

Pyrite crystallization in seep carbonates at gas vent and hydrate site

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Abstract

Pyrite formed by the synergistic metabolism of methane oxidizing archaea and sulfate reducing bacteria has been found in seep carbonates where hydrates usually occur in the subsurface and gas vents out from seafloor in many places worldwide. These bacteria collaborate to oxidize venting methane and reduce seawater sulfate. The hydrogen sulfide and carbon dioxide produced in this process causes pyrite and calcite crystallization (seep carbonate precipitation). We show, using the microscope analysis, that the pyrite crystallization has both bacterial fossilization and crystallization in seep carbonates collected from gas vent and hydrate sites off Louisiana Coast in the Gulf of Mexico and near Dongsha Island in the South China Sea. The pyrite shows bacterial and crystal forms scattered in the calcites. The crystal pyrite occurs as cubic crystals to construct framboid. The bacterial pyrite causes spheroids, rods in nanometer scale to aggregate to layered spheroids, rod-chains, and worm-like forms. These bacterial forms are identical to the characteristic form of live MOA/SRB colonies observed in gas vent and hydrate sites.

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1. Introduction

There is a great abundance of methane oxidizing archaea (MOA) and sulfate reducing bacteria (SRB) at gas vent and hydrate sites. Estimated abundance of MOA is 3×10^9 cells cm^{-3} and SRB is 6×10^9 cells cm^{-3} in the upper 5 cm of surface sediments at Hydrate Ridge on the Cascadian margin [1]. Direct microscopic counts of MOA and SRB cells in the Gulf of Mexico show 1.5×10^9 cells/g in hydrate-associated sediments, and 1.0×10^6 cells/ml in hydrate-decomposed fluids [2]. Michaelis et al. recently reported that live MOA and SRB mats are up to 10 cm thick at gas vent sites on the seafloor of the Black Sea [3]. These MOA and SRB collaborate to oxidize venting methane to carbon dioxide and reduce seawater sulfate to hydrogen sulfide [4], and cause calcite and pyrite to crystallize

(seep carbonate to precipitate) at gas vent and hydrate sites [5–9]. This collaboration of bacterial function is supported by fluorescence studies on live MOA and SRB [1,10–12].

The pyrite and calcite (seep carbonates) are main components in the products of the synergistic metabolism of MOA and SRB [5–9,13]. This paper analyzes the pyrite crystallization in seep carbonates collected from an active vent site in Green Canyon Block 238 in offshore Louisiana of the Gulf of Mexico and from the seafloor near Dongsha Island in the South China Sea using the scanning electron microscope (SEM) and optical microscope techniques. The results show that the pyrite occurs as bacterial and crystal forms in seep carbonates, suggesting that the pyrite crystallization is bacterial fossilization and crystallization (inorganic process) in gas vent and hydrate sites.

2. Sample and analytical method

Two samples described here were collected in May 2002 from an active gas vent area of Green Canyon Block 238 of the Gulf of Mexico (Fig. 1a and b), where the water depth is approximately 700 m and the seafloor is covered by red-

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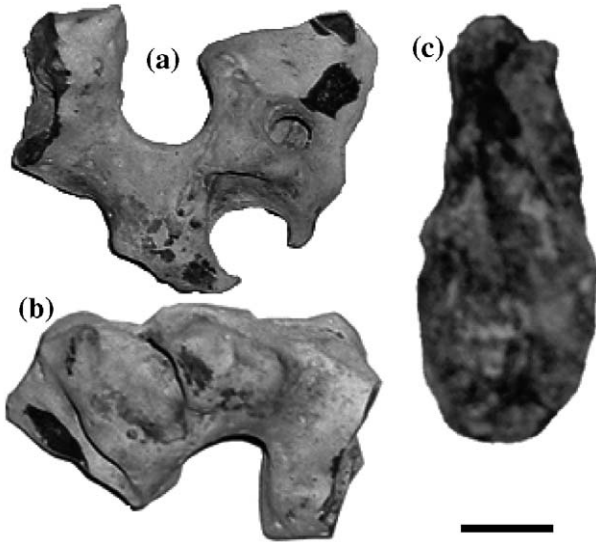


Fig. 1. Seep carbonate samples described this paper. (a) and (b) were sampled in May 2002 from an active gas vent site in Green Canyon Block 238 of the Gulf of Mexico using a clam-shell sampler at the end of a robot arm of Johnson-Sea-Link II submersible. (c) was sampled in April 2002 from the seafloor near Dongsha Island of the South China Sea using the tow-net sampler. The scale bars correspond to 1 cm in all images.

brown and white bacteria mats, using a clam-shell sampler at the end of a robot arm of Johnson-Sea-Link II submersible. Other one was sampled in April 2002 from the seafloor near Dongsha Island of the South China Sea (Fig. 1c), where water depth of sampling area is approximately 1000 m and the geophysical evidences of hydrate occurrence were found in the subsurface [14–17], using the tow-net sampler.

The samples were rinsed with fresh water at the time of collection. In preparation for the analysis of SEM and light microscope the samples were cleaned again by distilled water and were then air-dried. Some of samples were treated with 5% HCl to obtain a pyrite residue for SEM observation. The surfaces of all samples for SEM observation were coated with gold for 30 s using a procedure that does not produce artificial nanobacteria-like features [18]. SEM photographs were taken using the LEO-1530VP SEM operating at 10–20 kV with a 5 to 9 mm working distance. Light microscope photographs were taken using the LEICA-DMRX light microscope.

All minerals described here were verified by optical microscope and energy dispersive spectroscopy. Uniform, strongly negative carbon isotopic ratios were measured on the samples (-51.25% to -52.29% PDB), indicating that carbonates are precipitated by the synergistic metabolism of the MOA and SRB at gas vent and hydrate sites [19].

3. Pyrite microstructure

The transmitted light microscope image shows that the pyrite (gray to white) scatters in the calcite (black) with a concentration of less than 10%, and occurs as bacterial aggregated spheroids, irregular forms, chains, and little spots (Fig. 2). The bacterial spheroidal aggregates mostly consist of a center and an outer layer (Fig. 2a–e). The center is constructed of numerous smaller pyrite spheroids whose image has higher reflection than the outer layer, and contains calcites, while the outer layer consists of non-crystalline pyrite (Fig. 2b–f). These aggregated spheroids sometimes only develop either the center (Fig. 2f) or the outer layer (Fig. 2a and e). Details of these outer layers are depicted in Fig. 4.

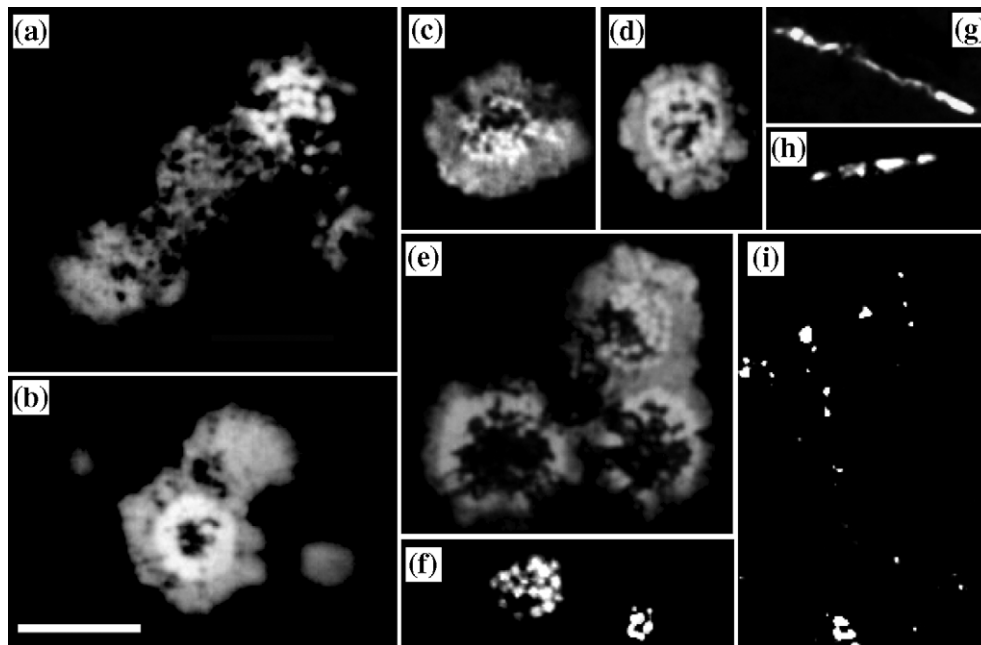


Fig. 2. Reflected light microscope images showing the pyrite occurrence. Panels (a–f) show the layered structure of pyrite spheroids, panels (g–h) show the rod-chains, and panel (i) shows pyrite spots scattered in the calcite. Several types of bacterial microstructure are present. See descriptions in text. Pyrite is in gray to white color and calcite is in black color. The scale bars correspond to 5 μm in all panels.

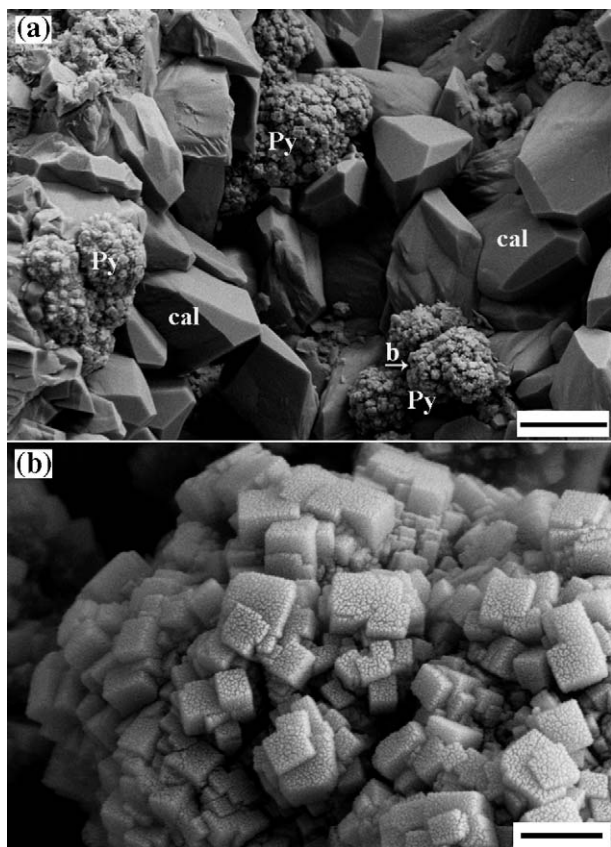


Fig. 3. SEM images of freshly broken surface in the left corner of the carbonate sample shown in Fig. 1a. The pyrite occurs as bacterial frambooids constructed of numerous smaller cubic crystal pyrite. Labels “Py” and “cal” in panel (a) indicate pyrite and calcite, respectively. Panel (b) is the enlargement of an area marked by a white arrow with “b” in panel (a). The scale bar corresponds to 10 μm in panel (a), and 1 μm in panel (b).

The pyrite also occurs as rods connecting to form chains (Fig. 2g and h), and as small spots scattered in the calcite (Fig. 2i). These layered structure and rod-chain are identical to the microstructures described in the live MOA and SRB colonies [1,10–12].

The SEM images of the freshly fractured surface of the sample (broken upper left of Fig. 1a) show that the pyrite occurs as frambooids constructed of numerous smaller cubic crystal pyrite (Fig. 3). The SEM images of the pyrite residue treated by the 5% HCl show the surface details of the outer layer of bacterial aggregated pyrite (Fig. 4). The pyrite occurs as bacterial frambooid and spheroid. The bacterial frambooid is composed of numerous smaller bacterial spheroids, the smaller spheroids tend to take on a roughly cubic form (Fig. 4e–f), suggesting that the cubic pyrite frambooid shown in Fig. 3 may be developed from these bacterial frambooids. The bacterial spheroid is composed of non-crystalline pyrite (Fig. 4). The allomorphic pyrite is composed of innumerable smaller bacterial spheroids with $<0.05 \mu\text{m}$ diameter (Fig. 4d and i) that is identical to the nanobacteria described in literatures [20–23]. Some bacterial worm-like pyrite disperses on the surface with $<0.1 \mu\text{m}$ diameter (Fig. 4d and k). This pyrite in nanometer scale is in fact properly classified as nanometer minerals ($<0.3 \mu\text{m}$).

4. Discussion and conclusion

The pyrite in seep carbonates described here occurs as fossilized bacteria and crystallized crystals. The crystal pyrite occurs as cubic crystals to construct frambooid. The fossilized bacteria occur as aggregated spheroids and chains. The spheroid consists of a center and an outer layer. The center is constructed of numerous smaller spheroids. The outer layer of spheroid is composed of innumerable smaller bacterial spheroids in nanometer scale. In addition, there are nanobacterial worm-like pyrite-rods dispersing on the surface. The aggregated chain consists of several bacterial rods. These layered structure and rod-chain are identical to the characteristic form of live MOA and SRB colonies observed at gas vent and hydrate sites [1,10–12]. The bacterial and crystal forms of pyrite observed here show bacterial and inorganic crystallization at gas vent and hydrate sites. The bacterial community in gas vent and hydrate sites appears to be operating in the following fashion: bacterial colonies convert seawater sulfate to H_2S and venting methane to CO_2 in the reduction zone. The abundant H_2S allows bacteria to be fossilized with reactive detrital iron minerals in sediments as well as crystallizes pyrite crystals. These observations will be useful both as a documentation of bacterial activity and mineralization at gas vent and hydrate sites, and as a suggestion of the bacterial fossilization versus inorganic crystallization involved.

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References

- [1] A. Boetius, K. Ravenschlag, C.J. Schubert, D. Rickert, F. Widdel, A. Gieseke, R. Amann, B.B. Jørgensen, U. Witte, O. Pfannkuche, *Nature* 407 (2000) 623.
- [2] B. Lanoil, R. Sassen, M.T. La Duc, S.T. Sweet, K.H. Nealson, *Appl. Environ. Microbiol.* 67 (2001) 5143.
- [3] W. Michaelis, R. Seifert, K. Nauhaus, T. Treude, V. Thiel, M. Blumenberg, K. Knittel, A. Gieseke, K. Peterknecht, T. Pape, A. Boetius, R. Amann, B.B. Jørgensen, F. Widdel, J.R. Peckmann, N.V. Pimenov, M.B. Gulin, *Science* 297 (2002) 1013.
- [4] D.L. Valentine, W.S. Reeburgh, *Environ. Microbiol.* 2 (2000) 477.
- [5] P. Aharon, *Geo-Mar. Lett.* 14 (1994) 69.
- [6] H.H. Roberts, P. Aharon, *Geo-Mar. Lett.* 14 (1994) 135.
- [7] S. Cavagna, P. Clari, L. Martire, *Sediment. Geol.* 126 (1999) 253.
- [8] D.S. Stakes, D. Orange, J.B. Paduan, K.A. Salamy, N. Maher, *Mar. Geol.* 159 (1999) 93.
- [9] J. Peckmann, A. Reimer, U. Luth, B.T. Hansen, C. Heinicke, J. Hoefs, J. Reitner, *Mar. Geol.* 177 (2001) 129.
- [10] V.J. Orphan, C.H. House, K.U. Hinrichs, K.D. McKeegan, E.F. DeLong, *Science* 293 (2001) 484.

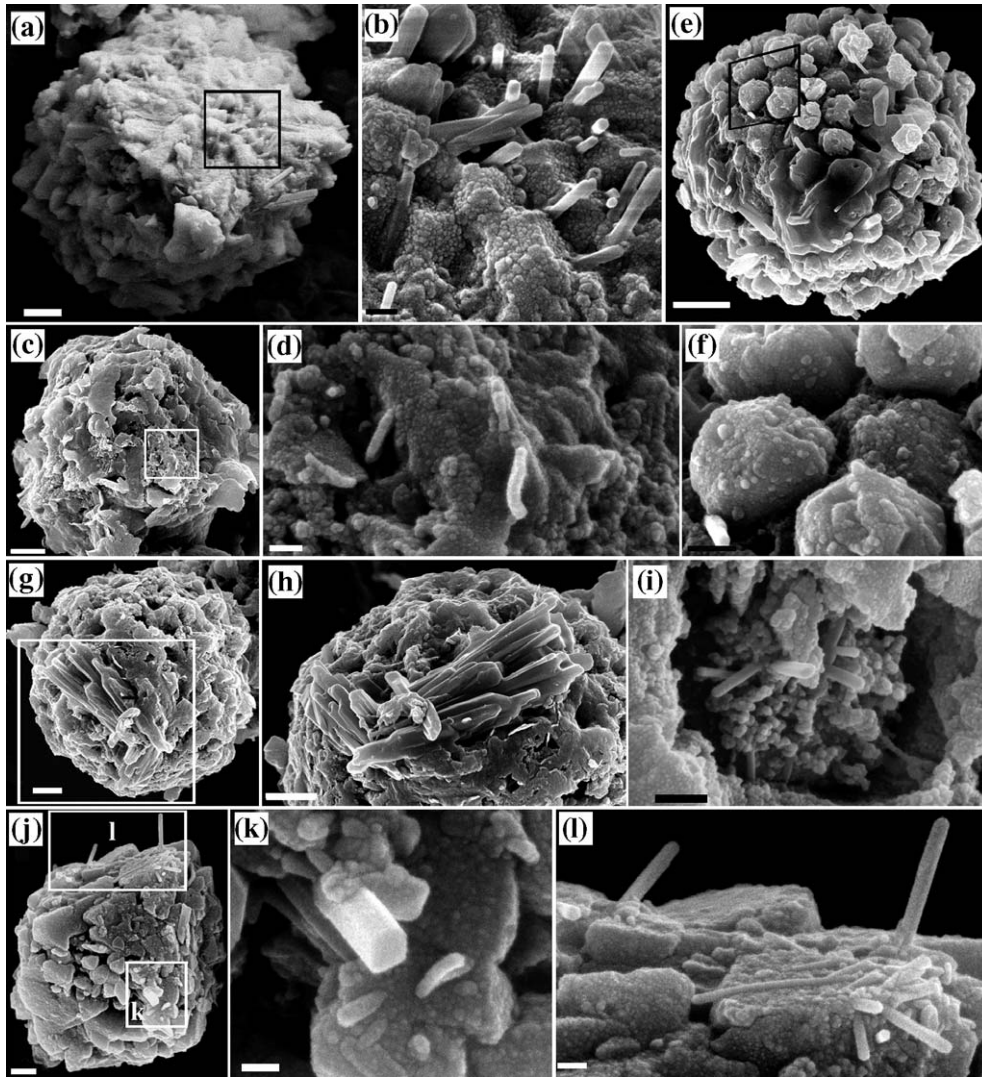


Fig. 4. SEM images of the pyrite framboid and spheroids showing pyrite crystallization and bacterial fossilization. Panels (a, c, g, j) show pyrite spheroid, and panel (e) shows pyrite framboid. Panel (b) is an enlargement of the white rectangle in panel (a). Panel (d) is an enlargement of the white rectangle in panel (c) that shows worm-like bacteria dispersing on the surface. Panel (f) is an enlargement of the white rectangle in panel (e) that shows the detail of the smaller spheroids tending to take on a roughly cubic form. Panel (h) is an enlargement of the white rectangle in panel (g). Panel (i) is an enlargement of a hole marked by black arrow in panel (g) showing acicular crystal and innumerable smaller spheroids. Panel (k) is an enlargement of the white rectangle with “k” in panel (j) showing worm-like bacteria. Panel (l) is an enlargement of the white rectangle with “l” in panel (j). The scale bars correspond to 1 μm (a, c, e, g), 0.2 μm (b, f, i), 0.1 μm (d, h, k, l), and 0.3 μm (j).

- [11] V.J. Orphan, C.H. House, K.U. Hinrichs, K.D. McKeegan, E.F. DeLong, *Proc. Natl. Acad. Sci. U. S. A.* 99 (2002) 7663.
- [12] A. Boetius, E. Suess, *Chem. Geol.* 205 (2004) 291.
- [13] J. Peckmann, V. Thiel, *Chem. Geol.* 205 (2004) 443.
- [14] J. Chow, J.S. Lee, R. Sun, C.S. Liu, N. Lundberg, *Geo-Mar. Lett.* 20 (2000) 3.
- [15] W.C. Chi, D.L. Reed, C.S. Liu, N. Lundberg, *Terr. Atmos. Ocean. Sci.* 9 (1998) 779.
- [16] T.M. Guo, B.H. Wu, Y.H. Zhu, S.S. Fan, G.J. Chen, *J. Pet. Sci. Eng.* 41 (2004) 11.
- [17] H.B. Song, J.H. Geng, H.K. Wang, W.S. Zhang, Y.X. Fang, T.Y. Hao, W.W. Jiang, *Chin. J. Geophys. (Chinese Edition)* 44 (2001) 687.
- [18] R.L. Folk, F.L. Lynch, *J. Sediment. Res.* 7 (1997) 597.
- [19] D.F. Chen, Y.Y. Huang, X.L. Yuan, L.M. Cathles III, *Mar. Pet. Geol.* 22 (2005) 613.
- [20] R.L. Folk, *J. Sediment. Res.* 63 (1993) 990.
- [21] R.L. Folk, *Sediment. Geol.* 126 (1999) 47.
- [22] R.L. Folk, F.L. Lynch, *Sedimentology* 48 (2001) 215.
- [23] R.L. Folk, E.T. Rasbury, *Terr. Nova* 14 (2002) 469.