



1 Biogenicity of Mn-mineralized Microbes from a Seafloor- Paleohydrothermal Vent System, Vani, Milos, Greece: Relevance to Mn-oxide Biomineralization

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Preservation of manganese oxide microfossils in the rock record is extremely rare and little is known about biogenicity of Mn-oxides in hydrothermal manganese deposits. Experimental synthesis of biogenic Mn-oxides under geologically relevant conditions suggest they are a complex mixture of nanoparticulate, relatively amorphous, or cryptocrystalline todorokite, birnessite, and busserite biominerals. Here we present a range of geological/mineralogical, morphological, chemical and molecular evidence that identify fossil bacteria and biominerals associated with a Quaternary hydrothermal Mn- deposit, located on Milos island, Greece.

The clearest evidence is given by: (1) The life-supporting geological environment—The low-temperature (approx. 100°C) and sunlit seafloor paleo-hydrothermal vent system at Vani is ideal situation for supporting biological processes; (2) The syngensis of hydrothermal minerals and microfossils—Mn oxide minerals are pseudomorphs after bacteria, and tubular biotextures also occur in gangue silica; (3) Mor-

phological bioindicators—FEG-SEM and TEM imaging reveals the presence of Mn-mineralized biofilms formed by extracellular polymeric substances and colonies of spherical, coiled and rod-shaped fossil bacteria, approximately 0.5 to 1 μm size; (4) Large oxygen isotope fractionation—Mn oxide separates give $\delta^{18}\text{O}$ values ranging from $\delta^{18}\text{O}$: -3.76% , to $\delta^{18}\text{O}$: $+9.1\%$, and suggest microbial activity during mineral precipitation; (5) Organic biomarkers—Lipids were extracted from the Mn-oxides using the Soxhlet apparatus and gas chromatography mass spectrometry showed that they were dominated by a variety of compounds that included branched fatty acids (C_{15} and C_{17}) and hopanoids derived from bacteria; (6) Biominerals—HR-TEM images show typical todorokite nanocrystalline needle morphology showing 9.8 and 1.4 \AA spaced lattice fringes. SAED patterns on these show strong circles at 2.4 \AA . EDS analyses on Mn oxide nanoparticles are also consistent with todorokite, with composition of about 67% MnO_2 in addition Ba, Mg, K, Na and Ca always present; in addition todorokite contains Pb ($\text{PbO} < 1 \text{ wt } \%$) and Zn ($\text{ZnO} < 1.5 \text{ wt } \%$).

These data strongly suggest that microbial processes have played a significant role in mineral precipitation in the Vani seafloor paleohydrothermal vent system and indicate a clear role for biological processes and metal sequestration in the shallow submarine hydrothermal environment.