Potential for preservation of microbial aggregates in Upper-Cretaceous age methane-derived authigenic carbonates from the Tepee Buttes, Colorado

Daniela Osorio-Rodriguez*, Victoria J. Orphan & John P. Grotzinger
California Institute of Technology, Pasadena, CA
*Correspondence: dosorior@caltech.edu

Overview

WHAT DO WE STUDY?

Aggregates formed by consortia between anaerobic methane-oxidizing archaea (ANME) and sulfate reducing bacteria (SRB), which have been shown to influence the formation of methane-derived authigenic carbonates as well as sulfide minerals in deep sea sediments.

WHERE?

At the Tepee Buttes Member (Campanian-Maastrichtian) of the Colorado Pierre Shale, considered a well preserved ancient analog of modern methane seeps, where a microbial influence on the formation of carbonates has been proposed.

HOW?

We used a combination of microscopy and analytical techniques to find morphological and geochemical evidence of fossil ANME-SRB aggregates at the Tepee Buttes. Samples from Hydrate Ridge (offshore Oregon), where methane seepage is currently active, were used as modern reference materials for comparison.

WHY?

For early Earth (and other planets if life ever evolved there), the discovery of ANME-SRB aggregates would be critical to understand how they influence the geochemistry of the environments where they live, what is their relative importance as mineralization agents, and how they may be contributing to their own preservation.

Evidence of ANME-SRB

SEDIMENTOLOGICAL: Mesoscale

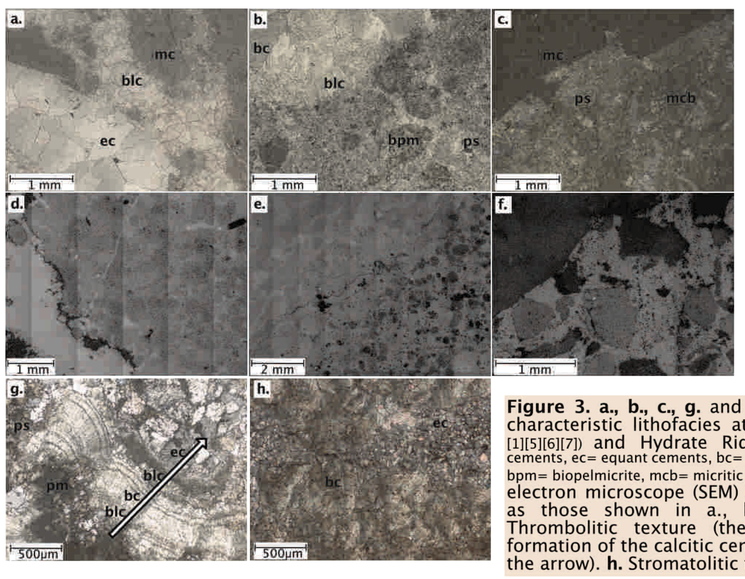


Figure 3. a., b., c., g. and **h.** Microphotographs of the characteristic lithofacies at the Tepee Buttes (a. and b.; [1][5][6][7]) and Hydrate Ridge (c.) mc=micrite, blc= bladed cements, ec= equant cements, bc= botryoidal cements, ps= pseudospar, bpm= biopelmicrite, mcb= micritic brecchia. **d. e.** and **f.** Scanning-electron microscope (SEM) images of lithofacies similar as those shown in a., b. and c., respectively. **g.** Thrombolitic texture (the time progression in the formation of the calcitic cements follows the direction of the arrow). **h.** Stromatolitic texture.

ISOTOPIC: Mass spectrometry

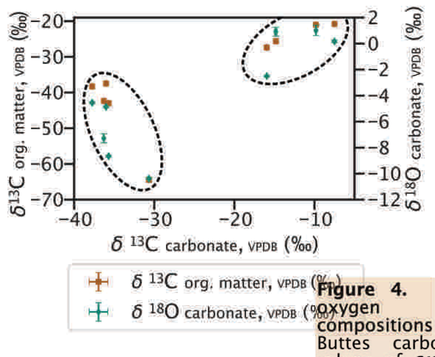


Figure 4. Carbon and oxygen isotopic compositions of the Tepee Buttes carbonates. Our values of $\delta^{13}C$ and $\delta^{18}O$ agree with those previously reported at the same locality ([6][7][8][9]). The $\delta^{18}O$ of the carbonate and the $\delta^{13}C$ of the organic matter are correlated. Their relationship to the $\delta^{13}C$ of the carbonate allows to differentiate two groups.

SEDIMENTOLOGICAL: Microscale / COMPOSITIONAL: EDS

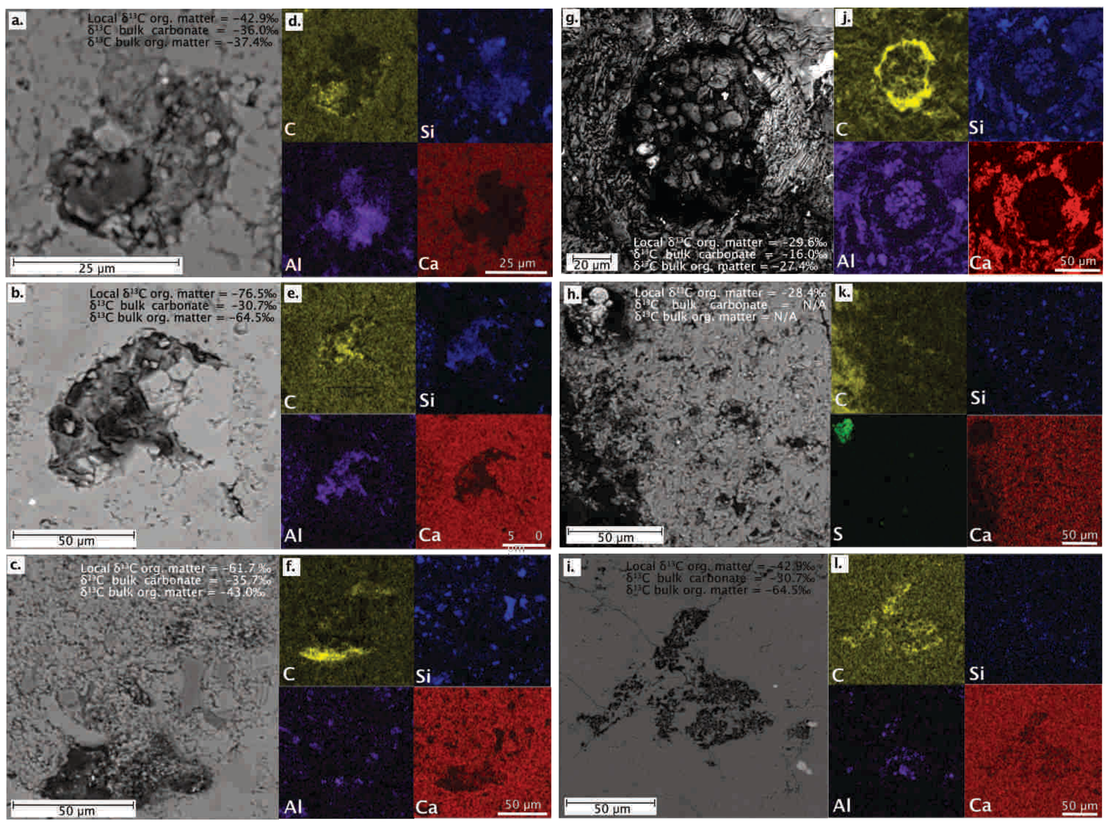


Figure 5. SEM images (black and white) and Electron-Dispersive X-Ray Spectroscopy maps (color) of selected targets examined by secondary-ion mass spectrometry (SIMS; shown below). **a. b.** and **c.** Potential ANME-SRB aggregates with high $\delta^{13}C$ depletions, unique of oxidation of methane. **g., h.** and **i.** Potential ANME-SRB aggregates with small local $\delta^{13}C$ depletions, which indicate that morphological and sedimentological criteria might not be enough to define the presence of these fosilized micro-organisms or bio-markers. **d., e., f., j., k.** and **l.** EDS maps of the same fields shown in a.,b., c., g. h. and i., respectively. All pictures correspond to Tepee Buttes Samples except for h. and k. (Hydrate Ridge).

ISOTOPIC: Secondary-ion mass spectrometry (SIMS)

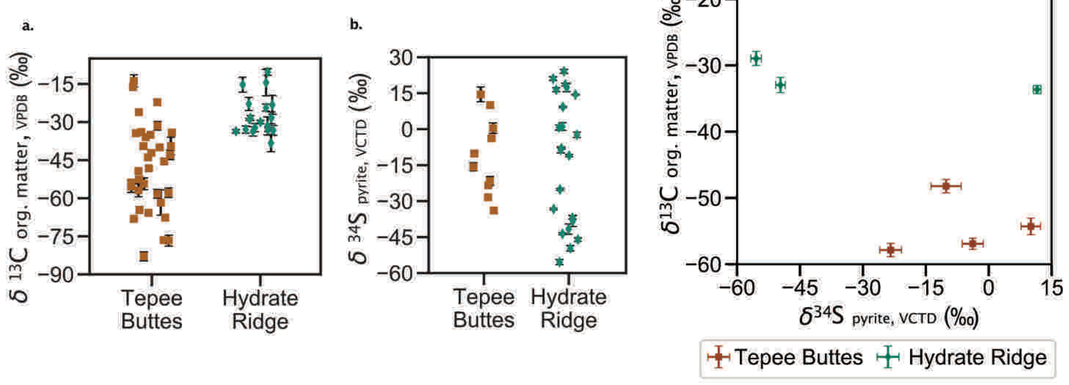


Figure 6. Carbon and sulfur isotopic compositions of 6 µm-spots analyzed by SIMS in the Tepee Buttes and Hydrate Ridge carbonates. **a.** $\delta^{13}C$ of organic matter at both locations. **b.** $\delta^{34}S$ values of micropyrite. **c.** Relationship between $\delta^{13}C$ of organic matter and $\delta^{34}S$ of pyrite.

Geologic setting

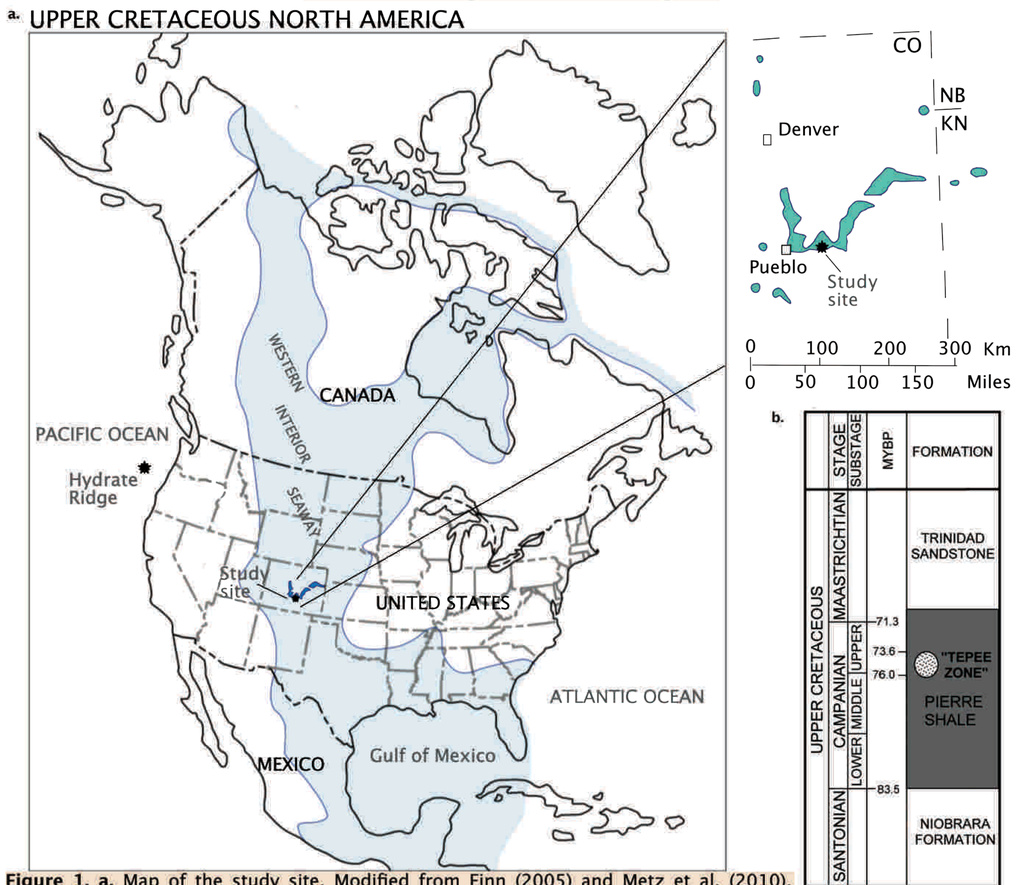


Figure 1. a. Map of the study site. Modified from Finn (2005) and Metz et al. (2010). **b.** Stratigraphic column that shows the position of the "Tepee Zone" at the Study site ([1]).

ANME-SRB-induced mineral formation

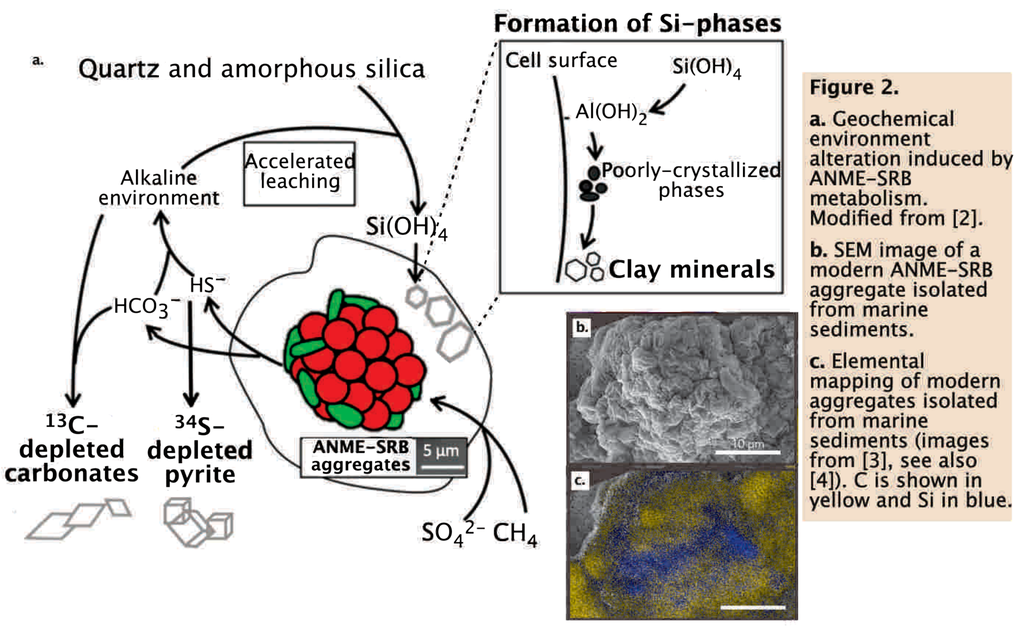


Figure 2.

a. Geochemical environment alteration induced by ANME-SRB metabolism. Modified from [2].

b. SEM image of a modern ANME-SRB aggregate isolated from marine sediments.

c. Elemental mapping of modern aggregates isolated from marine sediments (images from [3], see also [4]). C is shown in yellow and Si in blue.

Evidence of microbial preservation

COMPOSITIONAL: Raman spectroscopy

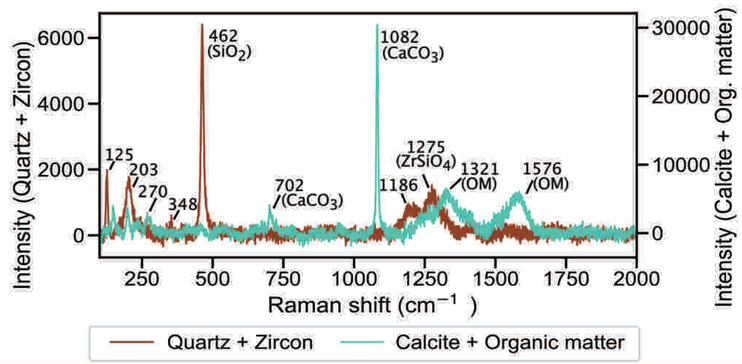


Figure 7. Raman spectra of the two distinctive phases (calcite and silica) present at the peloidal micrite lithofacies.

Paragenetic sequence

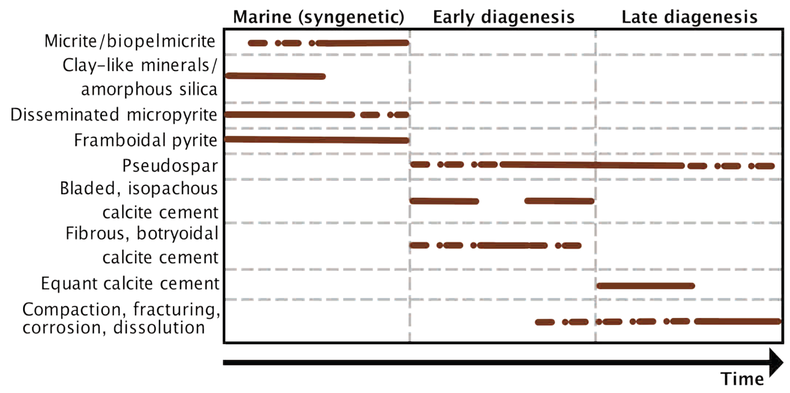


Figure 8. Inferred sequence of precipitation, cementation and diagenetic modifications of the Tepee Buttes carbonates.

Conclusions

- Stromatolitic and thrombolitic textures at the Tepee Buttes, and brecciated textures at Hydrate Ridge, harboring organic matter accumulations and aggregate-like features, were identified. The latter are micrometer-size, spherical structures with organic coatings and clay mineral accumulations found at both locations, consistent with the biomineralization model proposed for modern ANME-SRB aggregates.

-Our observations suggest that aggregate-like features and organic matter derived from methanotrophy are preferentially preserved in the peloidal micrite lithofacies and the stromatolitic cements associated with it, which is consistent with a previously proposed microbial origin for the peloids [1].

- Morphology and composition alone do not seem to be good criteria to establish the identity of ANME-SRB aggregates, given that the values of $\delta^{13}C$ of carbonates and organic matter at the Tepee Buttes indicate that most of the carbon is derived from methanotrophy, which does not hold true for Hydrate Ridge. The values of $\delta^{34}S$ of pyrite point to microbial sulfate reduction as the source of sulfide at both locations.

This is the first study that attempts to establish the potential presence of ANME-SRB fossil aggregates in ancient carbonates. Our results do not isolate a specific preservation mechanism, however, the combined morphological, compositional and isotopic criteria show the very likely influence of ANME-SRB activity.

Acknowledgements

We would like to thank Ken Williford and Adam Hoffmann from the NASA Jet Propulsion Laboratory for the training and assistance in the preparation of SIMS mounts. We would also like to thank George Rossman, Yunbin Guan, Fenfang Wu and Chi Ma for their help and technical support with the Raman spectrometer, SIMS, EA-IRMS and SEM/EDS, respectively, as well as Kyle Metcalfe, Antoine Crémière, Ted Present and the members of the Grotzinger and Orphan labs for discussions. This work was supported by the SIMONS Collaboration on the Origins of Life and the National Science Foundation.

References

[1] Shapiro, R. (2004). Recognition of fossil prokaryotes in Cretaceous methane seep carbonates: relevance to astrobiology. Astrobiology, 4(4), 438-449 [2] Chen, Y., Li, Y. L., Zhou, G. T., Li, H., Lin, Y. T., Xiao, X., & Wang, F. P. (2014). Biomineralization mediated by anaerobic methane-consuming cell consortia. Scientific reports, 4, 5696 [3] Metcalfe, K.S., Yu, H., Dekas, A.E., Chadwick, G.L., Michel, A.J., Fischer, W.W., and Orphan, V.J., Silicate precipitation mediated by ANME-SRB aggregates, in prep. **[4]** Marlow, J. J., Steele, J. A., Ziebis, W., Thurber, A. R., Levin, L. A., & Orphan, V. J. (2014). Carbonate-hosted methanotrophy represents an unrecognized methane sink in the deep sea. Nature Communications, 5, 5094 **[5] Shapiro, R., & Fricke, H. (2002). Tepee Buttes: Fossilized methane-seep ecosystems.** GSA Field Guide 3: Science at the Highest Level, Geological Society of America, Boulder, Colorado, 94-101 **[6] Kauffman, E. G., Arthur, M. A., Howe, B., & Scholle, P. A. (1996). Widespread venting of methane-rich fluids in Late Cretaceous (Campanian) submarine springs (Tepee Buttes), Western Interior seaway, USA. Geology, 24(9), 799-802 [7] Birgel, D., Peckmann, J., Klautzsch, S., Thiel, V., & Reitner, J. (2006). Anaerobic and aerobic oxidation of methane at Late Cretaceous seeps in the Western Interior Seaway, USA. Geomicrobiology Journal, 23(7), 565-577 [8]** Landman, N. H., Cochran, J. K., Larson, N. L., Brezina, J., Garb, M. P., & Harries, P. J. (2012). Methane seeps as ammonite habitats in the US Western Interior Seaway revealed by isotopic analyses of well-preserved shell material. Geology, 40(6), 507-510 **[9] Loyd, S. J., Sample, J., Defliese, W. F., Brooks, K., Hovland, M.,** Torres, M., Marlow, J., Hancock, L. G., Martin, R. , Lyons, T. & Tripati, A.E. **(2016). Methane seep carbonates yield clumped isotope signatures out of equilibrium with formation temperatures. Nature communications, 7, 12274. [10]** Elvert, M., Greinert, J., Suess, E., & Whiticar, M. J. (2001). Carbon isotopes of biomarkers derived from methane-oxidizing microbes at Hydrate Ridge, Cascadia convergent margin. GEOPHYSICAL MONOGRAPH-AMERICAN GEOPHYSICAL UNION, 124, 115-130 **[11]** Lin, Z., Sun, X., Peckmann, J., Lu, Y., Xu, L., Strauss, H., ... & Teichert, B. M. (2016). How sulfate-driven anaerobic oxidation of methane affects the sulfur isotopic composition of pyrite: a SIMS study from the South China Sea. Chemical Geology, 440, 26-41.