

A New Type of Carbonate Rocks on the Ocean Floor (Mid-Atlantic Ridge, 30°07' N)

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The Mid-Atlantic Ridge (MAR) is crosscut by a complicated system of transform faults. Intersection of these structures is marked by tectonically weakened zones, which serve as conduits for the exhumation of products of hydrothermal alteration of deep-seated rocks to the ocean floor surface if physicochemical conditions are favorable for the process. In 2000, the first active hydrothermal field (Lost City) with brucite–carbonate mineralization and an anomalous fluid composition was revealed at the intersection of the MAR and the Atlantis Fracture Zone [1]. At the same time, an inference was made on the possible wide distribution of such hydrothermal mineral associations on the ocean floor [2]. Currently, active investigations of the field are still in progress [3–5].

In 2005, study of the southern slope of the Atlantis massif near the Lost City field using the manned submersible Mir-2 during cruise 50 of the R/V *Akademik Mstislav Keldysh* discovered carbonate rock buildups (up to 1.5 m high) that were light-colored or covered with a black Fe–Mn crust [6, 7]. Ferromanganese crusts up to 2–3 mm thick are characteristic of the low-temperature (waning) stage of hydrothermal mineral formation. The floor area with carbonate rock exposures is located at a depth of 1016–1072 m. The area is covered with shells of extinct bivalve mollusks of the genus *Bathymodiolus azoricus* that are widespread in benthic associations of MAR active hydrothermal fields. This area of the ocean floor was named Lost Village [6, 7]. The field extends for 80–100 m from north to south and for 25–40 m from west to east. This new inactive hydrothermal field is also interesting because of its location

in immediate proximity to the Lost City active hydrothermal field. The nature of the hydrothermal fluid in this field and of the brucite–carbonate edifices (up to 60 m high) formed from the fluid poses many questions and remains debatable [1–5].

The aim of the present study is to establish mineralogical and geochemical features and the genesis of carbonate rocks of the inactive Lost Village hydrothermal field.

Carbonate rocks of this field are mainly composed of CaO and an appreciable admixture of MgO. In addition, Fe₂O₃ and MnO are found in the black surface crust (table).

The carbonate constituent of the Lost Village field is represented by a mixture of calcite and aragonite. The aragonite content varies from 3–5% near the surface of the studied specimen to 30–70% in its central part. X-ray diffractometry of point samples taken from the specimen surface (26 samples) established the presence of a pure CaCO₃ end member, as well as isomorphous CaCO₃–MgCO₃–FeCO₃–MnCO₃ mixtures (Fig. 1). The observed shift of the interplanar spacing in the studied samples is related to the replacement of Ca by

Content of major oxides (%) in carbonates of the Lost Village hydrothermal field (specimen 4806-3)

Oxide	Inner zone		Black crust
SiO ₂	1.35	1.95	0.38
Al ₂ O ₃	0.37	0.81	0.26
Fe ₂ O ₃	0.22	0.56	2.22
MgO	2.40	1.46	1.24
CaO	49.6	50.3	49.7
K ₂ O	0.083	0.14	0.076
TiO ₂	0.024	0.048	0.2
MnO	0.067	0.073	0.82
L.O.I.	44.8	43.6	44.0

Note: X-ray fluorescence analysis (T. G. Kuz'mina, analyst).

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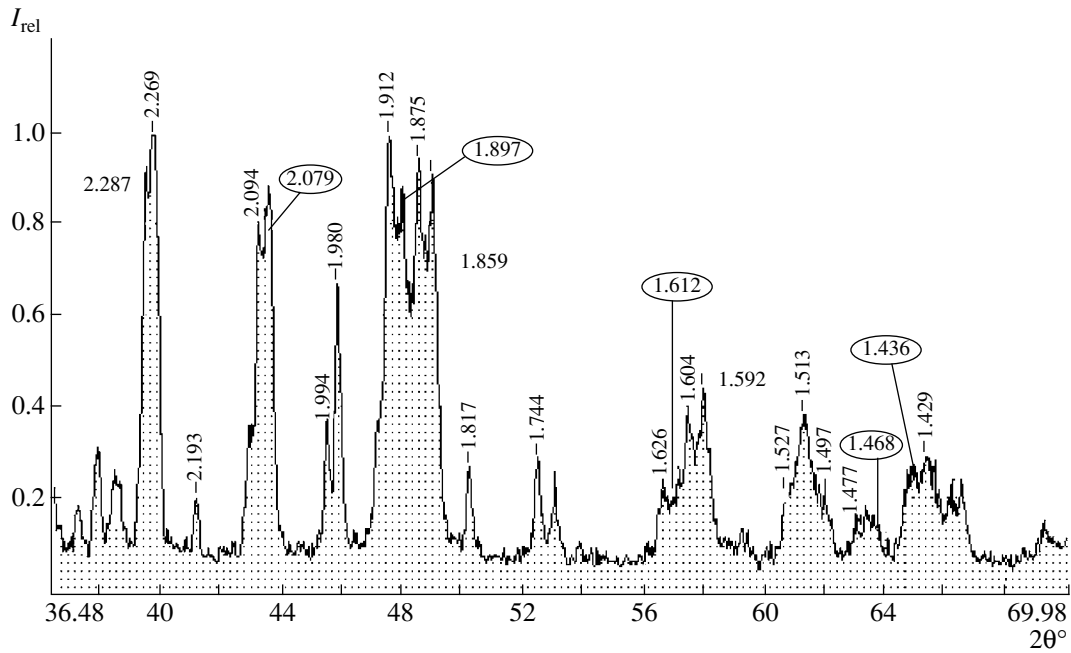


Fig. 1. A fragment of the typical diffractogram of isomorphically replaced calcites (sample 23) in the Lost Village field. The splitting of all basic diffraction reflections indicates the simultaneous presence of calcite with different cation compositions (DRON-2.0 with $\text{CuK}\alpha$ -radiation and graphite monochromator, IO RAS).

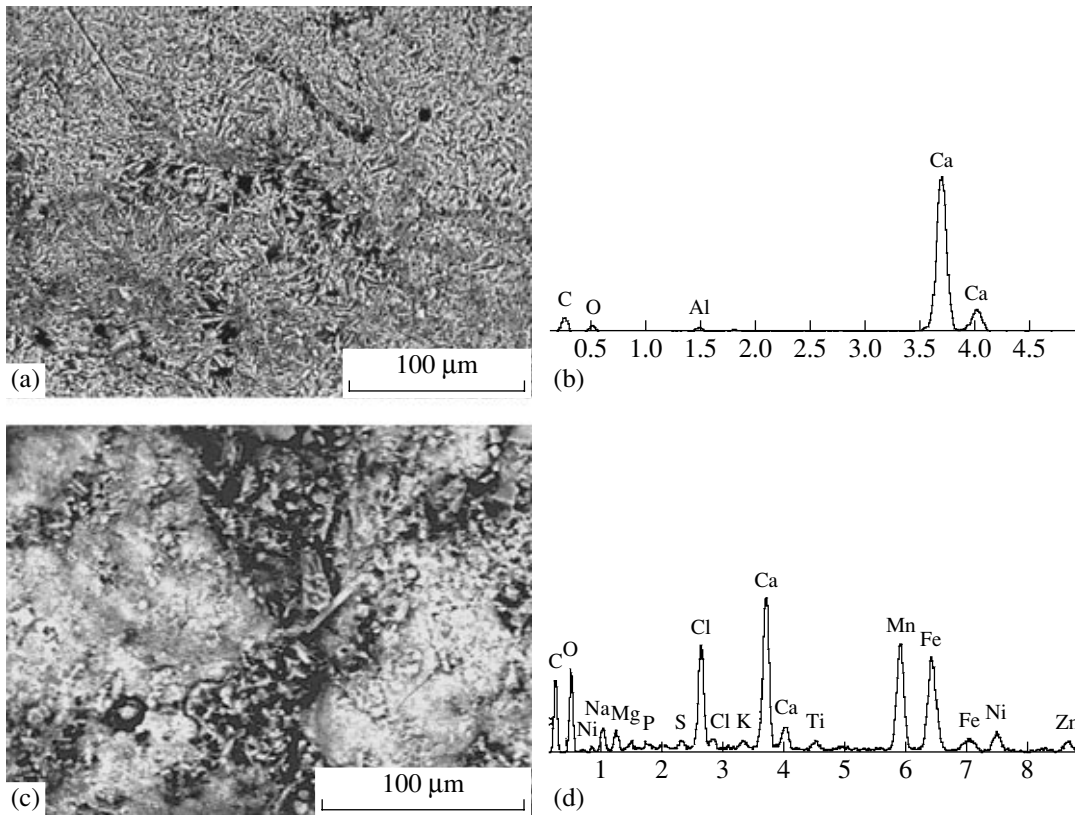


Fig. 2. Aragonite–calcite rock in the new inactive Lost Village hydrothermal field. (a, b) Central zone: dark and light areas are calcite and aragonite, respectively; (a) reflected electron image, (b) energy-dispersive spectra (EDS) of the calcite + aragonite mixture; (c, d) carbonates in close intergrowth with Fe–Mn minerals in the black surface crust; (c) reflected electron image, (d) EDS of the birnessite + vernadite mixture (SCAN JSM-5300 with INCA energy-dispersive spectrometer and LINK ISIS analyzer).

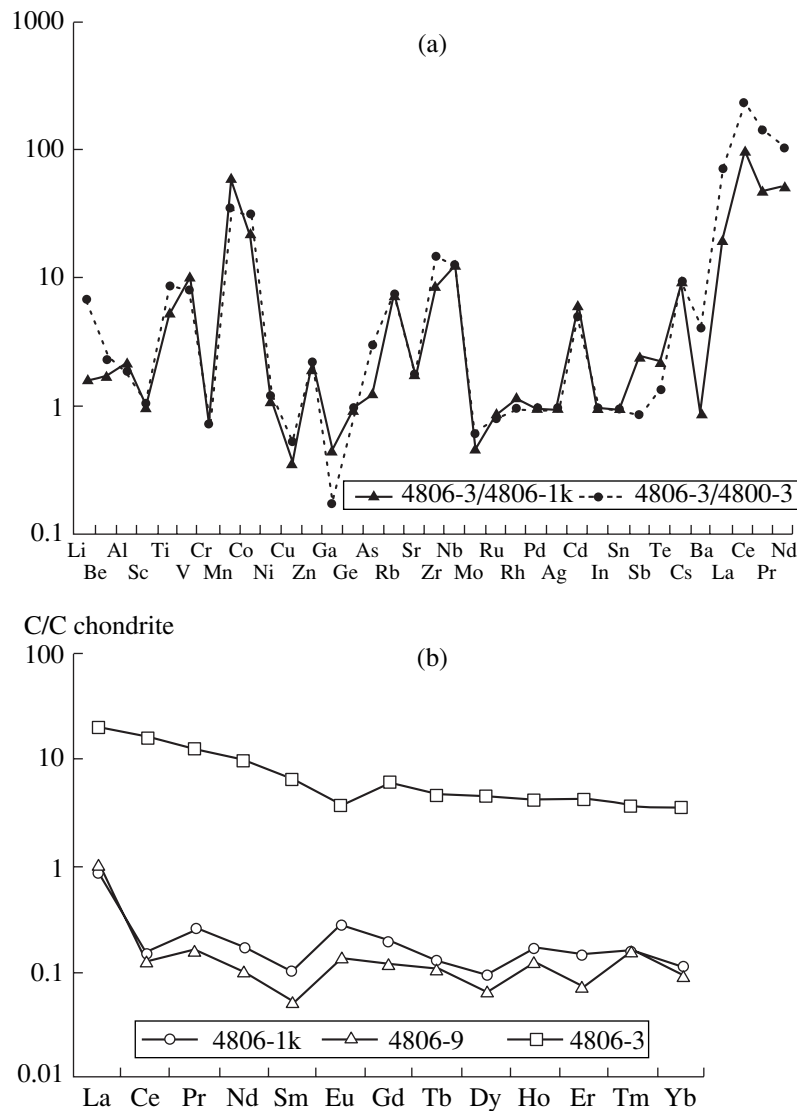


Fig. 3. Spidergrams: (a) composition of microelements in carbonates of the Lost Village hydrothermal field (specimen 4806-3) normalized to brucite-carbonate (specimen 4806-1k) and carbonate (specimen 4800-3) rocks of the Lost City active hydrothermal field; (b) REE composition in carbonates of the Lost Village (specimen 4806-3) and Lost City (specimens 4806-1k, 4800-3) fields normalized to chondrite (Boynton, 1984) (ISP MS, Perkin Elmer ELAN 6000).

Mg (up to 5.3%), Fe (up to 0.3%), and Mn (up to 0.1%) due to prolonged contact with the ambient ocean water. Isomorphically replaced calcites were found only in surface areas of the carbonate rocks. Aragonite in the inner parts of carbonate blocks makes up close intergrowth with calcite, which includes only Ca cations (Fig. 2).

Brucite is absent in both rocks of the Lost Village hydrothermal field and edifices of the Lost City field located far from sites of fluid seepage [8]. Birnessite and Fe-free vernadite occur in the black surface film as a fine intergrowth with X-ray amorphous material of an Fe-Mg-Mn composition (Fig. 2). Ferruginous protophase and nontronite were also found as thin films on carbonates from surface areas of the rock. Such a min-

eral assemblage is characteristic of low-temperature hydrothermal products.

As compared to minerals of the brucite-carbonate assemblage of the Lost City field, minerals of the aragonite-calcite assemblage of the Lost Village field are enriched in microelements (Fig. 3a) and LREE (Fig. 3b) derived from the ambient ocean water. In REE spectra of carbonates from the Lost Village field (Fig. 3b), the positive Eu anomaly typical of mid-ocean ridges is not retained and the negative Ce anomaly typical of oceanic carbonates has been leveled [9].

The Sr concentration in carbonate rocks of both fields exhibits values of the same order of magnitude (1288–3021 ppm). A high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is characteristic of brucite-free carbonate rocks. The Sr isotope ratio

in the aragonite–calcite assemblage of the Lost Village field is equal to 0.709 ± 11 (MC TRITON TIMS), which fits the limits known for the aragonite–calcite assemblage in active and inactive edifices of the Lost City field [4]. The values obtained are close to the average Sr isotope ratio in the present-day ocean water (0.70916) [10]. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is noticeably lower than in ocean water only in the brucite–carbonate mineral assemblage and varies from 0.706891 ± 13 to 0.707864 ± 17 [4]. These values prove the participation of magmatic rocks in the formation of the Lost City hydrothermal solution, from which brucite and carbonates precipitate as the primary generation of minerals in edifices.

In the Lost Village field, $\delta^{13}\text{C}$ values in carbonates vary from 0.96 to 1.42‰; $\delta^{18}\text{O}$ values, from 4.23 to 5.34‰ (Fig. 4). On the one hand, the values obtained fit the limits characteristic of marine sedimentary carbonates. On the other hand, they are close to the isotopic composition of carbonates from the brucite-free aragonite–calcite assemblage of the Lost City active field, which yielded close $\delta^{13}\text{C}$ (1.49–12.07‰) and $\delta^{18}\text{O}$ (4.29–5.50‰) values [1–4]. It should be noted that carbonates from the brucite-containing assemblage in the Lost City field are depleted in ^{13}C and ^{18}O ($\delta^{13}\text{C} = 0.4$ – 0.79 ‰, $\delta^{18}\text{O} = 0.51$ – 3.43 ‰) (Fig. 4). This fact once again highlights the difference in the geochemistry of carbonates of the primary hydrothermal brucite-containing assemblage and carbonates of the aragonite–calcite assemblage.

The geochemical studies carried out suggest a similar genesis of carbonate rocks in the Lost Village field and the Lost City edifices. It was established previously that the age of hydrothermal structures of the Lost City edifices varies from <50 yr to 30 ka [3, 8]. The youngest of them are represented by the brucite–aragonite–calcite assemblage formed around the hydrothermal springs. The diagenetic alteration of primary hydrothermal brucite–carbonate rocks under the influence of the ambient ocean water promotes a gradual complete dissolution of brucite, as well as partial dissolution and recrystallization of carbonates.

Brucite-free hydrothermal carbonates older than 50 yr (conditional value) in the Lost City edifices and, probably, the Lost Village field were in contact with the ambient ocean water for a long time. This is evidenced not only by mineralogical data, but also by higher contents of microelements and REE derived from ocean water, the Sr isotope ratio, and the carbon and oxygen isotopic compositions in carbonates.

The abundance of shell valves of *Bathymodiolus azoricus* mitilids, their drusoid accumulations on the floor, and the confinement of shell accumulations to carbonate buildups on the floor indicate that the shells dwelled in this region of the floor and were not transported from shallow zones. Discharge of the hydrothermal fluid was necessary for the existence of benthic assemblage with mitilids.

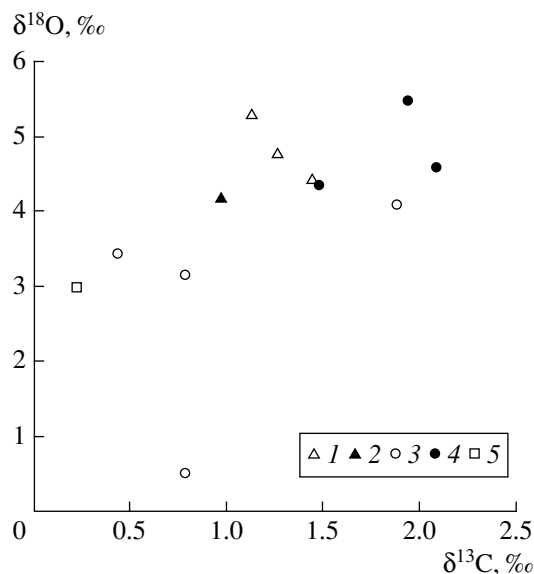


Fig. 4. Isotopic composition of carbonates ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of the inactive Lost Village hydrothermal field and the active Lost City hydrothermal field. (1, 2) Carbonates (aragonite + calcite) of the Lost Village field: (1) inner zone of light-colored dense carbonates, (2) carbonates near the contact with the outer thin black Fe–Mn crust; (3–5) carbonates of the Lost City field: (3) active zone of fluid seepage at the top of a giant (60 m) edifice (brucite–aragonite–calcite assemblage), (4) the same site, aragonite–calcite assemblage in the specimen taken at some distance from the source, (5) coral near the edifice base.

Termination of the hydrothermal activity provoked the death of the biotic assemblage and probably a partial change in the morphology and composition of carbonate rocks due to exchange with ocean water.

The studies showed that not only sedimentary and hydrothermal carbonates, but also carbonates of a mixed genesis can form on the ocean floor in the case of prolonged contact of the primary hydrothermal carbonates with the ambient ocean water.

The discovery of the first inactive hydrothermal field with carbonate mineralization in the MAR confirms the possibility of a wide distribution of low-temperature hydrothermal carbonates and their altered varieties on the ocean floor. This will require, in turn, significant revision of the model of geochemical cycles of Ca^{2+} and carbon in the ocean.

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