BIOGENIC VS GEOCHEMICAL PRECIPITATION OF MINERALS IN THE SUBMARINE HYDROTHERMAL VENTS OF PUNTA MITA, MEXICO

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SUMMARY – The submarine hydrothermal vents located in the vicinity of Punta Mita contain abundant deposition of calcite, pyrite. Also present are barite, carbonate hydroxyl-apatite, cinnabar and T1-sulfide. Textures indicate direct deposition for calcite and pyrite; however, pyrite also replaces magnetite in the host rock. Thermal water was filtered and microscopic analysis of the particles fiom the filters shows that the shape of the crystals varies from euhedral crystals of pyrite to globular aggregates that may be interpreted as a mixture of chemical and biogenic precipitation. Isotopic signature of sulfur in pyrite and carbon in calcite indicates that biogenic deposition is an important phenomenon in this hydrothermal system.

1. INTRODUCTION

The Fisura Las Coronas is located 500 m to the south of the Punta Mita peninsula (Fig. 1). Presently, hydrothermal fluid is being discharged at a temperature of 85°C along this feature. This activity takes place in a shallow ocean bottom from 9 to 13m depth. Due to the accessibility of the deposit, it was possible to sample the hydrothermal mounds and the host rock, which is composed of basalt, and unconsolidated sediments. Preliminary data on the structures, pH, and seismic activity in the study zone were reported by Núñez-Cornú et al. (2000). Shallow coastal hydrothermal activity, similar to that observed in Punta Mita, has been reported in' Punta Banda in Baja California (Vidal et al., 1978), associated to deep circulation of meteoric water.

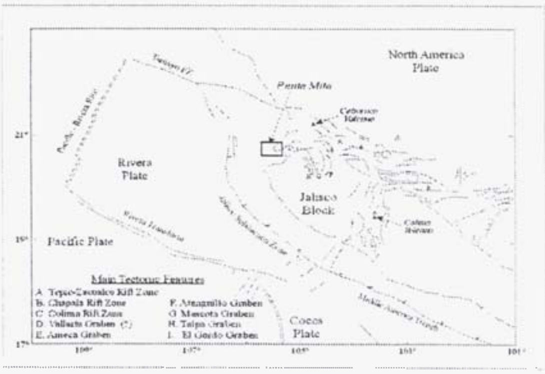

Fig. 1 Location of study area.

The occurrence of chemosynthetic microbial activities in the deep hydrothermal vents has been studied in detail (Jannasch, 1995). However, the presence of microbial activity in shallow hydrothermal vents has not been documented. Therefore, this study attempts to document the incidence of microbial activity in the deposition of minerals in the Punta Mita coastal vents.

2. PUNTA MITA SURFACE GEOLOGY

The Punta Mita area is located in the western coast of Mexico, in the NW border of the Jalisco Block. The tectonic history of this region is very complex and recent activity is shown as large structural features. The stratigraphic column contains units fiom the Paleozoic to the Quaternary (Fig. 2). Paleozoic rocks are represented by strongly deformed quartz-feldspatic and calcareous schist. The Cretaceous sequence contains limestone, and interlayered sandstone and siltstone with a carbonate matrix.

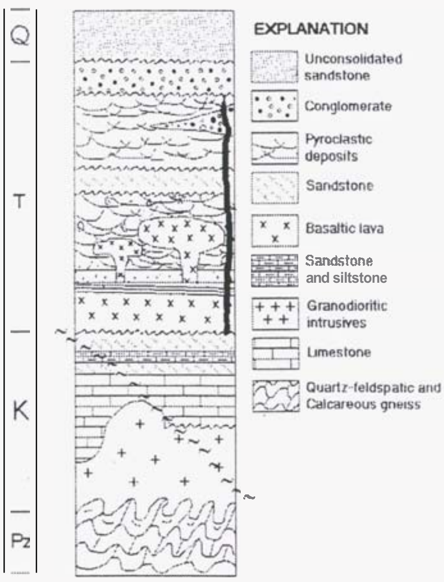

Fig. 2 Stratigraphic column in the Punta Mita area.

Tertiary rocks include intrusive, volcanic and sedimentary units. The base of the sequence consists of basaltic lava, pyroclastic flows and air fall deposits. This basaltic sequence is cut by almost vertical basaltic dikes that acted as feeders of pillow lava flows. The basalts are very vesicular and intensely altered to celadonite. This sequence is overlaid by an unconsolidated well-stratified air fall.

The Tertiary conglomerate includes fragments of granodiorite, granite, gneiss, ignimbrite and basalt. Locally, it presents silicification and is affected by vertical faults, especially between the Punta Mita and the Punta Negra area. The Quaternary deposits are mostly formed by medium grained stratified unconsolidated sandstone that has been recently uplifted. In the sea bottom, many vents are partially covered by unconsolidated platform sediments, and the discharge of gas is the only evidence of the hydrothermal activity. In some cases the deposited minerals form small mounds.

3. GEOCHEMISTRY OF THE FLUIDS

All water samples present different degrees of mixing with seawater; the least mixed are those with the largest flow rate. The chemistry of the water reveals a fluid more dilute than seawater; almost all trace elements are below detection limits, except for Mn, Ba and I, which are significantly enriched with respect to seawater (Prol-Ledesma et al., 2002).

The sampled gases show a predominance of nitrogen and methane, with low contents of carbon dioxide, argon, helium and hydrogen, and only traces of H_2S. Isotopic composition of carbon in methane yields a value of –42.8‰; this indicates a thermogenic origin for the organic gas.

4. MINERALOGY OF THE VENTS

Hydrothermal precipitates act as cement of the sands and also form mounds nearby the discharge areas. The fluid discharged by the vents deposits layers of sulfides, calcite and phosphate (Fig. 3).

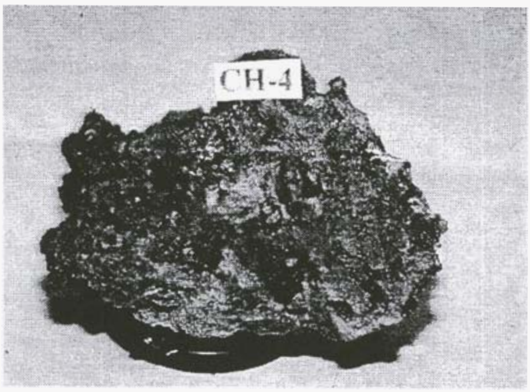

Fig. 3 Vent deposit from the Punta Mita submarine hydrothermal area.

4.1 Calcite

Calcite is by far the most abundant precipitate in this deposit and presents diverse textures. There is a first calcite generation with fibrous crystals up to 250 microns in length. The fibers occur as concentric aggregates with variable morphology: in the center they are mono-mineralic and less porous; in the more external zones the aggregates acquire a lobular morphology and increase their porosity, in such a way that the most external zone has arborescent texture. After this stage, a late fine-grained calcite generation appears. This calcite develops euhedral rhombohedral crystals (up to a few tens of microns in size) that cement the detrital and bioclastic grains. Cathodo-luminiscence and microprobe analyses do not show any variations in the chemical composition of all generations of calcite. The calcite composition is more than 95% $CaCO_3$, and the magnesium reaches only about 5%; strontium and sodium are present in small quantities, and iron, barium and manganese are not present in significant amounts. The low Ca/Mg ratio observed in many calcite crystals from the inner part of the vents indicate that they were not deposited from seawater. The carbon isotopic composition of the calcite varies from -39‰ to 0‰. The lowest value indicates that some calcite is produced by oxidation of methane and the values closer to 0 are evidence that some crystals were formed with seawater carbon.

4.2 Barite

Barite is developed as tabular, euhedral crystals having up to 50 microns in length that are usually arranged in radial or bow-tie groups. These groups occur during all the calcite deposition stages and within the vugs or in veins.

4.3 Carbonate-hydroxylapatite

Carbonate-hydroxylapatite was distinguished in the optical microscope and identified by XRD analysis. It is deposited in the inner part of the fluid channels, forming a series of bands in alternation with calcite. It also appears as a late filling in the porosity of the calcite aggregates.

4.4 Pyrite

Pyrite is the main sulfide mineral and occurs as thin colloform coatings (Fig. 4) in the inner part of the discharge channels and surrounding the vent openings.

Pyrite covers shells and pebbles that are cemented by calcite in the vents, and it was also observed as framboidal aggregates (up to 100 micrometers) disseminated in the calcite cement. Detrital magnetite grains are also locally replaced by pyrite. Backscattering electron images in the electronic microscope (SEM-BSE) show fine layering of the pyrite coatings (one micrometer approximate width) that alternate with carbonate in the thicker crusts.

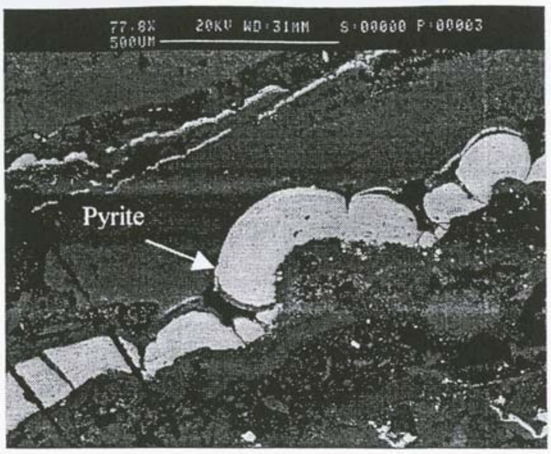

Fig. 4 Micrograph that shows layers of pyrite within calcite.

The range of $d^{34}S$ values in pyrite from the Punta Mita samples is from 10.7 to -4.9‰, and the D(seawater sulphate - sulphide) is from +32 to +27‰. These values indicate that sulphur form pyrite in Punta Mita comes fi-om the bacteriogenic reduction of seawater sulphate (Alfonso et al., *2002).*

4.5 Other sulphides

Cinnabar occurs in close association with pyrite, as aggregates up to 10 microns in size (bright minerals within the pyrite layers in figure 4), disseminated between pyrite and calcite layers (Prol-Ledesma et al., 2002). Small grains of an unidentified thallium mineral (up to 5 microns)'- were also observed in association with cinnabar. The only other sulphide present in the vents is galena, which is rather scarce and only few small grains have been identified within the pyrite layers.

4.6 Particulate matter

Particulate matter was collected with 0.4mm polycarbonate membrane filters and preserved in desiccators at a fridge temperature until analysis onshore. Filters containing hydrothermal particulate matter were surveyed under the scanning electron microscope in order to identify the chemistry of the particles. SEM examination revealed the presence of particles of different kind that suggests high degree of mixing and re-suspension: Planctonic organisms and organic matter appeared to be abundant; 25 micron particles of different carbonate faces and inorganic particles of silicates were also recognized. Barite crystals were also observed in the analysed filters. Distinctive euhedral grains of pyrite were identified as the result of precipitation fkom the solution (Fig. 5).

Fig. 5 Micrograph of the particulate matter in a filter from the Punta Mita water samples that shows a euhedral pyrite crystal.

Pyrite was also observed as globules that were possibly deposited by bacteriogenic reduction of seawater sulphate (Fig. 6). Cinnabar particles 8 micron in size are consistent with the mineralization conditions, observed in the discharge precipitate as well in the inner walls of the vent.

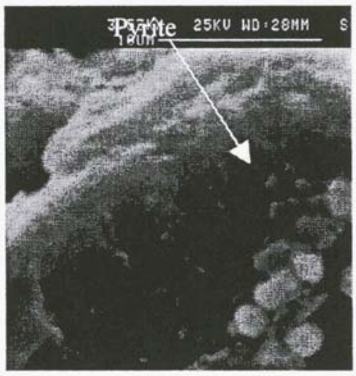

Fig. 6 Micrograph of the particulate matter from a filter from the Punta Mita water samples. The pyrite in this case forms globules deposited from the thermal fluid.

5. DISCUSION AND CONCLUSIONS

The textures of calcite and pyrite indicate that they are consistent with the, occurrence of microbial activity in the vents. Also, the carbonate (fluoro) apatite (CFA) precipitation may be favoured by the presence of bacterial products that would provide surfaces for its precipitation (Reimers et al., 1996). The isotopic values obtained for carbon in calcite down to -39‰ , and for pyrite from 10.7 to -4.9‰ cannot be explained on the basis of sole isotopic fractionation based on chemical deposition of these minerals.

Some of the methane is oxidized and calcite with carbon isotopic values similar to the methane is deposited in the vents. In addition to methane oxidation, calcite is deposited also from seawater carbonate

Sulphide is produced by bacterial reduction of the seawater sulphate. This causes deposition of pyrite, cinnabar and T1-sulphide.

6. REFERENCES

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