl washes, 1 L of 5% bleach solution was added and allowed to sit for ~8 h in order to remove any organic-bond sulfur species. After 8 h, the supernatant fluid was pipetted from the flask and discarded. Two additional NaCl washes followed the bleach step. To liberate the carbonate-associated sulfate as aqueous sulfate, 300 mL of 6 M HCl was slowly added to each sample and swirled. The flask was then left overnight to allow complete sample dissolution. The fluid was then filtered successively through 40, 11, and 0.45 µm pore diameter filters. Fluids filtered were then heated to ~80°C and a 30% BaCl2 solution was added. These samples were allowed to sit for 72 h to allow aqueous sulfate to be precipitated as barite. The solution was then filtered through a preweighed 0.45 µm filter using a vacuum-assisted flask to isolate the fluid from the barite. These filters were then dried for approximately 4 h at 80°C.

Elemental sulfur and sulfide sulfur were collected by microdrilling with a Dremel rotary tool fitted with a 1-mm diameter carbide drill bit. Approximately 6–8 mg of elemental sulfur and ~10–20 mg of metal sulfide were subjected to chromium reduction according to traditional methods69. Samples were heated and reacted with a 1 M CrCl3/HCl and ethanol solution under a N2 atmosphere. This reaction converted elemental sulfur and metal sulfide to gaseous H2S and the product gas was passed into a trap containing 50 mL of a 3% AgNO3/10% NH4OH solution. Reaction of sulfide gas with the trap solution yielded solid silver sulfide, which was used as analyte for isotope composition determination. Sulfur isotope analyses of CAS-extraction-produced barite and chromium-reduction-produced silver sulfide were conducted on a ThermoScientific Delta V Plus IRMS at the University of California, Riverside. The IRMS is connected to a Costech Analytical Technologies, Inc. elemental combustion system via a ThermoScientific CONFLO III interface. Samples were combusted in tin capsules with 2.000 mg (±0.500) of vanadium pentoxide (V2O5), added as a catalyst to ensure complete combustion. Sulfur isotope values are reported in %o using δ-notation relative to the VCDT standard. Replicate δ34S data are generally better than ±0.1‰ (2 s.d.).

Clumped isotope analyses. Select samples were microdrilled with a 1 mm carbide drill bit and approximately 50 mg collected for clumped isotope analyses. Then, 6–10 mg of powder was acidified with supersaturated phosphoric acid and the generated CO2 was passed through a series of cryogenic traps using an on-line automated preparation device (similar to that described in Passey et al.74) with digestion and clean-up methods identical to Loyd et al.82. The abundance of mass 47 CO2 was determined using a Thermo MAT 253 gas source isotope ratio mass spectrometer and reported in the conventional Δ47 notation in ‰ after being cast into the AR⃛. Isotopic ratios are calculated using the Brand parameter set and standardization utilized both equilibrated gases and carbonate standards. These Δ47 values were converted to temperature using low60 and high61 temperature endmembers. Replicate Δ47 data were generally better than ±0.013‰ (1 s.e.).

Data availability

All data pertinent to this study are provided in the manuscript.

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Author contributions

S.J.L. conceived project, J.R.K. provided samples and geologic context, K.H.C. conducted lab work, and A.T. conducted clumped isotope analyses. K.H.C., J.R.K., T.W.L., A.T. and S.J.L. contributed to data analysis, interpretation, and manuscript drafting.

Additional information

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