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Cinnabar, arsenian pyrite and thallium-enrichment in active shallow submarine hydrothermal vents at Paleochori Bay, Milos Island, Greece

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We herein report the discovery of active cinnabar-depositing hydrothermal vents in a submarine setting at Paleochori Bay, within the offshore southeastern extension of the Milos Island Geothermal Field, South Aegean Active Volcanic Arc. Active, low temperature (up to 115 °C) hydrothermal venting through volcaniclastic material has led to a varied assemblage of sulfide and alteration mineral phases in an area of approximately 1 km2. Our samples recovered from Paleochori Bay are hydrothermal edifices composed of volcaniclastic detrital material cemented by pyrite, or pure sulfide (mainly massive pyrite) mounts. Besides pyrite and minor marcasite, the hydrothermal minerals include cinnabar, amorphous silica, hydrous ferric oxides, carbonates (aragonite and calcite), alunite-jarosite solid solution and Sr-rich barite. Among others, growth textures, sieve-textured pyrite associated with barite, alunite-jarosite solid solution and hydrous ferric oxides rims colloform-banded pyrite layers. Overgrowths of arsenian pyrite layers (up to 3.2 wt. % As and/or up to 1.1 wt. % Mn) onto As-free pyrite indicate fluctuation in As content of the hydrothermal fluid. Mercury, in the form of cinnabar, occurs in up to 5 μm grains within arsenian pyrite layers, usually forming distinct cinnabar-enriched micro-layers. Hydrothermal Sr-rich barite (barite-celestine solid solution), pseudocubic alunite-jarosite solid solution and Mn- and Sr-enriched carbonates occur in various amounts and closely associated with pyrite and/or hydrous ferric oxides. Thallium-bearing sulfides and/or sulfosalts were not detected during our study; however, hydrous ferric oxides show thallium content of up to 0.5 wt. % Tl.

The following scenarios may have played a role in pyrite precipitation at Paleochori: (a) H2S originally dissolved in the deep fluid but separated upon boiling could have reacted with oxygenated seawater under production of sulphuric acid, thus causing leaching and dissolution of primary iron-rich grains from the volcaniclastic components of the sediments and resulting in precipitation of pyrite; (b) the iron may also have been derived by the near-neutral reduced hydrothermal brines and precipitate metal sulfides as a result of cooling, mixing with seawaters; the necessary iron content to form sulfides is mostly derived from primary iron-rich components of the basement; (c) biological activity may have resulted in pyrite deposition (e.g. sulfur is provided by a biogenic reduction of marine sulphate).

The mineralogy of hydrothermal precipitates considered in the present study resemble hydrothermal products from other shallow water venting areas elsewhere: Lihir and Ambitle Islands, Papua New Guinea, Kraternaya Bight, Kuriles, Russia, Punta Mita and Bahía Concepción, Mexico and Punta Banda at Baja California. The Paleochori vents contain the first documented occurrence of cinnabar on the sea floor in the Aegean area and provide an important link between offshore hydrothermal activity and the mercury-depositing mineralizing system on Milos Island. An interplay between bacterial activity, pH, Eh, temperature, precipitation rate and iron concentration resulted in precipitation of As-pyrite with interlayered cinnabar, hydrous ferric oxides enriched in thallium, alunite-jarosite solid solution and carbonates.