Evidence of Mn-oxide biomineralization, Vani Mn deposit, Milos, Greece

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ABSTRACT: We present evidence that precipitation of primary Mn-oxide minerals in the Vani volcanic hosted hybrid epithermal-VMS-type Mn-oxide and barite deposit was in part biogenically mediated. Manganese-oxides pseudomorphically replace small (1–5 μm) spherical cell-like structures, and branching filamentous constructions (< 60 μm long) probably representing manganese oxidizing bacteria. In addition, silicified consortia of spherical (5–10 μm), filamentous, sheathed, septate and spiral (~50–200 μm) fossilized bacteria, proposed to represent photosynthetic thermophilic cyanobacteria, were found in quartz paragenetically related to the Mn ore. Fluid inclusions indicate formation temperatures around 100°C. XRD and EMP analyses suggest X-ray-amorphous hollandite-group like Mn-oxide phases, and poorly crystalline todorokite and vernadite. These findings suggest a biological link between bacterial and mineralization processes.

KEYWORDS: biogenic Mn-oxides, todorokite, Milos, fossil bacteria

1 INTRODUCTION

Bacteria, as well as fungi, play a dominant role in the oxidation of dissolved Mn^{+2} in natural aqueous systems leading to Mn^{+4} oxide mineral precipitation (Tebo *et al*. 2004). In addition, manganese bio-oxides have been experimentally synthesized using Mn(II)-oxidising bacteria to catalyse Mn(II) oxidation (*see* Tebo *et al.* 2004 and references therein). Biogenic Mn-oxide mineral deposition has been reported in relation to modern submarine hydrothermal mineralization from the Lau Basin (Juniper & Tebo 1995), Juan de Fuca Ridge (Buatier *et al*. 2004). However, there has been little evidence so far of biogenically precipitated Mn-minerals associated with manganese deposits (Tebo *et al.* 2004). The Vani Mn-oxide deposit, Milos, offers an unique opportunity to study Mn-biomineralization because its sunlit shallow-marine seafloor venting paleo-hydrothermal system (Plimer 2000; this study) is ideal environment supporting biological processes (*e.g.* Reysenbach & Cady 2001). Vani has been considered by previous workers as a stratabound Mn deposit formed by subseafloor replacement of porous volcaniclastic rocks (Glasby *et al.* 2005; Liakopoulos *et al*. 2001; Hein *et al*. 2000), diagenetic processes (Skarpelis & Koutles 2004) and submarine hot spring-type processes (Plimer 2000).

This paper reports, for the first time, geological, mineralogical and fossil-bacteria evidence for Mn biomineralization in the volcanic-hosted transitional epithermal and shallow-marine exhalative system of Vani.

2 GEOLOGICAL EVIDENCE

The Vani Mn deposit occurs on the island of Milos, which is located on the active south Aegean Volcanic arc. Milos comprises U. Pliocene–Pleistocene calc-alkaline, volcanic and sedimentary successions that document the transition from the shallow submarine to subaerial volcanic environments (Stewart &McPhie 2006). Milos hosts the first documented example of hybrid VMS-epithermal Au–Ag (±base metals) deposits (Naden *et al*. 2005; Kilias *et al*. 2001).

The Vani Mn-ores are spatially associated with U. Pliocene–L. Pleistocene (2.5–1.5 Ma) submarine to subaerial dacitic volcanic complexes; mineralization is hosted in medial to distal fossiliferous (Haustator biblicatus sp.-Skarpelis & Koutles 2004; P. Koskeridou, *pers. Comm.*) synvolcanic sandstone, and within underlying dacitic hyaloclastite (Stewart &

McPhie 2006).

Manganese mineralization in Vani exhibits a range of ore deposit styles:

− *Sub-seafloor replacements, infillings and impregnations;* —these occur as stratiform to stratabound Mn-oxide sheets and lenses at at least three different levels within the hosting volcaniclastic succession.

− *Mound- and/or sheet-style shallow-water seafloor exhalative mineralization*—this occurs in the form of Mn-oxide rich chaotic melange of collapsed, toppled, eroded, and brecciated, and/or in situ white smoker chimneys and chimney rubble, debris and fragments (Fig. 1A). This ore type is buried in hydrothermally altered (adularia, sericite, chlorite, kaolinite, montmorillonite and silica; Likaopoulos *et al*. 2001) bioturbated sandstone. The morphology of this ore type is very similar to U. Pliocene to Pleistocene hydrothermal Mn chimneys from Central Pacific pelagic sediments (Usui *et a*l. 1997). Chimney textures and zonations are similar to those observed in modern ocean floor black smoker hydrothermal vents (*i.e.* Herzig & Hannington 1995; Fouquet *et al*. 1993), and the Palaeochori bay active hydrothermal field in southern Milos (Valsami-Jones *et al.* 2005).

– *Mn-oxide hydrothermal crusts (geyserite, exhalite)* occurring as cauliflower structures (Fig. 1C) and plates; these are identical to those found in the Hine-Hina field of the Lau Basin (Fouquet *et al*. 1993).

− *Structurally controlled stringer networks* that occur in the stratigraphic footwall of dacitic hyaloclastite, through the stratabound Mn-oxide ore and also in the volcaniclastic sandstone in the hanging wall. This network is enveloped by adularia-sericite-chlorite$\pm$pyrite alteration. The stockworks share the same textural and fluid characteristics with the Profitis Ilias transitional VMS-epithermal Au–Ag deposit south of Vani (Kilias *et al.* 2001; Naden *et al.* 2005), and modern epithermal systems (Hedenquist *et al.* 2000).

− *Subaerial Mn-rich mud pools*—these are rare in occurrence and exhibit preserved concentric rings that are interpreted to be bubble collapse structures (Fig. 1D) and may indicate localised subaerial exposure of the hydrothermal system.

3 MINERALOGICAL EVIDENCE

X-ray Diffraction and Electron Microprobe analyses suggest that Mn-oxides consist of X-ray-amorphous hollandite-group-like minerals (BaO: 2–14 wt %, PbO 1–11 wt %), romanechite-like and MnO_2-like phases; in addition XRD studies reveal the presence of poorly-crystalline todorokite and vernadite which are known as biogenic minerals (Tebo *et al.* 2004).

4 FLUID INCLUSION EVIDENCE

Aqueous two-phase fluid inclusions (L>V) in barite and quartz from stringer networks, chimneys and sheet-like ore show first melting temperatures (T_e) from –41.5 to –35 °C that cluster around –35 °C, hydrohalite melting (T_{hyd}) from –25.2 to –19 °C and $T_{m\text{-}ice}$ between –12.4 and 0.2 °C. Low temperature microthermometric data are comparable to those of seawater and may be modelled by the H_2O–NaCl–$MgCl_2$ system (Dubois & Marignac 1997). Liquid homogenization temperatures (T_h) range from 95 to 297 °C. Salinities show a wide range from 0.1 to 17 wt % NaCl + $MgCl_2$ eq. T_h–salinity relationships are best explained by extreme boiling and vaporization of seawater and seafloor exhalative hydrothermal activity around 100 ^oC (minimum T_h), and, mixing of seawater either with condensed boiled-off vapour or heated meteoric water. Pressure estimates suggest seawater depths of 40 to 50m and hydrostatic depths of at least 100-150m for

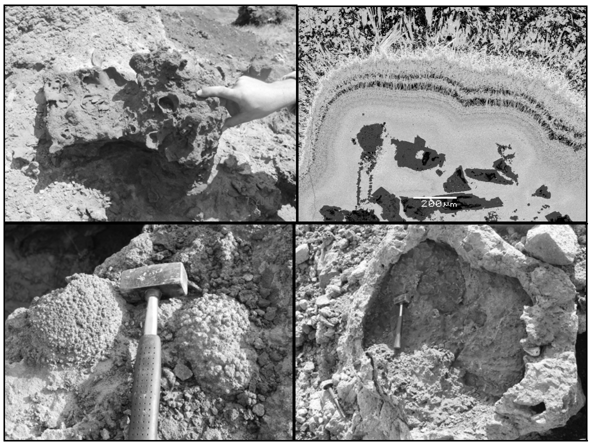

Figure 1: (A) Collapsed rubble of tubular Mn-chimneys and chimney fragments; chimney at the centre exhibits zoned walls;(B) SEM imaging of concentric zoning in a Mn-chimney: fine laminated alternating concentric aggregates of X-ray amorphous hollandite-group like Mn-oxide phases; (C) Mn-oxide hydrothermal crusts occurring as cauliflower structures; (D) Fossilized subaerial(?) boiling Mn-mud pool.

the stockwork/feeder zone. Combined with geological evidence this data indicate that Vani constituted a sunlit white smoker-type palaeohydrothermal system. The Vani palaeo-fluids are similar to the Palaeochori bay active seafloor exhalations (Valsami-Jones *et al*. 2005) in terms of salinity, temperature and phase.

5 FOSSIL BACTERIA EVIDENCE

SEM imaging and polarised light microscopy of samples from exhalative and hydrothermal edifices reveal manganese-mineralized and silicified textures resembling fossil biofilms and microbialites. These consist of small (1–5μm) spherical cell-like structures, and branching filamentous constructions (< 60 μm long). In addition, silicified consortia of spherical (5–10μm), filamentous, sheathed, septate and spiral (~50–200μm) structures were found in quartz veins related to manganese mineralization. We interpret many of these structures as fossil bacteria, or phenomena associated with bacteria. This is based on the identification criteria of Westall & Folk (2003):

− *Geological plausibility:* Sunlit seafloor venting hydrothermal systems like Vani are ideal environments for growth of bacteria under extreme conditions (Reysenbach & Cady 2001)

− *Size:* Most of the Mn mineralized, and silicified, structures in Vani (Fig. 2) fall within the size range of modern bacteria and cyanobacteria, respectively (Westall & Folk 2003).

− *Shape and Cell wall morphology:* The spherical structures, and the branching filamentous constructions in Vani Mn-ore have the morphological characteristics of modern Fe–Mn oxidising bacteria (Reysenbach & Cady 2001; Juniper & Tebo 1995); whereas the silicified spherical, filamentous, sheathed, septate and spiral (~50–200μm) structures are identical to living cyanobacteria (Fig. 2).

− *Cell division and reproduction textures:* Associations of two or more round shaped structures and branching is interpreted to represent bacterial cell division and vegetative reproduction respectively (Fig. 2B).

− *Colony formation and species consortia:* The great number of discrete clusters that resemble bacterial-like structures are interpreted as bacteria colony formation (Fig. 2B), while the consortia of many different species of round, oval, spiral and filamentous bacteriomorphs is consistent with modern bacterial occurrence.

− *Pseudomorphosis* (Southam & Saunders 2005): Hollandite-group-like minerals in Vani have pseudomorphs after bacteria (Fig. 2).

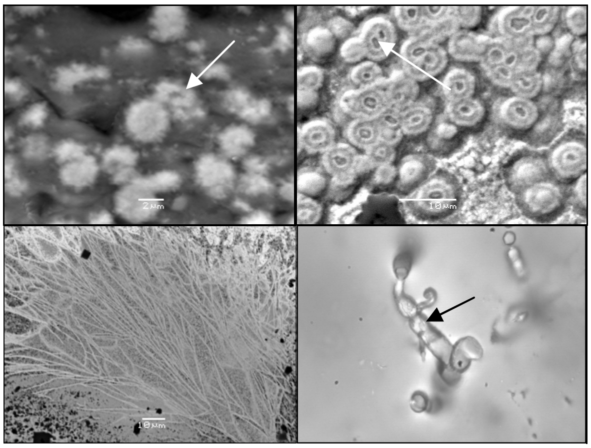

Figure 2: (A) Spherical, oval, deflated and irregular Mn-mineralized rod-like particles, possibly representing various bacterial metabolic stages from living to dead; arrow points to deflated structures suggested to be remnants of EPS; (B) Biofilm of Mn-mineralized bacterial cell colonies; arrow shows cell division structures; (C) SEM imaging of branching filamentous Mn-mineralized fossil bacteria; (D) Fossil filamentous and coccoid photosynthetic cyanobacteria hosted in vein-quartz; arrow shows structure as in vegetative reproduction (bar=10 μm)

6 CONCLUSIONS

Vani may represent the only example to date of a Quaternary shallow-marine (0–50m), emergent, hybrid epithermal-VMS-type Mn-oxide deposit, preserved on land. This geological setting combined with the identification of Mn-oxide and associated silica textures as fossil bacteria, the presence of todorokite and vernadite, and poorly-crystalline Mn-oxide phases, may support a bacterial origin for Vani Mn-ores. We envisage that photosynthetic cyanobacteria, and other manganese-oxidizing bacteria, have contributed to the formation of Vani by promoting chemical oxidation of Mn^{2+} and precipitation of Mn-oxides through the photosynthetic release of molecular oxygen and/or enzymatic chemical catalysis.

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