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HAL Id: insu-01352929
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Submitted on 10 Aug 2016

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Fossil evidence for serpentinization fluids fueling chemosynthetic assemblages

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Edited by Norman H. Sleep, Stanford University, Stanford, CA, and approved March 24, 2011 (received for review June 30, 2010)

Among the deep-sea hydrothermal vent sites discovered in the past 30 years, Lost City on the Mid-Atlantic Ridge (MAR) is remarkable both for its alkaline fluids derived from mantle rock serpentinization and the spectacular seafloor carbonate chimneys precipitated from these fluids. Despite high concentrations of reduced chemicals in the fluids, this unique example of a serpentine-hosted hydrothermal system currently lacks chemosynthetic assemblages dominated by large animals typical of high-temperature vent sites. Here we report abundant specimens of chemosymbiotic mussels, associated with gastropods and chemosymbiotic clams, in approximately 100 kyr old Lost City-like carbonates from the MAR close to the Rainbow site (36°N). Our finding shows that serpentinization-related fluids, unaffected by high-temperature hydrothermal circulation, can occur on-axis and are able to sustain high-biomass communities. The widespread occurrence of seafloor ultramafic rocks linked to likely long-range dispersion of vent species therefore offers considerably more ecospace for chemosynthetic fauna in the oceans than previously supposed.

**Bathymodiolus** | Ghost City | ultramafic-hosted | mid-ocean ridge | ecogeochemistry

High-temperature hydrothermal vents occur at very geographically restricted sites in the deep-sea, localized on spreading ridges and arc-related volcanoes. Typically, such vent fluids are metal- and H<sub>2</sub>S-rich and precipitate metallic sulfide chimneys on the seafloor (1, 2). These vents usually support high-biomass invertebrate communities, dominated by a small number of endemic species forming symbioses with diverse chemautotrophic bacteria (e.g., vibrio tubeworms, bresiliid shrimp, provaniid gastropods, vesicomyid clams, and bathymodiolin mussels) (1, 3). These symbioses exploit chemical energy from a variety of fluids enriched in reduced compounds in Lost City hydrothermal fluid indicates that these, and similar peridotite-hosted vents, hold the energetic potential to support large aggregations of *Bathymodiolus* mussels, a genus widely distributed along the MAR axis (22). B. *aff. azoricus* at Lost City hosts the same symbiont phylotypes as the methanotrophic and thiotrophic endosymbionts of both *B. azoricus* and *B. puteoserpentis* from on-axis sites on the MAR (18), where the methanotrophic symbiont fixes carbon from methane and the chemolithoautotroph uses sulfide to fix CO<sub>2</sub> (23–25). In addition to methane, DeChaine et al. (18) suggest that B. *aff. azoricus* at Lost City could also be utilizing hydrogen, although hydrogen-oxidizing symbionts have yet to be identified. These authors further


The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1009383108/-/DCSupplemental.

7698–7703 | PNAS | May 10, 2011 | vol. 108 | no. 19

www.pnas.org/cgi/doi/10.1073/pnas.1009383108

[Image 0x-33 to 19x783]
Eight carbonate blocks were dredged during the MoMAR-Ghost City Carbonates to the ridge axis, but it also expands the range of marine environments of low-temperature hydrothermal circulation in serpentinized high-temperature vent fluids. This finding not only reveals the existence of metal-poor fluid venting, contrasting with all known MAR-axis associated with a distinct type of environment associated with mal vent field, the Ghost City carbonates and fossils were clearly MAR. Although geographically close to the Rainbow hydrothermal field (22, 26), recent data (27), moreover, suggest that fluids issuing from flanges on the flanks of Lost City chimneys may indeed have a higher H2S/temperature ratio than the end-member fluid. Given the potential availability of these reduced compounds in the Lost City vent fluids for symbionts and free-living chemotrophic microbial populations (28, 29), there is therefore no reason to suppose that Lost City-type fluids should exclude the formation of dense chemosynthetic faunal assemblages.

The findings contained in this paper support the hypothesis that Lost City-type fluids can sustain such communities, while providing further evidence for the suggestions of Kelley et al. (17, 30) that low-temperature hydrothermal circulation on slow-spreading ridges has a widespread distribution. We report previously unrevealed blooms of two species of chemosynthetic bivalves and four gastropod species. This fossil assemblage is 110,000 years old (based on radiometric isotopes) and contains similar species to the Rainbow mussel beds from high-temperature vents elsewhere on the mid-Atlantic ridge. The authigenic carbonates and the infilling pelagic sediment show good separation between the Lost City and Rainbow samples (Fig. 2 E and F and Fig. S4). The infilling pelagic sediments have δ13C values of 3.63 ± 0.25‰ and δ18O values of 0.93 ± 0.17‰ (n = 4). Mixed calcite/aragonite authigenic cements have δ18O and δ13C values of 4.88 ± 0.19‰ and −0.66 ± 1.18‰, respectively (n = 9) (Table 1). The authigenic carbonates and the infilling pelagic sediment show good separation between δ13C and δ18O on a canonical discriminant analysis (CDA) scatterplot, allowing distinction. One of these subsamples is characterized by a δ234U_initial value (150 ± 1‰; Table 2) close to the modern seawater signature (146.6 ± 2.6‰) (31), which suggests that its U/Th ratio may be considered as the most representative of the formation age of Ghost City carbonates. The corresponding U/Th age (110 ± 0.9 kyr) lies in the same range as the older chimneys from Lost City (122 ± 12 kyr) (32) and suggests that…

**Ghost City Carbonates**

Eight carbonate blocks were dredged during the MoMAR-DREAM cruise (MoMAR 08 Leg 2, August–September 2008) from the northwestern flank of the Rainbow massif, which is situated on a nontransform offset at 36°14.15N, 33°53.50W (Fig. 1 and S1). This site, which we name Ghost City, is 1,200 m northeast of the Rainbow vent field at around 2,100 m water depth. The dredge from which the carbonates were collected sampled a transect around 800 m long on the seafloor and recovered, in addition to the carbonates, three shells of thysanid bivalves, numerous pieces of serpentinized peridotite, and some troctolites and gabbros. The carbonates are white to ivory in color, ranging from 750 to 25 cm2 in volume, and most have thin (up to 1 mm) exterior ferric oxihydroxide (ferrihydrite with Mn component) black crusts upon which solitary corals have grown (Fig. 2 A and B and Fig. S2). The carbonate textures range from “layered” (Fig. 2 C and Fig. S3), with significant porosity (close to 40%, n = 4), to “massive.” This carbonate matrix, which encloses mussel shells with a density of up to 4 shells per 10 cm2, lacks metallic oxide or sulfide minerals and consists of varying proportions of authigenic carbonate cements and infilling pelagic calcitic and aragonitic fossils (foraminifera, coccoliths, and a few pteropods; Fig. 2 D and Fig. S3). The authigenic carbonate cements consist of aragonite, commonly occurring as radial aggregates of acicular crystals, calcite, and sparser rosettes of glendonite crystals (Fig. 2 E and F and Fig. S4). The infilling pelagic sediments have δ13C values of 3.63 ± 0.25‰ and δ18O values of 0.93 ± 0.17‰ (n = 4). Mixed calcite/aragonite authigenic cements have δ18O and δ13C values of 4.88 ± 0.19‰ and −0.66 ± 1.18‰, respectively (n = 9) (Table 1). The authigenic carbonates and the infilling pelagic sediment show good separation between δ13C and δ18O on a canonical discriminant analysis (CDA) scatterplot, supporting distinct mineralization process (Fig. 3 and Table S2). Isotopic measurements of a series of subsamples from one authigenic carbonate crust gave U/Th ages ranging from 46 ± 0.3 kyr to 193 ± 11 kyr (n = 4) (Table 2). These samples, however, display a wide range of initial δ234U values (from approximately 129 to 183‰), suggesting that their U/Th ages may be possibly biased due to postformation interaction with seawater or diagenesis (31). One of these subsamples is characterized by a δ234U_initial value (150 ± 1‰; Table 2) close to the modern seawater signature (146.6 ± 2.6‰) (31), which suggests that its U/Th ratio may be considered as the most representative of the formation age of Ghost City carbonates. The corresponding U/Th age (110 ± 0.9 kyr) lies in the same range as the older chimneys from Lost City (122 ± 12 kyr) (32) and suggests that...
Carbonate samples from Ghost City. (A) Sectioned block formed of authigenic carbonate cements covered by ferric oxyhydroxide dark crust upon which (B) solitary corals have grown. (Scale bars, 1 cm.) (C) Photomicrograph showing anastomosing aragonite laminae defining fluid flow channels (center and right) and a piece of mussel shell (bottom left). The channels have thin aragonite walls, some with thin collomorphic coatings; others are in-filled with micritic carbonate. A thin rim of aragonite acicular crystals seems to be the latest cement phase, covering mussel shells, channel walls (top left), and micritic infill (center right). (Scale bars, 1 mm.) (D) Photomicrograph showing articulated mussel specimens and gastropods enclosed within authigenic carbonate. (Scale bars, 1 mm.) (E and F) SEM photomicrographs of carbonates showing aragonite acicular crystals (E) and rosette of glendonite crystals (F). (Scale bars, 20 μm.)

Ghost City carbonate formation is significantly older than the first evidence of Rainbow vent activity (23 ± 1.5 kyr) (33). Additionally, the same carbonate sample exhibits a radiogenic strontium isotope ratio (87Sr/86Sr) of 0.70916 ± 0.00006, close to seawater ratios.

Among known authigenic carbonates from oceanic environments where ultramafic rocks are exposed, such as vein-filling aragonites in serpentinites (34, 35), samples from Ghost City are texturally and mineralogically most similar to those from Lost City, particularly the carbonates of old (up to 25 kyr) inactive chimneys (12). According to these authors, the Lost City inactive structures display well-defined fluid flow paths, retaining significant porosity (up to approximately 35%) and are characterized by dark or black exteriors that contrast to white, ivory, or gray interiors. The outer walls of these structures become dark due to manganese precipitation associated with aging and are colonized by serpulid worms and corals (13). In older inactive chimneys the internal microchannels are progressively in-filled with micritic calcite; brucite, which is undersaturated in seawater, tends to disappear in these chimneys (12). Another feature indicative of prolonged postformation interaction with seawater is near seawater Sr isotope values in carbonate minerals, as seen in both the Lost City inactive chimneys (13) and Ghost City samples. One mineralogical distinction of Ghost City carbonates is the presence of glendonite. Glendonite in Ghost City carbonate crust exhibits a characteristic star shape and is associated with acicular aragonite crystals surrounding the benthic fossils. Glendonite is a pseudomorph after ikaite, a very unstable hydrous calcium carbonate associated with cold water (<6°C) depositional systems, including glacimarine and deep water settings (36, 37). Original ikaite precipitation is favored by elevated alkalinity, high pH (>10) and dissolved phosphate enrichments. Glendonite was not reported in Lost City carbonates, but the presence of ikaite in the walls of active chimneys was suspected from the observation of rapid dissolution of elongated carbonate crystals during sampling (13). The oxygen and carbon isotope values of the Ghost City authigenic carbonates are consistent with those observed in serpentinization contexts. The 18O enrichment during fluid/rock interaction results in carbonates with high 18O values (>2‰) (11, 38). The Ghost City carbon isotope signatures (δ13C = −2.6 to 0.7‰) are comparable to those measured in carbonates from serpentinite-hosted systems, like the South Chamorro Seamount (δ13C = −2.1 to −1.3‰) and the Conical Seamount (δ13C = −2.9 to −0.1‰) in the Mariana forearc (39–41), and lie within the wide range of carbonate isotopic signatures reported for Lost City (−7 to +13‰) (11). Carbonates with the lower
isotopic signature reflect a mixed inorganic carbon source with contributions from seawater ($\delta^{13}C_{DIC} \sim 0\%$) and an isotopically lighter-DIC source. Owing to the very low concentration of inorganic carbon in serpentinization fluids, the most likely origin for this $^{13}$C depleted DIC is the oxidation of methane. Methane in serpentinization fluids are characterized by light carbon isotopic signatures (e.g., $\delta^{13}C_{CH4} = -7\%$ in the Zambales ophiolite, $-10.3\%$ at Logatchev, $-16.7\%$ at Rainbow, and $-11.9\%$ at Lost City) (42–45), which can be further fractionated by methanotrophic microbes converting methane into inorganic carbon. While abiotic methane oxidation is kinetically inhibited at low temperature (46), microbial oxidation of methane can occur in subseaﬂoor habitats with various electron acceptors (e.g., oxygen and sulfate) during the mixing of seawater with end-member fluids (47, 48). According to Proskurowski et al. (48), the fractionation factor resulting of anaerobic or aerobic methane oxidation can be as high as 1.039 (49, 50) and will result in further depletion of the initial carbon isotopic ratio by at least $-13\%$. Only a small fraction (approximately 5%) of this $^{13}$C depleted methane is thus sufficient to explain the slightly negative carbon isotopic signature of some Ghost City carbonates. An additional contribution from biogenic methane formed during the subseaﬂoor mixing of seawater and the end-member fluid, as described in Proskurowski et al. (48), cannot be ruled out. This assumption is supported by the identification of methanotrophic and anaerobic methane-oxidizing Archaea at Lost City, particularly in the less active chimneys where seawater mixing is occurring (28). In Lost City-type conditions, seawater is the only source of $\text{HCO}_3^-$, and mixing is required to compensate the poor supply of this ion from the fluid. As a consequence, the substantial isotopic fractionation resulting of biogenic methane formation that was observed at basalt-hosted diffuse vents (48) may not be achieved due to limiting inorganic carbon conditions. The relative importance of biogenic methane is therefore difficult to estimate from Ghost City samples’ isotopic ratios.

The geological context, as well as petrographic and isotopic data, provides supporting evidence that the Ghost City carbonate samples were formed 110,000 years ago from venting of metal-poor fluids. Despite the proximity with the Rainbow high-temperature vents field, the lack of polymetallic sulfide precipitates in the Ghost City carbonate samples precludes a high-temperature metal-rich hydrothermal fluid contribution in their formation. More likely, these fluids were formed from low-temperature hydrothermal circulation related to serpentinization and were probably close in composition to those currently venting at Lost City.

**Ghost City Fossils**

We counted 146 specimens of the mussel *Bathymodiolus* aff. *azoricus* on the exposed surfaces of the eight Ghost City carbonate blocks (Fig. 4 and Fig. S4). The shells range in length from 5 mm to 84 mm, which is comparable to living *B. azoricus* shells from high-temperature hydrothermal vent fields on the MAR (51). Very few of the Ghost City mussel shells are fragmented, and quite a few specimens have articulated valves, with a ratio of 3.6 disarticulated to articulated shells ($n = 73$). Some of the small articulated mussel shells are nested within larger articulated specimens (Fig. 2D) are indicative of in situ growth and a lack of post mortem transport. This interpretation is supported by the isotope composition of the Ghost City *B. aff.*

**Table 2. U-Th ages for Ghost City carbonate samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corrected U-Th age (kyr) ± 2σ</th>
<th>Initial $^{234}$U (%) ± 2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>195 ± 11</td>
<td>183 ± 10</td>
</tr>
<tr>
<td>S2</td>
<td>110 ± 0.9</td>
<td>150 ± 1</td>
</tr>
<tr>
<td>S3</td>
<td>65 ± 11</td>
<td>170 ± 1</td>
</tr>
<tr>
<td>S4</td>
<td>46 ± 0.3</td>
<td>129 ± 1</td>
</tr>
</tbody>
</table>

azoricus shells ($\delta^{18}O = 4.93 \pm 0.40\%$, $\delta^{13}C = -0.30 \pm 1.99\%$, $n = 3$; Table 1), values that are more similar to the Ghost City authigenic carbonates than living *Bathymodiolus* shells from the Rainbow high-temperature hydrothermal vent site (CDA analysis; Fig. 3 and Table S2). The other benthic fossils enclosed within the Ghost City carbonate samples (Fig. 4) comprise serpulid tubes (>30); the vesicomyid clam Phreagena sp. ($n = 2$); the thyasirid clam Thyasira sp. ($n = 1$); the limpet Paralepetopsis aff. ferrugivora ($n = 15$); and the snails *Protoliria* aff. *thorvaldssoni* ($n = 32$), *Phymorhynchus* sp. ($n = 1$), *Anatoma* sp. ($n = 2$), and *Lurfax vitreus* ($n = 1$). These also show variable preservation, but in general the shells that were originally aragonitic (the gastropods and clams) show more dissolution and recrystallization than the mixed calcite/aragonite mussel shells, an observation consistent with prolonged seawater interaction (Fig. S5). The Ghost City mollusk assemblage shares five taxa with living MAR axial high-temperature vent communities (3, 52–54), including two locally at Rainbow (*Bathymodiolus* and *Protoliria*), and two taxa associated with sedimented vent sites (Table S3). The Ghost City *Phreagena* sp. is also found at the recently described Clamstone site, an inactive (approximately 25 kyr BP) serpentine-hosted sedimented vent field near Rainbow (approximately 1.2 km east of Ghost City, at a depth of 1,980 m) (55). Thyasirid clams that may be conspecific with the Ghost City *Thyasira* sp. occur at Clamstone (55), Anya’s Garden, a sedimented vent site in the Logatchev area (52, 56, 57), and have also been reported in
soft sediments at Lost City (20). Thus, the Ghost City mollusk fauna is a mixture of MAR vent species from sedimented sites and more typical chimney habitat mussel bed communities. Although Ghost City fauna has a higher biomass, the mollusc species list is not greatly different from Lost City communities, with three mollusk species shared between the two sites: *B. azoricus*, *Thyasira* species, and the gastropod *Lurifax* (see Table S3).

### High-Biomass Vent Communities Supported by Serpentinization Fluids

The Ghost City carbonates demonstrate that (i) high-biomass populations of *Bathymodiolus* mussels and other symbiont-hosting mollusks can be supported by metal-depleted and likely alkaline fluids, similar to the serpentinization-related vent fluids described at Lost City; and (ii) these communities have been present on the axis of the MAR for at least 110,000 years. The flexible *B. azoricus* dual symbiosis responds to variations in the methane-to-sulfide ratio in the environment (24, 25), making this species particularly well adapted to the variety of fluid chemistries that are found on the MAR (8, 58). The Ghost City fossil mollusks might therefore also have relied on methanotrophy and, potentially, on sulfide, or even hydrogen, oxidation as primary energy sources, the most likely explanation is to be searched for in the rotary drill with a diamond-tipped Burr. The shell sample powders were pretreated with 1.5 % NaClO for 30 min to remove organic contaminants, rinsed three times with distilled water following a protocol modified after (64, 65). All carbonate powders were acidified in 100% phosphoric acid at 50 °C under vacuum. The produced CO$_2$ was collected and analyzed using a mass spectrometer. Isotopic data are reported in conventional delta notation relative to the Vienna Pee Dee Belemnitne (VPDB).

### Carbon and Oxygen Stable Isotopes Analyses

Analyses of three *Bathymodiolus* aff. *azoricus* shells and 13 carbonate matrix (authigenic carbonate and infill-sulfide) samples were acquired on a VG Micromass 620 mass spectrometer. Additionally, five shells of living *B. azoricus* from the Rainbow vent field were analyzed. Powdered samples from mussel shells for the isotopic analyses (3–4 mg) were obtained from the cleaned outer layer using a rotary drill with a diamond-tipped Burr. The shell sample powders were pretreated with 1.5 NaClO for 30 min to remove organic contaminants, rinsed three times with distilled water following a protocol modified after (64, 65). All carbonate powders were acidified in 100% phosphoric acid at 50 °C under vacuum. The produced CO$_2$ was collected and analyzed using a mass spectrometer. Isotopic data are reported in conventional delta notation relative to the Vienna Pee Dee Belemnitne (VPDB).

### Uranium/Thorium and Strontium Analyses

Analyses were made in the Pôle Spectrométrie Océan (Brest) on a Neptune MC-ICPMS. For uranium and thorium isotope measurements, about 2 mg of carbonate sample was dissolved in 7.5M HNO$_3$ and spiked with a mixed U/Th spike (66). U and Th were separated chemically using conventional anion exchange techniques adapted from previous studies (67). U and Th concentrations and isotope ratios were then measured in the MC-ICPMS. The carbonate age was corrected for detrital contamination (inherited $^{230}$Th) using measured $^{232}$Th concentrations and assuming a typical $^{232}$Th/$^{238}$Th ratio (150,000) for the contaminant detrital phase, but this correction was insignificant on the calculated age (about 1%). Strontium was isolated using Sr resin and the isotope ratios were measured using the MC-ICPMS. Isotope ratios were normalized to $^{88}$Sr/$^{87}$Sr = 0.1194 and corrected from $^{86}$Sr/$^{88}$Sr interferences on the $^{87}$Sr and $^{86}$Sr signal, respectively.

### Acknowledgments

We thank captain and crew of R/V Atlantis; the remotely operated vehicle Victor operation group; the MoMARDREAM scientific party for their support during the MoMARDREAM cruise; E. Rongemaile, N.-C. Chu, and E. Ponzevera for analytical work; E. Krylova for vescimyid and thyasirid bivalve identification; and A. Wéren for benthic gastropod identification. T.M. Shank and A.L. Meistertzheim are also thanked for their helpful comments. The manuscript also benefited from helpful comments from G. Proskurowski and one anonymous reviewer. Centre National de la Recherche Scientifique (CNRS)-INSU, CNRS-INEE, IFREMER, and GENAVIR acknowledge financial support from TOTAL and UPMC to the chair “Extreme environment, biodiversity and global change.”


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