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Authigenic carbon entombed in methane-soaked sediments from the northeastern transform margin of the Guaymas Basin, Gulf of California

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Abstract

Extensive ROV-based sampling and exploration of the seafloor was conducted along an eroded transform-parallel fault scarp on the northeastern side of the Guaymas Basin in the Gulf of California to observe the nature of fluids venting from the seafloor, measure the record left by methane-venting on the carbonates from this area, and determine the association with gas hydrate. One gas vent vigorous enough to generate a water-column gas plume traceable for over 800 m above the seafloor was found to emanate from a ~10-cm-wide orifice on the eroded scarp face. Sediment temperature measurements and topography on a sub-bottom reflector recorded in a transform-parallel seismic reflection profile identified a subsurface thermal anomaly beneath the gas vent. Active chemosynthetic biological communities (CBCs) and extensive authigenic carbonates that coalesce into distinct chemoherm structures were encountered elsewhere along the eroded transform-parallel scarp.

The carbon isotopic composition of methane bubbles flowing vigorously from the gas vent (-53.6 ± 0.8‰ PDB) is comparable to methane found in sediment cores taken within the CBCs distributed along the scarp (-51.9 ± 8.1‰ PDB). However, the δ^{13}C value of the CO_2 in the vent gas ($+12.4 \pm 1.1$‰ PDB) is very distinct from those for dissolved inorganic carbon (DIC) (-35.8‰ to -2.9‰ PDB) found elsewhere along the scarp, including underneath CBCs. The δ^{13}C values of the carbonate-rich sediments and rocks exposed on the seafloor today also span an unusually large range (-40.9‰ to $+12.9$‰ PDB) and suggest two distinct populations of authigenic carbonate materials were sampled. Unconsolidated sediments and some carbonate rocks, which have lithologic evidence for near-seafloor formation, have negative δ^{13}C values, while carbonate rocks that clearly formed in the subsurface have positive δ^{13}C values (up to $+23.0$‰) close to that measured for CO_2 in the vent gas. There appears to be two carbon sources for the authigenic carbonates: (1) deeply-sourced, isotopically heavy CO_2 (~+12‰); and (2) isotopically light DIC derived from local anaerobic oxidation of methane at the sulfate–methane interface in the shallow subsurface. Addition of isotopically light methane-derived carbon at the seafloor may completely mask the isotopically heavy CO_2 signature ($+12.4$‰) in the underlying sediments. Thus,

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the authigenic carbonates may have formed from the same methane- and carbon dioxide-bearing fluid, but under different migration and alteration conditions, depending on how it migrated through the sediment column.

Keywords: Authigenic carbonate; Diagenesis; Gas vents; Guaymas Basin

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1. Introduction

1.1. Seafloor authigenic carbonates

Authigenic carbonate concretions and nodules are abundant on the seafloor in continental margin settings. The carbon and oxygen isotopic composition of these authigenic carbonates is commonly investigated because it might provide information about their environment of formation. Because authigenic carbonate minerals form from dissolved inorganic carbon (DIC) (reaction (1)), their carbon isotopic composition indicates the nature of the DIC available at the time of carbonate formation (e.g., Ritger et al., 1987; Paull et al., 1992).

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O. \qquad (1)$$

There are at least three early diagenetic biogeochemical processes that have potential roles in the formation of DIC: (1) aerobic oxidation of methane, (2) anaerobic oxidation of methane, and (3) sulfate reduction of sedimentary organic matter. Methane oxidation within sediments surrounding seafloor seep sites, gas vents, and gas hydrate occurrences can produce profound biological and diagenetic changes within the seafloor sediments. As methane approaches the seafloor, rapid changes in the redox state occur which affect carbonate equilibrium. The fate of the methane is in part a function of the rate at which it is moving through the seafloor.

In areas of active gas venting, methane that comes into contact with oxygenated seawater will be oxidized aerobically:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O. \qquad (2)$$

While aerobic oxidation may be of importance for oxidation of methane within the water column (e.g., Valentine et al., 2001), reaction (2) produces acidity and thus is not conducive to authigenic carbonate precipitation.

In the more isolated sub-seafloor environment where upward migrating methane meets sulfate diffusing downward from overlying seawater, populations of microorganisms engage in anaerobic oxidation of methane (AOM, Reeburgh, 1980; Boetius et al., 2000; Valentine and Reeburgh, 2000):

$$CH_4 + SO_4^{-2} \rightarrow HCO_3^- + HS^- + H_2O. \qquad (3)$$

This reaction (3) converts carbon originally in methane into HCO_3^-; spiking the pore-water DIC pool with ^{13}C-depleted carbon and increasing the alkalinity of the water at the sulfate–methane interface (SMI, Borowski et al., 1997, 1999). This alkalinity increase will stimulate the formation of authigenic carbonates, and the bisulfide that is generated may support chemosynthetic communities. Because methane carbon is known for its distinct carbon isotope values ($\delta^{13}C = -40$‰ to -90‰; Schoell, 1980), carbonates that have formed from pore-water DIC supplemented by AOM (reaction (3)) have light isotopic values (Ritger et al., 1987; Paull et al., 1992; Rodriquez et al., 2000). AOM-related authigenic carbonates can have clear isotopic signatures indicating formation from methane-derived carbon.

Sulfate reduction of sedimentary organic matter is another widespread process occurring in most marine sediments (Claypool and Kaplan, 1974):

$$2CH_2O + SO_4^{-2} \rightarrow 2HCO_3^- + H_2S. \qquad (4)$$

Reaction (4) also increases pore-water alkalinity. Because sulfate reduction occurs throughout the sulfate-bearing sediment column, its effects are distributed over a broader area rather than being focused at a relatively narrow zone as in the case of AOM at the SMI (reaction (3)). Thus, sulfate-reduction of organic matter is a less effective mechanism to stimulate local carbonate precipitation than AOM.

Authigenic carbonate minerals that are attributed to AOM have been found around numerous seafloor seeps (Peckmann et al., 2001; Roberts, 2001; Henry et al., 2002; Aloisi et al., 2004). Diagenetic carbonate nodules also form at depth by other poorly understood processes (Matsumoto, 1989; Pisciotto and Mahoney, 1981; Kelts and McKenzie, 1982; Hicks et al., 1996; Rodriguez et al., 2000; Malone et al., 2002; Claypool et al., 2003) during shallow diagenesis. Most diagenetic