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Redox conditions and authigenic mineralization related to cold seeps in central Guaymas Basin, Gulf of California

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Abstract

Authigenic carbonate crusts, surface muds and bivalve shell fragments have been recovered from inactive and active recently discovered cold seep sites in central Guaymas Basin. In this study, for first time, redox conditions and fluid sources involved in mineral precipitation were investigated by analyzing the mineralogy and textures of surface samples, along with skeletal contents, and C, O and S isotopes variations. The δ¹³C values of aragonitic bivalve shells and non-skeletal carbonate
from some surface muds (1‰ to -3.7‰ V-PDB) suggest that carbonate precipitated from ambient
dissolved inorganic carbon, whereas fibrous aragonite cement and non-skeletal carbonate from
other sites are highly depleted in $^{13}$C (down to -47.6‰ V-PDB), suggesting formation via anaerobic
oxidation of methane, characteristic of methane seepage environments. $\delta^{18}$O in most of the
carbonates varies from +1.4‰ to +3.2‰ V-PDB, indicating that they formed from slightly modified
seawater. Some non-skeletal carbonate grains from surface muds have lower $\delta^{18}$O values (-12.5‰
to -8.2‰ V-PDB) reflecting the influence of $^{18}$O-depleted pore water. Size distribution of pyrite
framboids (mean value: 3.1 $\mu$m) scattered within diatomaceous sinter suggests formation from
anoxic-sulfidic bottom waters. $\delta^{34}$S in pyrite is of -0.3‰ V-CDT compared to +46.6‰ V-CDT in
barite, thus implying a fluid sulfate–sulfide fractionation of 21.3‰ that argues in favor of microbial
sulfate reduction as the processes that mediated pyrite framboid formation, in a semi-closed
system. Barite formation occurred through the mixing of reducing and Ba-rich seep fluids with a $^{34}$S-
enriched sulfate pool that resulted from microbial sulfate reduction in a semi-closed system. The
chemical composition of aragonite cement, barite and pyrite suggest mineral precipitation from
modified seawater. Taken together, our data suggest that mineralization at the studied seep sites is
controlled by the mixing of seawater with minor amounts of hydrothermal fluids, and oxygen-
depleted conditions favoring anaerobic microbial processes.

**Keywords**: Oxygen and carbon isotopes; Sulfur isotopes; Cold seepage; Hydrothermal venting;
Anaerobic oxidation of methane; Microbial sulfate reduction.

1. Introduction

Cold seeps systems, characterized by seepage of fluids enriched in methane and other
hydrocarbons from deep reservoirs to the seafloor, are common features at geologically passive
and active margins (Robertson, 1996; Milkov, 2000; Canet et al., 2013; Tong et al., 2013; Himmler
et al., 2015; Mazzini et al., 2016). Biogeochemical conditions in those settings depend on the flux of
methane, availability of sulfate, temperature and redox conditions. These conditions promote the
development of chemosynthetic communities mainly dependent on methane and/or sulfur, driving
microbial reactions that alter sulfur and carbon pools and whose pathways involve the formation of authigenic minerals (MacDonald et al., 1990; Levin, 2005; Paull et al., 2007, Teske et al., 2014; McKay et al., 2016). The precipitation of carbonates (high-magnesium calcite –HMC–, aragonite or dolomite) close to the seafloor at cold seeps results from anaerobic oxidation of methane (AOM), a process conjointly carried out by methane-oxidizing archaea and sulfate reducing bacteria in which methane is oxidized using sulfate as an electron acceptor releasing bicarbonate and sulfide into pore-water. This reaction raises pore-water dissolved inorganic carbon from a $^{13}$C-depleted pool and increases alkalinity (Aloisi et al., 2000; Paull et al., 2007; Liu et al., 2016). Hydrogen sulfide-free conditions and pyrite formation in cold seep settings are augmented by microbial sulfate reduction (MSR) and the associated oxygen depletion. Pyrite formed via this process is commonly depleted in $^{34}$S and develops framboidal texture (Núñez-Useche et al., 2016; Liu et al., 2016). Barite precipitation can also take place as a consequence of the reaction between barium-rich, reducing seep fluids and sulfate-rich seawater (Paytan et al., 2002; Torres et al., 2003; Aloisi et al., 2004; Canet et al., 2013). Dissolved Ba in cold seep fluids commonly originates from dissolution under reducing conditions of biogenic barite accumulated in organic-rich sediments deposited under highly productive water columns (Aloisi et al., 2004). In addition, leaching during hydrothermal alteration of basalt can also result in Ba enrichment relative to ambient seawater (Chan et al., 1976; Kim and McMurtry, 1991).

Because authigenic mineral formation in cold seeps is closely linked to the redox and chemical conditions, the texture, mineralogy and chemistry of these deposits provide excellent archives of the environmental conditions and the chemistry of the fluids involved in their origin. Moreover, considering the link between hydrocarbon-rich seeps, gas hydrate formation and sub-seafloor hydrocarbon reservoirs (e.g. Macgregor, 1993), the understanding of the occurrence of authigenic mineralization is crucial for the exploration of sea-floor resources (Pacheco-Muñoz et al., 2005; Chen et al., 2015).

The Gulf of California (GC) is an active oblique rift system constituted by short extensional trough segments connected by major transform faults. It encompasses the transition between the spreading East Pacific Rise to the south and the right-lateral transform motion of the Cerro Prieto
and San Andreas fault systems to the north (Fig. 1). According to Wang et al. (2009), the nascent spreading center in the northern GC is associated with dynamic, buoyancy-driven upwelling and melting. Seafloor spreading is well established in at least three of the eight tectonically active, pull-apart basins that comprise the GC, including the Guaymas Basin (Lizarralde et al., 2007). The latter is a near-shore basin located in the central portion of the GC and constitutes a narrow rift segment.

Because active seafloor hydrothermal vent systems were discovered in the Guaymas Basin (e.g. Gieskes et al., 1982), it is the most studied basin of the GC. Hydrothermal activity related to rifting-related magmatism affects the approximately 2 km-thick cover of organic-rich, diatomaceous sediments. These have accumulated with high sedimentation rate and consist both of biogenic particles derived from the productive surface water and terrigenous input. The interaction of magmatism and sediments causes seepage of H₂S, CH₄ and other hydrocarbons at a range of different temperatures and precipitation of different authigenic mineral phases (Einsele et al., 1980; Lonsdale and Becker, 1985; Paull et al., 2007; Berndt et al., 2016). Although cold seep systems are ubiquitous in the Guaymas Basin, most of studies have focused on the hydrothermal deposits.

This contribution is the first study dealing with the nature of the mineralization in recently discovered cold seep sites in central Guaymas Basin. It presents new petrographic, mineralogical (including mineral chemistry) and geochemical (C and O stable isotopes) data of pelagic mud, bivalve shells and authigenic fragments from cold seep sites from the central trough of the Guaymas Basin recovered during cruise SO241 (Berndt et al., 2015). The objective of this study is to shed new light on the redox conditions and processes triggering methane-related authigenic carbonate and barite mineralization and to provide insights into the physicochemical characteristics of the fluid mixing that drives mineral precipitation, in view of the unique geological setting of the GC with the interplay between hydrothermal processes and cold-seeps. Moreover, this research contributes to improve the understanding of the environmental conditions during seepage activity.

2. Guaymas Basin tectonic and geological setting and study area

The Guaymas Basin is located in the central part of the GC and is a young, tectonically and hydrothermally active sedimentary basin (Einsele et al., 1980; Aragón-Arreola et al., 2005). Its
evolution is linked to the complex tectonic framework of the GC that onset between the Middle Miocene and the Lower Pliocene, when the subduction of the Farallon Plate under the North America Plate along Baja California was deactivated and the plate boundary evolved to a right-lateral fault system (Spencer and Normark, 1989; Michaud et al., 2007). This switch from a subduction to oblique rifting caused extension that resulted in the opening of the proto-GC and the subsequent formation of oceanic crust (Martín-Barajas and Delgado-Argote, 1995). Propagation northwards of the East Pacific Rise since 5 Ma caused the formation of small divergent basins interconnected by large dextral-oblique faults (Lonsdale, 1989).

Presently, the Guaymas Basin represents a heavily sedimented basin of the central GC, located south of a kink in the obliquity of extension where rifting is more parallel to the relative plate motion (Axen et al., 2006). It is a recent spreading center constituted by two northeast-trending grabens, called the northern and southern trough. They are axial rift valleys developed with an en echelon fault arrangement that overlaps at a non-transform offset. The basin is bounded by the Guaymas Transform Fault to the east, the Carmen and Tortuga transform faults to the west, and the Baja California and Sonora continental slopes to the north and south, respectively (Lonsdale and Becker, 1985; Aragón-Arreola et al., 2005). It has a basement consisting of recently accreted crust (Lonsdale, 1985, Albertin, 1989, Aragón-Arreola et al., 2005) and a thick sedimentary cover (at least 500 m) composed of terrigenous and biogenic sediments resulting from an unusually high sedimentation rate (1-2 m/k.y.; Calvert, 1966; Schrader, 1982). However, much lower sedimentation rates of 0.74 m/k.y (inside a hydrothermal vent field located 1 km southeast of the northern Guaymas rift axis) and of 0.79 m/k.y. (along the rift axis) have been recently calculated based on $^{210}$Pb (Berndt et al., 2016).

In general, biogenic grains, mainly represented by diatom frustules, are associated with high marine productivity and plankton blooms linked to seasonal coastal upwelling activity (Sancetta, 1995; Pride et al., 1999; Chang et al., 2015). Nutrient-rich surface waters are the result of the mixing between the oxygen-poor, nutrient-rich Subtropical Subsurface Water and the well-oxygenated North Pacific Intermediate Water, flowing into the GC during the summer and El Niño events (Bray et al., 1986). Aforementioned eutrophic conditions trigger the development of an
oxygen minimum zone at a depth range of 500–1000 m, with a minimum dissolved O$_2$ concentration of 0.13 mL/L, as well as the deposition of organic C-rich sediments (Goldhaber, 1974; García et al., 2006).

Magmatic intrusions associated with seafloor spreading drive hydrothermal circulation and subsequent alteration of the carbonaceous and diatomaceous unconsolidated sediments (Einsele et al., 1980; Lonsdale and Becker, 1985). Hydrothermal activity is manifested in the seafloor as numerous vents occurring along the rift (from trough axis up to 10 km away). Seismic data show areas interpreted as conduits for the ascending hydrothermal fluids and/or those released by gas hydrate destabilization, giving place to cold seep systems (Holbrook et al., 1996; Berndt et al., 2016). Water-column plumes rising from the seafloor are also documented in the basin by acoustic methods (Merewether et al., 1985). In such hydrothermal environments, organic matter buried in sediments undergoes thermocatalytic transformation and results in a methane- and light hydrocarbon-rich sedimentary environment (Welhan and Lupton, 1987). Cold seep systems are also characterized by chemosynthetic fauna assemblages and rich microbial diversity (Teske et al., 2002; McKay et al., 2016). Buoyant fluids that rise from the seafloor and mix with cold and oxygenated bottom water cause a steep physicochemical gradient in the surficial sediments (Gundersen et al., 1992). Diverse thermal and chemical conditions trigger a variety of mineralization processes and control microbial reactions such as MSR and AOM occurring in the bottom and within the upper sediments (Paull et al., 2007; Teske et al., 2014; McKay et al., 2016).

The portion of the central Guaymas Basin where samples were collected is characterized by the presence of three cold seep sites previously named Ring-seep, Northern-seep, and Central-seep (Berndt et al., 2015). They correspond to conspicuous blanked zones in the seismic record that reach up to the surface of the sediments and that have been interpreted as resulting from sediment mobilization above sill intrusions (Lizarralde et al., 2011). They also have typical chemosynthetic seep fauna such as vesicomyid bivalves, tubeworms and bacterial mats, as well as authigenic carbonates related to an AOM zone at shallow subsurface depths (as shallow as 8 cm below the sediment surface) evidenced by pore-water peaks of alkalinity and H$_2$S (Berndt et al.,
2015). Particularly for the Northern-seep, these authors reported pore-water enriched in silica and
depleted in $\text{PO}_4^{3-}$ and $\text{NH}_4^+$ relatively to seawater. For the studied area of the basin, Berndt et al.
(2015) determined a high geothermal temperature gradient varying between $0.127 \ ^\circ\text{C/m}$ and
$15.109 \ ^\circ\text{C/m}$.

3. Sampling and methods

3.1. Sample selection and location

The material studied is part of the stock of samples collected in Central Guaymas Basin during
the RV Sonne 241 cruise carried out in 2015 (Berndt et al., 2015). Samples were selected from the
Ring-seep, Northern-seep, and Central-seep locations and include authigenic mineralization
fragments, surface muds and bivalve shell fragments (Fig. 1; Table 1). They were taken using a
gravity corer, a multicorer device and a video guided hydraulic grab system HyBis from five
sampling stations. The shells are housed at Colección Nacional de Paleontología, Museo María del
Carmen Perrilliat, Instituto de Geología, UNAM.

3.2. Methods

Polished thin sections of three authigenic mineralization fragments were prepared and
described using a standard petrographic microscope. During this study, the diameter of 60 pyrite
framboids was measured by eyepiece micrometer under reflected light mode. Later, thin sections
were critical point-dried and coated with a thin layer of carbon in order to be analyzed with an
electron probe microanalyzer (EPMA) JEOL JXA-8900 XR, at the Laboratorio Universitario de
Petrología of the Instituto de Geofísica, Universidad Nacional Autónoma de México (UNAM). This
equipment allowed us to obtain back-scattered electrons (BSE) images, together with X-ray energy
dispersive spectroscopy (EDS) qualitative analyses and wavelength dispersive spectroscopy (WDS)
for a quantitative analyses of the mineral grains. The following conditions were used during this
analysis: 20 KeV, beam diameter of 1 $\mu$m and a counting time of 30 s. Additionally, rock chips were
studied with- a Hitachi TM-1000 table-top scanning electron microscope (SEM) which included EDS
analysis, at the Laboratorio de Petrografía y Microtermometría of the Instituto de Geofísica, UNAM.
Standards used for calibration of the equipment included pure metals and synthetic and natural minerals (carbonates and sulfates) from the set of standard SPI # 02753-AB serial No. 02-148.

For geochemical and mineralogical analysis, all samples were washed with distilled water and dried at 25 °C for 24 h. The bulk mineralogy of twelve samples was determined via X-ray diffraction (XRD) using an EMPYREAN diffractometer equipped with a fine focus Cu tube, nickel filter, and PIXCell 3D detector operating at 40 mA and 45 kV at the LANGEM (Laboratorio Nacional de Geoquímica y Mineralogía), Instituto de Geología, UNAM. For this, samples were ground with an agate pestle and mortar to <75 µm and mounted in back-side aluminum holders. The analyses were carried out on randomly oriented samples by the step scan method using the measurement range (2θ) of 5 to 70° with an integration time of 40 s and step size of 0.003°. Phase identification was made with PDF-2 and ICSD databases. Rietveld refinement of the data was done with the Highscore software using a pseudo-Voigt profile function. Some specimen-dependent parameters were refined, including the zero error, displacement error, polynomial fitting for the background, peak positions, peak areas, peak shape, scale factors, atomic coordinates and preferred orientation. Weighted R profile (Rwp) and Goodness of fit (Gof) discrepancy indices were calculated. For samples with an important proportion of amorphous components, semi-quantitative results were based on the intensity of the corundum peak as a standard for a relative intensity ratio (RIR; Chung, 1974; Hillier, 2000). Mg in calcite was determined using XRD measurement and Rietveld refinement method (Rietveld, 1969) by calculation of lattice parameters (Titschack et al., 2011).

Stable-isotope analyses (δ¹³C, δ¹⁸O) were performed on seven powdered samples of both calcareous sediment and authigenic material and five carbonate samples from bivalve shells extracted by a dental drill. These analyses were performed at the LANGEM, Instituto de Geología, UNAM. Approximately 0.9 mg of each sample was reacted under vacuum with orthophosphoric acid at 25 °C for 54 h following the guidelines of McCre (1950). The released CO₂ was analyzed with a mass spectrometer Thermo Finnigan MAT 253 coupled with Gas Bench II. The carbon isotope results are expressed in ‰ relative to the V-PDB standard and have a reproducibility better than 0.2‰ (1 SD).
Sulfur isotopes ($\delta^{34}$S) were measured in barite and pyrite at the Centres Científics i Tecnològics, Universitat de Barcelona. For this, barite was concentrated and pyrite was obtained by scratching the surface of polished samples and avoiding contamination. The measurement was performed with a Delta-C Finnigan MAT continuous flow isotope-ratio mass spectrometer coupled with a TC-EA Carlo Erba 1108 elemental analyzer, according to the method of Giesemann et al. (1994). Results are expressed in ‰ relative to the V-CDT standard. Analytical precision is within ± 0.2‰ (1 SD).

4. Results

4.1. Macroscopic characterization of samples

Samples of the authigenic deposits analyzed in this study are illustrated in Figure 2. SO241/56 is a large block of authigenic carbonate crust, white-colored, with a very high degree of porosity resulted from both worm bioturbation activity and dissolution driven by fluids release (HyBis sample Nº 4; Figs. 2A–B; Table 1). It contains plant root remains (Fig. 2B) and bivalve shell fragments (Fig. 2B) inside the burrows.

Samples SO241/17 and SO241/17a (HyBis sample Nº 2) correspond to highly porous, friable fragments, white to light gray-colored, with siliceous matrix (Figs. 2C–D; Table 1). They are partially covered with bacterial mats. Porosity is interpreted as fluid-expulsion structures.

As for surface mud samples (Table 1), they consist predominantly of silt-size particles and a minor proportion of sand-size grains, including non-skeletal carbonate grains; following the classification of Folk (1980), they are silts and sandy silts. Otherwise, recovered bivalve shells correspond to the species Archivesa gigas (Dall, 1896) (Bivalvia: Vesicomyidae), except for one assigned to the species Lucinoma annulata (Reeve, 1850) (Bivalvia: Lucinidae) (Fig. 3; Table 1).

4.2. Petrography, mineralogy and mineral chemistry

Two petrography types of authigenic deposits were recognized in the surface sediments recovered from the Guaymas Basin: (a) fine-grained carbonate mud, and (b) diatomaceous sinter.
Fine-grained carbonate mud (sample SO 241/56; Fig. 2A–B) contains sparse planktonic foraminifera and diatoms (Figs. 4A–C and 5A–D). According to XRD analysis, this carbonate mud contains aragonite (95.5%), low magnesium calcite (LMC) (1 wt.%) and quartz (1 wt.%). It also contains marine precipitated halite (4 wt.%) (Tables 5A–B). Aragonite occurs as (1) acicular crystals, randomly oriented forming a microcrystalline matrix (Figs. 4A-C and 5A), and (2) acicular crystals, up to 600 µm in length and 50 µm in width, constituting fibrous and botryoidal cement that fills matrix porosity, cracks and skeletal grains (Figs 4A-C and 5A-C). The EPMA analyses of the latter crystals reveal magnesium contents up to 0.12% MgCO$_3$ molar (Fig. 6A; Table 2). Therefore, chemically, these aragonite crystals are almost pure calcium carbonate. Iron and manganese concentrations reach 0.02% FeCO$_3$ molar and 0.05% MnCO$_3$ molar, respectively. Their elemental concentration is as follows: ~1400–3400 ppm for Sr, ~1900–3500 ppm for Na, up to ~200 ppm for Ba and ~100-400 ppm for K.

Tiny pyrite framboids are common and disseminated within the microcrystalline matrix. They have diameters ranging between 1.5 and 8.1 µm (mean 3.5 µm; standard deviation 2.4 µm) (Fig. 7; Table 3). Chemically, pyrite is rich in several trace elements, mainly in molybdenum (~4100–4500 ppm), vanadium (~1300–2700 ppm), cobalt (~900-1100 ppm) and nickel (~100–200 ppm) (Table 4).

Diatomaceous sinter (samples SO 241/17 and SO 241/17a; Fig. 2C–D) is highly porous, showing a fine-grained matrix composed of opal nanospheres (0.1–4 µm in diameter) (Fig. 5D). The full width at half maximum (FWHM), a measure of the degree of lattice ordering of silica phase (Herianita et al., 2000), indicates that it is opal-A (FWHM >6.0°, 2θ). XRD analysis reveals the presence of opal (~84–100 wt.%), zeolite (11 wt.%) and halite (5 wt.%) in this authigenic deposit (Table 5A). Besides abundant diatoms and silicoflagellates, allochems include common radiolarians, planktonic foraminifera and pellets, and sparse ostracods (Figs. 4D–I and 5E–F).

Common and well-rounded clasts attain up to 600 µm in diameter (mean 200-300 µm) and show a siliceous matrix embedding similar skeletal grains (Fig. 4E). Minor barite occurs as platy aggregates, with tabular barite crystals commonly between 20 and 40 µm, rarely up to 100 µm in length, within the opal matrix and filling the interior of diatoms and radiolarians (Figs. 5E–G). According to EPMA analyses, barite crystals have a large variation in their chemical composition,
with barium content ranging between 84.44 and 91.55 % BaSO$_4$ molar and strontium between 5.02 and 11.96 % SrSO$_4$ molar (Fig. 6B; Table 6). Barium and strontium show a good negative correlation ($R^2 = 0.940$) reflecting the isomorphous substitution between these elements in the barite–celestite solid solution (cf. Hanor, 1968). Calcium and sodium are in rather low concentrations, up to ~5100 and ~1200 ppm, respectively. Lead is always below the detection limit (Table 6). Framboidal pyrite with diameter ranging between 1.9 and 7.5 µm (mean 3.1 µm; standard deviation 2.8 µm) are common in the matrix (Fig. 7; Table 3). Pyrite microcrystals have elevated contents of molybenum (3900–5100 ppm), vanadium (1200–3300 ppm), cobalt (300-1500 ppm), and some nickel (100–200 ppm) (Table 4).

Regarding silt and sandy silt sediments (samples SO 241/2, 241/3 and 241/33), they are composed of plagioclase (3–44 wt.%), quartz (2–8 wt.%), phyllosilicates (0–30 wt.%), LMC (1–9 wt.%), HMC (0–89 wt.%), gypsum (0–6 wt.%), barite (0–6 wt.%), pyrite (0–1wt.%), halite (0–5 wt.%), zeolite (0–28 wt.%), and opal (~0–1 wt.%). One sample from the North-seep site contains magnesium calcite (89.2 wt.%) and another from the Ring-seep is rich in barite (6.4 wt.%). Bivalve shells are composed mainly of aragonite (98–100%) and minor quantities of LMC (0–2%).

4.3. Carbon, oxygen and sulfur isotopes

The stable isotopic composition of the studied carbonates (including fibrous cement, non-skeletal carbonates from surface muds and shell fragments) has a wide variation, with $\delta^{13}C$ values ranging from -47.6‰ to +1.0‰, and $\delta^{18}O$ from -12.5‰ to +2.7‰ (‰ relative to the V-PDB standard) (Fig. 8; Table 7). In the $\delta^{13}C$ vs. $\delta^{18}O$ plot two clusters of values can be identified (Fig. 8A). The first encompasses fibrous aragonite cement showing $^{13}C$-depleted values (down to -47.6‰). Conversely, this cement have high $\delta^{18}O$ values (up to +2.6‰). The second one is constituted by the bivalve shells yielding $\delta^{13}C$ values from -3.7‰ to +1.0‰ and $\delta^{18}O$ values from +1.4‰ to +2.7‰.

Non-skeletal carbonates from surface muds have isotopic values distributed in a wide range. Three samples from the Ring-seep area yields a $\delta^{13}C$ range overlapping with that of the most $^{13}C$-depleted bivalve shells, between -3.7 and -1.2‰. They also have the lowest $\delta^{18}O$ values, ranging

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from -12.5‰ to -8.2‰. Contrastingly, two other samples (from the Ring-seep and North-seep areas) have depleted $^{13}\text{C}$ values (down to -40.6‰) and $\delta^{18}\text{O}$ values in the range of the fibrous aragonite cement and bivalve shells (+2.0‰ and +3.20‰). In general, there is not a covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Fig. 8A). The analyzed authigenic barite crystals have a high $\delta^{34}\text{S}$ value of +46.6‰, whereas pyrite frambooids show a slightly negative $\delta^{34}\text{S}$ value of -0.3‰ (‰ relative to the V-CDT standard) (Fig. 8C).

5. Discussion

5.1. Implications of mineralogy, texture and skeletal components

Carbonate components of the authigenic deposits consist of fine-grained mud particles and fibrous-botryoidal cement, which are mostly aragonitic in composition but also contain LMC (Figs. 4A–C and 5 A–C; Tables 5A–B). Otherwise, the grains of the muds correspond to LMC, HMC and aragonite (Tables 5A–B). These minerals are also important constituents of the methane-seep carbonates in the Consag Basin (northernmost end of the Gulf of California; Canet et al., 2013). In these environments, authigenic carbonate precipitation occurs within sediment form pore-water that is highly supersaturated with respect to the carbonate phase. This process is favored by the increase in carbonate alkalinity that results from microbially-mediated AOM (Aloisi et al., 2000; Paull et al., 2007; Liu et al., 2016). Furthermore, the abundance of aragonite and HMC implies that precipitation took place mainly under high $\text{SO}_4^{2-}$ activity and Mg/Ca ratio (Burton, 1993). According to Liu et al. (2016), aragonite minerals start to precipitate when the methane flux is 20 times higher than the base case. Although data concerning methane flux in the studied sites are not available, the presence of aragonite is consistent with an intense methane flux. Given the presence of plant root remains, burrows and bivalve shell (Fig. 2A–B), these deposits must have formed at or just below the sediment–water interface.

The presence of framboidal pyrite (Fig. 5G–H) within aragonite mud and diatomaceous sinter is consistent with mineral precipitation via MSR, a process commonly coupled to AOM (Paull et al., 2007; Liu et al., 2016). Anoxic-sulfidic conditions at least during pyrite formation are suggested by...
the tiny pyrite framboids in the studied authigenic deposits (Fig. 7; Table 3). The small diameter
(down to 1.5 µm) and narrow size distribution of pyrite framboids reflect formation within the lower
water column, close to the sediment-water interface (e.g. Wilkin et al., 1996, 1997; Wignall and
Newton, 1998; Bond and Wignall, 2010; Ding et al., 2014; Núñez-Useche et al., 2016). Barite
formed authigenically within the diatomaceous sinter (Figs. 4H and 5E–G) and is present in surface
mud from the North-seep area (Tables 5A–B). Barite forms in cold seeps through the reaction
between reducing, barium-rich seep fluids and sulfate-rich seawater (Paytan et al., 2002; Torres et
al., 2003; Aloisi et al., 2004; Canet et al., 2013). The predominance of calcium carbonate over
barite in the studied samples suggests, according to Aloisi et al. (2004), a high methane/barium
ratio with sulfate availability limited by AOM, which, moreover, is in agreement with the abundance
of pyrite.

The species of bivalves found at the different sampling locations are widely distributed inside
the Gulf of California (Fig. 3). The members of the family Lucinidae are considered deeply infaunal,
found in a wide variety of sediment grain sizes, but rich in organic matter (Coan et al., 2000). For
instance, a living specimen has been recovered from silty clay sediments deposited at a depth
range of 1370–1382 m from a site at the mouth of the gulf at water temperature of 4 °C and oxygen
concentration of 0.5 ml/l (Parker, 1963). The family Vesicomyidae includes epifaunal nestlers
species, frequently associated with hard substrate or compact clay in deep water and low-oxygen
environments (Coan et al. 2000). *Archivesica* and the remainder taxa of the subfamily Pliocardiiinae
typically inhabit extreme, such as hydrothermal vents, cold seeps and other sulphide-rich reducing
environments; relying on chemoautotrophic endosymbiotic bacteria for nutrition (Coan et al. 2000;
Krylova and Sahling, 2010).

Diatoms and in minor proportion silicoflagellates are the dominant skeletal grains in the studied
authigenic deposits (Figs. 4D–G and 5C, E–F and H). Their high abundance has also been reported
from different sites in the basin, where in biogenic sediments are prevalent (Thunell et al., 1996;
Ziveri and Thunell, 2000; Barron et al., 2005; Chang et al., 2015). In particular, the flux of diatoms is
commonly linked to enhanced seasonal primary productivity and upwelling. Currently, such
biosiliceous productivity occurs during winter owing to the turnover of surface water induced by
strong northwesterly winds (Sancetta, 1995; Pride et al., 1999; Chang et al., 2015). Diatoms suppose a significant contribution to the opal enrichment in the studied sediments, and the opal-A matrix found in the studied samples (Figs. 4D–G and 5D) could be associated with reprecipitation of mobilized Si from dissolved diatoms in deeper levels. Furthermore, it is possible an abiogenic source associated with the discharge of fluids; for instance the silica-rich upwelling fluids. The report of an abiogenic silica phase not derived from a sedimentary source in seafloor hydrothermal deposits from other sites of the Guaymas Basin (Von Damm et al., 1985; Peter and Scott, 1988) is in agreement with this observation. However, such mineralization took place at higher temperatures.

The halite found in some samples (Table 5a) is probably the result of sample drying rather than an authigenic phase. On the other hand, the presence of zeolites (clinooptilolite-heulandite) mostly in clay-bearing samples (Table 5a) suggests they are secondary minerals, likely formed in situ from the alteration of aluminosilicate precursor materials. However, in sample SO 241/17, which contains no clay but has a high percentage of opal related with diatoms and radiolarians tests, zeolites may have directly precipitated from silica-rich interstitial water. According to some studies (e.g. Hay and Sheppard, 2001; Li and Schoonmaker, 2003; Volpi et al., 2003), the excess of biogenic silica can be a significant factor in forming zeolites (mainly clinoptilolite) on the seafloor. However, we lack petrographic evidence to verify this hypothesis.

5.2. Geochemical approach to mineralization processes

5.2.1. Isotope geochemistry

Fibrous aragonite cement, as well as non-skeletal carbonate from surface muds from North-seep site and some from the Ring-seep area are extremely negative, yielding values as low as -47.6‰ (Fig. 8; Table 7). These δ^{13}C data are consistent with those of authigenic carbonates precipitated from pore-water dissolved inorganic carbon resulting from AOM (e.g. Paull et al., 2007; Aloisi et al., 2010; Canet et al., 2013). Moreover, they are in line with the carbon isotope composition of methane (down to -51‰) found in other sites of the Guaymas Basin (Teske et al.,
Indeed, $^{13}$C depletion is a common geochemical feature of authigenic carbonates from cold seep environments (Greinert et al., 2002; Han et al., 2004; Campbell, 2006; Canet et al., 2006, 2013; Himmler et al., 2015). For instance, in the northeastern transform margin of the Guaymas Basin, an area where a high geothermal gradient due to magmatic-driven hydrothermal systems, Paull et al. (2007) reported large methane-related carbonate build-ups (“chemoherm structures”) with distinct negative $\delta^{13}$C values (<-25‰). At gas-seep locations of the Consag Basin, Canet et al. (2013) reported cryptocrystalline cement of HMC and dolomite with $\delta^{13}$C between -45.4 and -22.3‰.

On the other hand, $\delta^{13}$C from bivalve shells (*Archivesica gigas* and *Lucinoma annulata*) and non-skeletal carbonate from surface muds vary in a narrow range between -3.7 and +1.0‰ (Fig. 8A; Table 7). These values are close to the average composition reported from marine mollusks (McConnaughey and Gillikin, 2008), which suggest the preferential shell incorporation of ambient dissolved inorganic carbon rather than of AOM-derived carbon. In contrast, in deep-sea hydrothermal vents, previous studies report shells of the bivalve *Archivesica gigas* with a mean $\delta^{13}$C value of -35.7‰ (e.g. Soto, 2009) that point out the contribution of the AOM-derived carbon to the CO$_2$ pool of the Guaymas Basin.

In the Ring-seep area, sulfur isotopes indicate that MSR mediated H$_2$S formation, likely coupled to AOM. Authigenic barite crystals yield extremely high $\delta^{34}$S values (+46.6‰), similar but even greater to those reported from cold seeps in the Sea of Okhotsk–Pacific Arctic ocean (up to +38.6‰; Greinert et al., 2002) and in the northeastern Wagner Basin–northern Gulf of California (up to +44.8‰; Canet et al., 2013). The obtained value is well above the sulfur isotopic composition of present-day seawater sulfate (+21‰; Rees et al., 1978; Paytan et al., 2002) (Fig. 8C) and the aqueous sulfate from pore- and seawater from other cold seep sites in the Consag Basin (between +14.8 and +23.6‰; Canet et al., 2013). This fact suggests that barite formation occurred through the mixing of seep fluids (reducing and barium-rich), with a $^{34}$S-enriched sulfate pool residual after MSR. Indeed, according to Torres et al. (2003), a component of isotopically heavy sulfate derived from microbial processes in anoxic sediments resulted in the enrichment is $^{34}$S of modern cold seep barite. Assuming pyrite precipitation ($\delta^{34}$S = -0.3‰) from seawater, calculation of the fractionation
between seawater sulfate and sulfide ($\Delta^{34}S$) gives a value of 21.3‰ that indeed match those found by MSR under controlled laboratory conditions (between 4 and 66‰; Ohmoto et al., 1990; Canfield, 2001; Sim et al, 2011). During this anaerobic process, bacteria degrade organic carbon and reduce marine sulfate to sulfide, preferentially incorporating $^{32}S$ in the latter and therefore resulting in low $\delta^{32}S$ values for pyrite. Remarkably, the measured $\delta^{34}S$ value in pyrite is not as negative as the found in other sulfides link to MSR (e.g. -13.3‰, Alfonso et al., 2005; -51.2‰, Núñez-Useche et al., 2016). This can be explained by formation of the analyzed pyrite frambooids in a semi-closed system with depletion of the sulfate pool, bacteria uptake of $^{34}SO_4$ and incorporation of $^{34}S$ into pyrite.

Oxygen stable isotope data from both skeletal and non-skeletal carbonate also shows a relatively wide range, between -12.5‰ and +2.7‰ (Fig. 8A; Table 7). The highest values (+1.4 to +2.7‰) correspond to bivalve shells, fibrous aragonite cement and some non-skeletal carbonate from surface muds from the Ring-seep and North-seep areas. For bivalve shells, values close to 0‰ are expected for common marine skeletal carbonates. In case of the fibrous aragonite cement crystals and the aforementioned non-skeletal carbonate from surface mud (remarkably depleted in $^{13}C$), their $\delta^{18}O$ values also seem to reflect the oxygen isotope composition of ambient water. They are similar to those obtained from methane-derived authigenic carbonates of cold seep locations in the northeastern transform margin of the Guaymas Basin ($\delta^{18}O$ between 0.0 and 6.5‰; Paull et al., 2007), the Consag Basin ($\delta^{18}O$ between +1.3 and +1.4‰; Canet et al., 2013) and in the northern continental slope of the South China Sea ($\delta^{18}O$ between +1.4 to and +5.1‰; Tong et al., 2013). Noteworthy, non-skeletal carbonates from surface muds of the Ring-seep have carbon isotope values (from -3.7 to -1.2) falling within the range of $\delta^{13}C$ for bivalve shells but are depleted in $^{18}O$ ($\delta^{18}O$ from -12.5 to -8.2‰).

The oxygen isotopic composition of marine carbonates is controlled by the $\delta^{18}O$ of water from which they precipitated and the temperature during their formation. In Guaymas Basin, the bottom water temperature averages 2.9–3.0 °C (Paull et al., 2007; McKay et al., 2016). Therefore, if the equilibrium calibrations established by Böhm et al. (2000) are applied to the bivalve shell isotope analyses considering this temperature, a range of $\delta^{18}O$ for water of -2.8 to -1.6‰ (relative to SMOW) is obtained (Fig. 8B). A similar range between -2.0 and -0.9‰ is also determined using the
equation of Kim et al. (2007) calibrated for inorganic aragonite (Fig. 8B). In case of the fibrous aragonite cement crystal, the oxygen isotopic composition of water was roughly estimated by applying the equation of Kim et al. (2007) for inorganic aragonite. Considering that fine-grained aragonite mud samples were taken 0-30 cm below the bottom surface, a temperature range of 2.9 to 5.0 °C was used for this calculation. Accordingly, the δ^{18}O_{SMOW} obtained values vary between -2.1 and -0.5‰ (Fig. 8B).

Aforementioned δ^{18}O values do not match with pore-water compositions reported from the northeastern transform margin of the Guaymas Basin, which vary between -0.5 and +1.8‰ (Paull et al., 2007). In fact, these values are also slightly lower than modern seawater values and imply that bottom and upper sediment pore-water in the studied cold seep sites is modified seawater. Contrastingly, isotopically light oxygen values from non-skeletal carbonate from surface mud from Ring-seep are more consistent with higher temperature and/or ^18O-depleted fluids, likely meteoric water or pore solutions after gas hydrate crystallization (e.g. Veizer et al., 1999; Aloisi et al., 2000; Tong et al., 2013). However, additional evidence is needed to certainly determine the origin of these isotopically light oxygen values.

5.2.2. Mineral chemistry

Aragonite is by far the most common carbonate marine cement and its trace element geochemistry can be used to infer fluid composition and mineralization conditions (e.g. James and Ginsburg, 1979; Anadón et al., 2013; Canet et al., 2013). In the case of the studied fibrous aragonite cement crystal, their trace element content (Table 2) is in the lower range of the composition of modern and Pleistocene marine cement of botryoidal aragonite from various localities (cf. James and Ginsburg, 1979; Aissaoui, 1985; Anadón et al., 2013). In comparison with fibrous aragonite cement from the Consag Basin (Sr: 6190–11788 ppm, Magnesium: 96–1182 ppm; Sodium: 964–5327 ppm, Manganese: 46–418 ppm; Canet et al., 2013), the studied cements are depleted in Sr and Mn, slightly depleted in magnesium and similar in sodium (Table 2). With respect to aragonite experimentally precipitated from seawater (molar ratios: Sr/Ca=0.0101, Mg/Ca=0.0050–0.0064, Ba/Ca=0.000013–0.000022; Holcomb et al., 2009), the mean content of
these elements in the fibrous aragonite cement crystals is lower for Sr/Ca and Mg/Ca and higher for Ba/Ca (Table 2). Moreover, applying to the presented data the partition coefficients (Kd) for inorganic aragonite precipitated at 5°C (Kd\textsubscript{Sr}: 0.417, Kd\textsubscript{Mg}: 0.0149, Kd\textsubscript{Ba}: 1.81; Gaetani and Cohen, 2006), the obtained metal/Ca values for water in equilibrium with aragonite range from 0.0039 to 0.0095 (mean 0.0057) for Sr/Ca\textsubscript{w}, from 0 to 0.0798 (mean 0.0471) for Mg/Ca\textsubscript{w} and from 0 to 0.000072 (mean 0.000015) for Ba/Ca\textsubscript{w}. Although this also includes lower values, in general, the calculated Sr/Ca\textsubscript{w} values encompass the values of modern seawater (0.00850–0.0090; Bruland, 1983 in Chester, 2000; de Villiers, 1999). Otherwise, the obtained Mg/Ca\textsubscript{w} ratios are below those of modern seawater (5.15–5.18; Milliman, 1974; Bruland, 1983 in Chester, 2000), whereas some calculated Ba/Ca\textsubscript{w} ratios are higher than those (0.000003–0.00001; Broecker and Peng, 1982 in Rosenthal and Katz, 1989; Bruland, 1983 in Chester, 2000). The low Mg/Ca\textsubscript{w} and some of the high Ba/Ca\textsubscript{w} ratios agree with the low measured Mg abundance and high concentration of barium of submarine hydrothermal solutions from the Southern Trough of the Guaymas Basin (Von Damm et al., 1985). However, it should be noted that even higher Ba/Ca ratios have been reported for cold seep fluids, without impact of hydrothermal solutions. For instance, Torres et al. (2001) calculated a Ba/Ca of 0.005 for pore fluids at cold seep sites in the Cascadia margin. On the summit of Hydrate Ridge (site 1250), Ba/Ca ratios of pore waters varying between 0.0110 and 0.0497 have been related to high barium concentrations in the near-surface fluids due to the upward flow of sulfate-depleted and barium-rich fluids (Tréhu et al., 2003). Therefore, the data suggest that aragonite cement crystals from Guaymas Basin precipitated mainly from modified seawater, perhaps with some degree of mixing with altered hydrothermally solutions.

Regarding framboidal pyrite from fine-grained aragonite mud and diatomaceous sinter, it is relatively enriched in trace elements relative to modern seawater (see Large et al., 2014). The enrichment of molybdenum, nickel and cobalt found in pyrite framboids (Table 4) could be a consequence of the anoxic-sulfidic conditions. Under such a redox setting, these redox-sensitive trace elements (RSTE) are scavenged from seawater and pore-water and taken up directly from solution by Fe-sulfide (Huerta-Diaz and Morse, 1992; Algeo and Maynard, 2004; Tribovillard et al., 2006; Gregory et al., 2015). Large et al. (2014) proposed that the pattern of enrichment of RSTE in
authigenic pyrite is a function of the availability of these elements in seawater. For instance, sedimentary pyrite formed under euxinic conditions in the Cariaco Basin has elevated contents of Mo and Ni (although lower than those found in Central Guaymas Basin), reflecting the abundance of these elements in modern oceans (Lyons et al., 2003, Piper and Perkins, 2004). Accordingly, the very high concentration of RSTE measured in the analyzed pyrite framboïds likely reflects their abundance in pore fluids and scavenging by pyrite.

In the case of barite crystals, when their molar ratios (Table 6) are compared with those of marine barite from modern sediments from a wide range of depositional environments (molar ratios: Sr/Ba=0.00001–0.04461, mean 0.0316; Sr/Ca=0.03-41.46, mean 13.7; Ca/Ba=0.00039-1.281, mean 0.0024; Averyt and Paytan, 2003), they have elevated Sr/Ba, and Sr/Ca and Ca/Ba ratios within the lower range of variations. They also have Sr/Ba ratios well above those the found in modern barite from core top sediments (0.036 in average; Paytan et al., 2007). However, on average, barite crystal from Guaymas have Sr/Ba ratios in the range of those reported for other cold seep barite (Monterey, Naehr et al., 2000; Okhotsk, Greinert et al., 2011; San Clemente basin, Torres et al., 2002). A significant concentration of strontium in barite crystals could mean active barium substitution by this element (e.g. Torres et al., 2002), higher temperature conditions during formation and/or higher Sr/Ba ratios in seep fluids (Fu et al., 1994). Preferential dissolution of previously formed Sr-rich barite under conditions of sulfate depletion link to active AOM could explain elevated Sr/Ba in the pore fluid of the studied cold seeps from Guaymas. However, it is not possible to preclude the involvement of hydrothermal fluids in the mineralization process.

6. Conclusions

Cold seep-related authigenic deposits from Central Guaymas Basin consist of fine-grained aragonite and diatomaceous sinter. Surface muds contain non-skeletal carbonates that correspond to LMC and HMC. In some samples, magnesium calcite and barite are important constituents. Bivalve shells correspond to the species Archivesica gigas (Dall, 1896) (Bivalvia: Vesiomyidae)
and *Lucinoma annulata* (Reeve, 1850) (Bivalvia: Lucinidae). Their presence in the sediments suggests oxygen-depleted, sulfide-rich reducing, and organic matter-rich environments.

The δ13C values of aragonite bivalve shells and non-skeletal carbonate from some surface muds (from 1‰ to -3.7‰) are close to the average composition reported for marine mollusks and suggest that their precipitation took place from ambient dissolved inorganic carbon. Contrarily, fibrous aragonite cement crystals, non-skeletal carbonate from surface muds from North-seep site, and some from the Ring-seep area are highly depleted in 13C, yielding values as low as -47.6‰. Hence, those carbonates formed via AOM, evidencing that methane-rich fluids seep out of the seafloor. The predominance of calcium carbonate over barite, as well as the occurrence of pyrite, suggest a high methane/barium ratio with limited sulfate availability.

According to oxygen stable isotope data, carbonate of bivalve shells, fibrous aragonite cement and non-skeletal carbonate from surface muds (δ18O from +1.4‰ to 3.2) precipitated from slightly modified seawater. This fact agrees with the trace element content of the aragonite cement evidencing seawater with some degree of modification. On the other hand, non-skeletal carbonate of surface mud from Ring-seep have low δ18O values (from -12.5‰ to -8.2‰), suggesting their formation from 18O-depleted fluids like meteoric water or pore solutions after gas hydrate formation.

The narrow size distribution of pyrite framboids (size ranging between 1.9 and 7.5 µm, mean 3.1 µm) contained in the authigenic deposits indicates that their formation mainly occurred from anoxic-sulfidic bottom waters, likely caused by the increase in dissolved sulfate during AOM. In the Ring-seep area, a calculated seawater sulfate–sulfide fractionation of 21.3‰ argues in favor of MSR as the processes that mediated pyrite formation. It took place in a semi-closed system with depletion of the sulfate pool. The very high concentration of RSTE in pyrite likely reflects their abundance in pore fluids and scavenging by sulfide. On the other hand, barite formation took place within the sediments by mixing of reducing and barium-rich seep fluids with 34S-enriched seawater that resulted from MSR in a semi-closed system.

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Figure captions

Figure 1. Location of sampling sites in the Central Guaymas Basin. Numbers correspond to sites in Table 1.

Figure 2. Authigenic material collected from Central Guaymas Basin: Sampling sites: Images A–B, site SO 241/56 (central-seep); images C–D, site SO 241/17 (ring-seep). The location of the sampling sites is shown in Fig. 1. Abbreviations: Rt, plant root remains; Fss, fluid-escape structures. (A) Fine-grained aragonite mud fragments. Note the high porosity (sample SO 241/56). (B) Close-up of the image in A showing plant root remains inside the burrows. (C)–(D) Diatomaceous sinter with fluid-escape structures (samples SO 241/17 and SO 241/17a, respectively, both from site SO 241/17).

Figure 3. Bivalve shells collected from the Central Guaymas Basin: Sampling sites: Image A, site SO 241/2; images B–D, site SO 241/3; image E, site SO 241/33. The location of the sampling sites is shown in Fig. 1. (A), (C)–(E) Valves of *Archivesica gigas* (Dall, 1896) (Bivalvia: Vesicomyidae) (samples SO 241/2-1s, SO 241/3-1s, SO 241/3-2s, SO 241/33s, respectively). (B) Valve of *Lucinoma annulata* (Reeve, 1850) (Bivalvia: Lucinidae) (sample SO 241/3-1s).

Figure 4. Thin section photomicrographs of authigenic deposits from Central Guaymas Basin. Sampling sites: Image A–C, site SO 241/56, Fine-grained aragonite mud; images D–I, site SO 241/17, Diatomaceous sinter. The location of the sampling sites is shown in Fig. 1. Abbreviations: Arg-m, aragonite mud; Arg-c, Aragonite cement; Brt, Barite; Pf, planktonic foraminifera; Mat, Matrix; Dia, diatoms; Rad, radiolarians; Ost, ostracods; Pel, pellets; Cl, clasts. (A) Lithified aragonite mud and fibrous aragonite cement filling porosity (sample SO 241/56). (B) Aragonite mud and aragonite cement filling intraskeletal porosity (sample SO 241/56). (C) Planktonic foraminifera cemented by aragonite. (D)–(E) Highly porous matrix embedding diatoms, radiolarians, pellets and rounded clasts (sample SO 241/17a). (F)–(G) Highly porous matrix embedding diatoms (sample SO 241/17).
(H) Radiolarian test partially filled with barite crystals (sample SO 241/17). (I) Ostracod shell (sample SO 241/17a).

**Figure 5.** Scanning electron microscopy photomicrographs of authigenic deposits from Central Guaymas Basin: Image A–C, site SO 241/56, Fine-grained aragonite mud; images D–H, site SO 241/17, Diatomaceous sinter. The location of the sampling sites is shown in Fig. 1. Abbreviations: Arg-m, aragonite mud; Arg-c, Aragonite cement; Brt, Barite; Op-m, opal-A microspheres; Brt, barite; Py, pyrite; Dia, diatoms. (A) Fibrous aragonite cement crystals (sample SO 241/56). (B) Lithified aragonite mud and fibrous aragonite cement (sample SO 241/56). (C) Diatoms and Fibrous aragonite cement crystals (sample SO 241/56). (D) Opal-A microspheres constituting the matrix (sample SO 241/17a). (E)–(F) Diatoms and platy barite crystals (sample SO 241/17a). (G)–(H) Platy barite crystals and disseminated pyrite framboids (sample SO 241/17).

**Figure 6.** Composition diagrams of carbonates (A) and barite (B) of cold seep-related, authigenic mineralizations from Central Guaymas Basin. (A) Magnesium content of calcite vs a calcite cell parameter diagram based on the calibration published by Titschak et al. (2011) using Rietveld refinement. The standard deviation is included in the size of the symbols. (B) Barite compositions plotted on a BaSO$_4$ vs. SrSO$_4$ binary diagram.

**Figure 7.** Mean versus standard deviation plot of pyrite framboid size. The boundary between zones for euxinic and/or anoxic and dysoxic environments is deduced from modern depositional settings (Wilkin et al., 1996).

**Figure 8.** Stable isotope diagrams: (A) Plot of carbon and oxygen stable isotope composition ($\delta^{13}$C and $\delta^{18}$O; with respect to the V-PDB standard) of the seep-related carbonate samples; (B) $\delta^{18}$O$_{SMOW}$ composition of bivalve shells and fibrous aragonite cement and calculated $\delta^{18}$O$_{SMOW}$ for water using the equations of Böhm et al. (2000) and Kim et al. (2007); the gray rectangles indicate the range of
values; (C) Histogram showing the distribution of $\delta^{34}$S values (with respect to the V-CTD standard) of authigenic barite and pyrite from Central Guaymas Basin.
Table 1. Location of sampling sites in Central Guaymas Basin

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Table 2. Selected chemical analyses (#1 to #6) and descriptive statistics summary (for n = 17 analyses) of aragonite crystals of the central Guaymas Basin (sample SO 241/56). Calculated metal/Ca molar ratios are also shown. Electron-microprobe data.

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<tr>
<td>Total</td>
<td>99.02</td>
<td>100.69</td>
<td>98.85</td>
<td>102.16</td>
<td>99.18</td>
<td>98.04</td>
<td>—</td>
<td>—</td>
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<td>—</td>
</tr>
<tr>
<td>CaCO3 mol%</td>
<td>98.91</td>
<td>98.47</td>
<td>98.77</td>
<td>98.15</td>
<td>98.49</td>
<td>98.90</td>
<td>98.91</td>
<td>98.41</td>
<td>98.01</td>
<td>0.28</td>
</tr>
<tr>
<td>MgCO3</td>
<td>0.00</td>
<td>0.06</td>
<td>0.00</td>
<td>0.09</td>
<td>0.06</td>
<td>0.02</td>
<td>0.12</td>
<td>0.07</td>
<td>0.00</td>
<td>0.04</td>
</tr>
<tr>
<td>MnCO3</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.05</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>FeCO3</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>Sr ppm</td>
<td>1400</td>
<td>1700</td>
<td>1400</td>
<td>2100</td>
<td>2300</td>
<td>1500</td>
<td>3400</td>
<td>2100</td>
<td>1400</td>
<td>602</td>
</tr>
<tr>
<td>Na</td>
<td>2000</td>
<td>2900</td>
<td>2200</td>
<td>3400</td>
<td>2500</td>
<td>1900</td>
<td>3500</td>
<td>2800</td>
<td>1900</td>
<td>545</td>
</tr>
<tr>
<td>Ba</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>200</td>
<td>0</td>
<td>200</td>
<td>100</td>
<td>100</td>
<td>57</td>
</tr>
<tr>
<td>Mn</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>300</td>
<td>100</td>
<td>0</td>
<td>69</td>
</tr>
<tr>
<td>Mg</td>
<td>0</td>
<td>200</td>
<td>0</td>
<td>200</td>
<td>200</td>
<td>0</td>
<td>300</td>
<td>200</td>
<td>0</td>
<td>93</td>
</tr>
<tr>
<td>K</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>200</td>
<td>400</td>
<td>200</td>
<td>400</td>
<td>300</td>
<td>100</td>
<td>123</td>
</tr>
</tbody>
</table>

| Sr/Ca | Molar/ratios | 0.00163 | 0.00198 | 0.00171 | 0.00233 | 0.00273 | 0.00179 | 0.00395 | 0.00239 | 0.00163 | 0.00069 |
| Mg/Ca | 0.00000 | 0.00065 | 0.00000 | 0.00096 | 0.00066 | 0.00015 | 0.00119 | 0.00070 | 0.00000 | 0.00039 |
| Ba/Ca | 0.0000664 | 0.000015 | 0.0000000 | 0.0000800 | 0.0000464 | 0.0001303 | 0.0001303 | 0.000276 | 0.0000000 | 0.0000420 |

Key: Max. = maximum value; Min. = minimum value; S.D. = standard deviation.
Table 3. Pyrite framboïd size statistic parameters of the central Guaymas Basin

<table>
<thead>
<tr>
<th>Sample</th>
<th>Petrographic type</th>
<th>N</th>
<th>$d_m$ ($\mu$m)</th>
<th>S.D. ($\mu$m)</th>
<th>$d_{\text{min}}$ ($\mu$m)</th>
<th>$d_{\text{max}}$ ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO 241/56</td>
<td>Fine-grained aragonite mud</td>
<td>60</td>
<td>3.5</td>
<td>2.4</td>
<td>1.5</td>
<td>8.1</td>
</tr>
<tr>
<td>SO 241/17</td>
<td>Diatomaceous sinter</td>
<td>70</td>
<td>3.1</td>
<td>2.8</td>
<td>1.9</td>
<td>7.5</td>
</tr>
</tbody>
</table>

**Key:** $N =$ Number of measured framboïds; $d_m =$ Mean framboïd diameter; S.D. = Standard deviation of framboïd diameter; $d_{\text{min}} =$ Minimum framboïd diameter in sample; $d_{\text{max}} =$ Maximum framboïd diameter in sample.
Table 4. Chemical composition of pyrite framboids of the central Guaymas Basin. Electron-microprobe data (n = 5).

<table>
<thead>
<tr>
<th>Sample</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>52.57</td>
<td>53.10</td>
<td>53.65</td>
<td>52.91</td>
<td>53.10</td>
</tr>
<tr>
<td>Fe</td>
<td>46.32</td>
<td>46.83</td>
<td>45.81</td>
<td>47.07</td>
<td>45.75</td>
</tr>
<tr>
<td>V</td>
<td>0.27</td>
<td>0.13</td>
<td>0.12</td>
<td>0.33</td>
<td>0.13</td>
</tr>
<tr>
<td>Ni</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Mo</td>
<td>0.45</td>
<td>0.41</td>
<td>0.39</td>
<td>0.51</td>
<td>0.45</td>
</tr>
<tr>
<td>Pb</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Co</td>
<td>0.11</td>
<td>0.09</td>
<td>0.23</td>
<td>0.18</td>
<td>0.15</td>
</tr>
<tr>
<td>Cr</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>99.75</td>
<td>100.58</td>
<td>100.23</td>
<td>101.03</td>
<td>99.64</td>
</tr>
</tbody>
</table>

| V      | ppm  | 2700 | 1300 | 1200 | 3300 | 1300 |
| Ni     | 100  | 200  | 100  | 100  | 200  |
| Mo     | 4500 | 4100 | 3900 | 5100 | 4500 |
| Pb     | 100  | 0    | 100  | 0    | 200  |
| Co     | 1100 | 900  | 300  | 1800 | 1500 |
| Cr     | 100  | 0    | 100  | 200  | 200  |
| U      | 10   | 0    | 10   | 0    | 20   |
| Th     | 0    | 10   | 0    | 10   | 10   |

Petrographic types: analyses #1 and #2 (fine-grained aragonite mud; sample SO 241/56); #3 to #5 (Diatomaceous sinter; sample SO 241/17).
Table 5a. Bulk-rock mineralogy data of the studied samples based on XRD analyses and Rietveld refinement.

<table>
<thead>
<tr>
<th>#</th>
<th>Sample</th>
<th>Type of sample</th>
<th>LMC</th>
<th>HMC</th>
<th>Ar</th>
<th>Pl</th>
<th>Qtz</th>
<th>Gy</th>
<th>Brt</th>
<th>Ph</th>
<th>Hl</th>
<th>Zeo</th>
<th>Op</th>
<th>Py</th>
<th>GOF**</th>
<th>Rwp***</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SO 241/56</td>
<td>Fine-grained aragonite mud</td>
<td>0.7(5)</td>
<td>95.5(7)</td>
<td>0.3(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.33</td>
<td>4.02</td>
</tr>
<tr>
<td>2</td>
<td>SO 241/2-1</td>
<td>Surface mud</td>
<td>9.3(8)</td>
<td></td>
<td>0.1(1)</td>
<td>44.4(4)</td>
<td>7.7(2)</td>
<td>1.1(2)</td>
<td>30.1(5)</td>
<td>6.9(2)</td>
<td>0.4(1)</td>
<td>0.76</td>
<td></td>
<td>3.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>SO 241/33</td>
<td>Surface mud</td>
<td>1.3(3)</td>
<td>89.2(8)</td>
<td>4.2(4)</td>
<td>3.0(2)</td>
<td>1.6(2)</td>
<td>0.1(2)</td>
<td>0.5(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1(2)</td>
<td>0.97</td>
<td>4.16</td>
</tr>
<tr>
<td>4</td>
<td>SO 241/3-1</td>
<td>Surface mud</td>
<td>7.8(1)</td>
<td>0.6(4)</td>
<td>13.0(2)</td>
<td>25.8(3)</td>
<td>8.1(2)</td>
<td>6.2(2)</td>
<td>26.8(6)</td>
<td>10.6(4)</td>
<td>1.1(2)</td>
<td>1.10</td>
<td></td>
<td>4.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>SO 241/3-2</td>
<td>Surface mud</td>
<td>7.0(2)</td>
<td>0.3(1)</td>
<td>1.0(5)</td>
<td>22.1(3)</td>
<td>4.6(4)</td>
<td>0.7(2)</td>
<td>0.3(1)</td>
<td>29.6(2)</td>
<td>4.7(5)</td>
<td>27.9(4)</td>
<td>0.9(9)</td>
<td>0.9(6)</td>
<td>1.07</td>
<td>3.68</td>
</tr>
<tr>
<td>6</td>
<td>SO 241/3-3</td>
<td>Surface mud</td>
<td>4.8(1)</td>
<td>47.0(9)</td>
<td>1.4(3)</td>
<td>10.9(3)</td>
<td>3.6(3)</td>
<td>1.1(4)</td>
<td>6.4(1)</td>
<td>22.1(7)</td>
<td>2.0(2)</td>
<td>0.7(2)</td>
<td>0.94</td>
<td></td>
<td>3.37</td>
<td></td>
</tr>
<tr>
<td>7*</td>
<td>SO 241/17</td>
<td>Diatomaceous sinter</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>8*</td>
<td>SO 241/17a</td>
<td>Diatomaceous sinter</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>SO 241/2-1s</td>
<td>Shell</td>
<td>1.0(7)</td>
<td>99.0(7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.31</td>
<td>4.66</td>
</tr>
<tr>
<td>10</td>
<td>SO 241/33s</td>
<td>Shell</td>
<td>1.0(5)</td>
<td>99.1(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.42</td>
<td>5.93</td>
</tr>
<tr>
<td>11</td>
<td>SO 241/3-2s</td>
<td>Shell</td>
<td>0.7(4)</td>
<td>99.3(6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.33</td>
<td>4.98</td>
</tr>
<tr>
<td>12</td>
<td>SO 241/3-3s</td>
<td>Shell</td>
<td>0(0)</td>
<td>100.0(9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.03</td>
<td>4.33</td>
</tr>
</tbody>
</table>

**Key:** Low-Magnesium calcite (LMC); high-Magnesium calcite (HMC); Ar (aragonite); Pl (plagioclase); Qtz (quartz); Gy (gypsum); Brt (Barite); Ph (Phyllosilicates); Op (opal-A); Hl (halite); Zeo (zeolite: clinoptilolite-heulandite); Py (pyrite). rwp= Rietveld Weighted R profile discrepancy index, GOF= goodness of fit.

Between parenthesis Standard Deviation Estimated (ESD) during the last Rietveld refinement cycle.

*Semiquantitative results (RIR method) for samples with abundant amorphous component.
Table 5b. Carbonate mineralogy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Cal</th>
<th>% Ar</th>
<th>% LMC</th>
<th>% molar MgCO$_3$</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
<th>% HMC</th>
<th>% molar MgCO$_3$</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO 241/56</td>
<td>96.2</td>
<td>99.0</td>
<td>1.0</td>
<td>4</td>
<td>4.972</td>
<td>17.104</td>
<td>366.20</td>
<td>0</td>
<td>—</td>
<td>—</td>
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<td>—</td>
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<tr>
<td>SO 241/2-1</td>
<td>9.4</td>
<td>1.0</td>
<td>99.0</td>
<td>1</td>
<td>4.989</td>
<td>17.062</td>
<td>367.78</td>
<td>0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SO 241/33</td>
<td>94.7</td>
<td>4.4</td>
<td>1.4</td>
<td>2</td>
<td>4.984</td>
<td>17.060</td>
<td>367.05</td>
<td>94.2</td>
<td>4.936</td>
<td>16.838</td>
<td>355.38</td>
<td></td>
</tr>
<tr>
<td>SO 241/3-1</td>
<td>21.4</td>
<td>60.7</td>
<td>36.4</td>
<td>0</td>
<td>4.990</td>
<td>17.065</td>
<td>368.05</td>
<td>2.9</td>
<td>4.997</td>
<td>16.761</td>
<td>353.86</td>
<td></td>
</tr>
<tr>
<td>SO 241/3-2</td>
<td>8.3</td>
<td>12.1</td>
<td>84.3</td>
<td>0</td>
<td>4.990</td>
<td>17.067</td>
<td>368.06</td>
<td>3.6</td>
<td>4.945</td>
<td>16.849</td>
<td>356.84</td>
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</tr>
<tr>
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<td>53.2</td>
<td>2.6</td>
<td>9.0</td>
<td>1</td>
<td>4.988</td>
<td>17.055</td>
<td>367.44</td>
<td>88.4</td>
<td>4.934</td>
<td>16.816</td>
<td>354.55</td>
<td></td>
</tr>
</tbody>
</table>

Key: *% mol MgCO$_3$ Calculated using the calibration of Titschack et al. (2011), based on a and c lattice parameters values refined by Rietveld method. Calcite lattice parameter a varied between 4.990(Å) and 4.934(Å). The smallest calculate value of lattice parameter c was 16.761(Å) and the largest 17.104(Å). Cell volume varied between 368.06(Å$^3$) and 353.86(Å$^3$). The standard deviation of these values is always <0.02. The standard deviation of carbonate percentages is about ±1 for all samples. Calcite with MgCO$_3$ less than 5 mol% was considered low-Magnesium calcite (LMC). Calcite with MgCO$_3$ more than 5 mol% was considered high-Magnesium calcite (HMC). Cal (calcite); Ar (aragonite).
Table 6. Selected chemical analyses (#1 to #6) and descriptive statistics summary (for n = 14 analyses) of barite crystals of the central Guaymas Basin (sample SO 241/17). Calculated elemental molar ratios are also shown. Electron-microprobe data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
<th>Max.</th>
<th>Mean</th>
<th>Min.</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaO wt. %</td>
<td>59.95</td>
<td>59.77</td>
<td>60.02</td>
<td>59.55</td>
<td>59.74</td>
<td>59.05</td>
<td>60.02</td>
<td>59.23</td>
<td>57.34</td>
<td>0.82</td>
</tr>
<tr>
<td>SrO</td>
<td>4.76</td>
<td>2.26</td>
<td>2.22</td>
<td>4.23</td>
<td>4.24</td>
<td>3.03</td>
<td>5.49</td>
<td>3.67</td>
<td>2.22</td>
<td>1.03</td>
</tr>
<tr>
<td>CaO</td>
<td>0.37</td>
<td>0.62</td>
<td>0.53</td>
<td>0.53</td>
<td>0.46</td>
<td>0.55</td>
<td>0.71</td>
<td>0.56</td>
<td>0.37</td>
<td>0.10</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.19</td>
<td>0.33</td>
<td>0.32</td>
<td>0.25</td>
<td>0.17</td>
<td>0.31</td>
<td>0.33</td>
<td>0.25</td>
<td>0.12</td>
<td>0.06</td>
</tr>
<tr>
<td>PbO</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>SO₃</td>
<td>33.83</td>
<td>35.07</td>
<td>35.79</td>
<td>34.26</td>
<td>36.94</td>
<td>37.60</td>
<td>37.60</td>
<td>36.19</td>
<td>33.83</td>
<td>1.30</td>
</tr>
<tr>
<td>Total</td>
<td>99.10</td>
<td>98.03</td>
<td>98.88</td>
<td>98.81</td>
<td>101.56</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>BaSO₄ mol%</td>
<td>87.55</td>
<td>91.10</td>
<td>91.55</td>
<td>87.75</td>
<td>88.24</td>
<td>89.73</td>
<td>91.55</td>
<td>88.66</td>
<td>84.44</td>
<td>1.99</td>
</tr>
<tr>
<td>SrSO₄</td>
<td>10.28</td>
<td>5.09</td>
<td>5.02</td>
<td>9.21</td>
<td>9.28</td>
<td>6.82</td>
<td>11.96</td>
<td>8.10</td>
<td>5.02</td>
<td>2.17</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>1.49</td>
<td>2.58</td>
<td>2.22</td>
<td>2.12</td>
<td>1.87</td>
<td>2.28</td>
<td>2.91</td>
<td>2.31</td>
<td>1.49</td>
<td>0.41</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.68</td>
<td>1.23</td>
<td>1.20</td>
<td>0.91</td>
<td>0.61</td>
<td>1.17</td>
<td>1.23</td>
<td>0.93</td>
<td>0.45</td>
<td>0.24</td>
</tr>
<tr>
<td>Ca ppm</td>
<td>2700</td>
<td>4400</td>
<td>3800</td>
<td>3800</td>
<td>3300</td>
<td>4000</td>
<td>5100</td>
<td>4000</td>
<td>2600</td>
<td>700</td>
</tr>
<tr>
<td>Pb ppm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Na ppm</td>
<td>700</td>
<td>1200</td>
<td>1200</td>
<td>900</td>
<td>600</td>
<td>1100</td>
<td>1200</td>
<td>900</td>
<td>500</td>
<td>200</td>
</tr>
</tbody>
</table>

**Key:** Max. = maximum value; Min. = minimum value; S.D. = standard deviation.
Table 7. Carbon and oxygen stable isotope analyses of carbonates of the central Guaymas Basin.

<table>
<thead>
<tr>
<th>#</th>
<th>Sample</th>
<th>Type of sample</th>
<th>Mineral</th>
<th>$\delta^{13}C_{VPDB}$ ($‰$)</th>
<th>$\delta^{18}O_{VPDB}$ ($‰$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SO 241/56 c1</td>
<td>Fibrous aragonite cement in authigenic carbonate</td>
<td>Ar</td>
<td>-47.6</td>
<td>+2.6</td>
</tr>
<tr>
<td>2</td>
<td>SO 241/56 c2</td>
<td>Fibrous aragonite cement in authigenic carbonate</td>
<td>Ar</td>
<td>-45.2</td>
<td>+1.5</td>
</tr>
<tr>
<td>3</td>
<td>SO 241/2-1</td>
<td>Carbonate from surface mud</td>
<td>Cal</td>
<td>-1.5</td>
<td>-11.4</td>
</tr>
<tr>
<td>4</td>
<td>SO 241/33</td>
<td>Carbonate from surface mud</td>
<td>Cal</td>
<td>-40.6</td>
<td>+3.2</td>
</tr>
<tr>
<td>5</td>
<td>SO 241/3-1</td>
<td>Carbonate from surface mud</td>
<td>Cal</td>
<td>-3.7</td>
<td>-12.5</td>
</tr>
<tr>
<td>6</td>
<td>SO 241/3-2</td>
<td>Carbonate from surface mud</td>
<td>Cal</td>
<td>-1.2</td>
<td>-8.2</td>
</tr>
<tr>
<td>7</td>
<td>SO 241/3-3</td>
<td>Carbonate from surface mud</td>
<td>Cal</td>
<td>-36.5</td>
<td>+2.0</td>
</tr>
<tr>
<td>8</td>
<td>SO 241/2-1s</td>
<td>Bivalve; <em>Archivesica gigas</em></td>
<td>Ar</td>
<td>+0.9</td>
<td>+2.3</td>
</tr>
<tr>
<td>9</td>
<td>SO 241/33s</td>
<td>Bivalve; <em>Archivesica gigas</em></td>
<td>Ar</td>
<td>+1.0</td>
<td>+2.7</td>
</tr>
<tr>
<td>10</td>
<td>SO 241/3-2s</td>
<td>Bivalve; <em>Archivesica gigas</em></td>
<td>Ar</td>
<td>-2.6</td>
<td>+1.4</td>
</tr>
<tr>
<td>11</td>
<td>SO 241/3-1s</td>
<td>Bivalve; <em>Archivesica gigas</em></td>
<td>Ar</td>
<td>-3.7</td>
<td>+1.6</td>
</tr>
<tr>
<td>12</td>
<td>SO 241/3-1b s</td>
<td>Bivalve; <em>Lucinoma annulata</em></td>
<td>Ar</td>
<td>-3.3</td>
<td>+1.8</td>
</tr>
</tbody>
</table>

Key: Ar = aragonite; Cal = calcite.
A

\[ \text{BaSO}_4 \text{ (mol \%)} \]

\[ \text{SrSO}_4 \text{ (mol \%)} \]

\[ 4.98 \]

\[ 4.96 \]

\[ 4.94 \]

\[ 4.92 \]

\[ 4.90 \]

\[ 4.88 \]

\[ 4.86 \]

\[ 4.84 \]

\[ 4.82 \]

\[ 4.80 \]

\[ 4.78 \]

\[ 4.76 \]

\[ 4.74 \]

\[ 4.72 \]

\[ 4.70 \]

\[ 4.68 \]

\[ 4.66 \]

\[ 4.64 \]

\[ 4.62 \]

\[ 4.60 \]

\[ 4.58 \]

\[ 4.56 \]

\[ 4.54 \]

\[ 4.52 \]

\[ 4.50 \]

\[ 4.48 \]

\[ 4.46 \]

\[ 4.44 \]

\[ 4.42 \]

\[ 4.40 \]

\[ 4.38 \]

\[ 4.36 \]

\[ 4.34 \]

\[ 4.32 \]

\[ 4.30 \]

\[ 4.28 \]

\[ 4.26 \]

\[ 4.24 \]

\[ 4.22 \]

\[ 4.20 \]

\[ 4.18 \]

\[ 4.16 \]

\[ 4.14 \]

\[ 4.12 \]

\[ 4.10 \]

\[ 4.08 \]

\[ 4.06 \]

\[ 4.04 \]

\[ 4.02 \]

\[ 4.00 \]

\[ 3.98 \]

\[ 3.96 \]

\[ 3.94 \]

\[ 3.92 \]

\[ 3.90 \]

\[ 3.88 \]

\[ 3.86 \]

\[ 3.84 \]

\[ 3.82 \]

\[ 3.80 \]

\[ 3.78 \]

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\[ 3.74 \]

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\[ 3.34 \]

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\[ 2.04 \]

\[ 2.02 \]

\[ 2.00 \]

\[ 1.98 \]

\[ 1.96 \]

\[ 1.94 \]

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\[ 1.48 \]

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\[ 1.08 \]

\[ 1.06 \]

\[ 1.04 \]

\[ 1.02 \]

\[ 1.00 \]

\[ 0.98 \]

\[ 0.96 \]

\[ 0.94 \]

\[ 0.92 \]

\[ 0.90 \]

\[ 0.88 \]

\[ 0.86 \]

\[ 0.84 \]

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\[ 0.80 \]

\[ 0.78 \]

\[ 0.76 \]

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\[ 0.72 \]

\[ 0.70 \]

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\[ 0.62 \]

\[ 0.60 \]

\[ 0.58 \]

\[ 0.56 \]

\[ 0.54 \]

\[ 0.52 \]

\[ 0.50 \]

\[ 0.48 \]

\[ 0.46 \]

\[ 0.44 \]

\[ 0.42 \]

\[ 0.40 \]

\[ 0.38 \]

\[ 0.36 \]

\[ 0.34 \]

\[ 0.32 \]

\[ 0.30 \]

\[ 0.28 \]

\[ 0.26 \]

\[ 0.24 \]

\[ 0.22 \]

\[ 0.20 \]

\[ 0.18 \]

\[ 0.16 \]

\[ 0.14 \]

\[ 0.12 \]

\[ 0.10 \]

\[ 0.08 \]

\[ 0.06 \]

\[ 0.04 \]

\[ 0.02 \]

\[ 0.00 \]

\[ 15 \%

\[ 10 \%

\[ 5 \%

\[ 0 \%

\[ % \text{ mol MgCO}_3 \]

\[ 0 \]

\[ 5 \]

\[ 10 \]

\[ 15 \]

\[ \text{a (Amstrongs)} \]

\[ \text{BaSO}_4 \text{ (mol \%)} \]

\[ \text{SrSO}_4 \text{ (mol \%)} \]

Fine-grained aragonite mud

Carbonate grains from surface muds

Red: LMC; Blue: HMC

B
Dysoxic

Euxinic

Anoxic

Mean diameter (µm)

Standard deviation (µm)

Framboids from:
- fine-grained aragonite mud
- diatomaceous sinter
A

B

C

Symbols for A and B

- Fibrous aragonite cement
- Carbonate grains from surface muds
- Bivalve shells
- Water

Böhm et al. (2000)
Kim et al. (2007)

Present-day seawater sulfate

Barite
Highlights

- In cold seeps of Guaymas Basin, aragonite, barite and pyrite precipitated from modified seawater.
- Aragonite is highly depleted in $^{13}$C suggesting formation via anaerobic oxidation of methane.
- Barite formed through mixing of reducing, Ba-rich seep fluids with a $^{34}$S-rich sulfate pool.
- Pyrite framboids formed under anoxic-sulfidic water via microbial sulfate reduction.