BIOMINERALISATION IN NEW ZEALAND GEOTHERMAL AREAS

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SUMMARY – Several experiments are currently underway to investigate the role of bacteria in the formation of unique textures in sinter deposits at New Zealand geothermal areas,. Preliminary results are presented fiom three areas: Wairakei, Rotokawa, and Waiotapu. In the Main Drain at Wairakei, thermophilic filamentous bacteria are growing at ~62°C at a rapid pace and are progressively sheathed or replaced by amorphous *silica*, building large 3-D fan-shaped structures. Siliceous microstromatolites at Rotokawa, located in the outwash from hot springs *(60* – 85°C), grow at a much slower rate maintaining a level just above the water surface. Growth is initiated on protruding pumice stones and wood fragments. At Champagne Pool, Waiotapu, siliceous microstromatolites grow on native sulphur accumulated around the pool edge or on protruding parts of the pool bottom. Their rate of growth (0.02– 0.03 mm day^{-1}) and size is greater than at Rotokawa. Orange precipitates in the pool, previously identified as flocculated antimony rich sulphides and sulphur, appear to be entirely biomediated. It is not known whether the bacteria are actively metabolising sulphur or antimony or whether biomineralization is passive. These biomineralization effects strongly increase surface areas for potential metal – mineral – microbe interactions and thus effect metal distributions in sinter deposits.

1. INTRODUCTION

New Zealand geothermal areas are well known for their spectacular surface features. The overall distribution of hot springs, geysers, mud pots, sinter flats and altered ground in each of these areas is a function of *structural,* topographic and hydrological parameters. However, micro-organisms have a role in determining local morphology and mineral textures, as well as, the spatial distribution of chemical components. Thermophilic organisms are remarkable for their ability to thrive in the solute-rich, high temperature waters of hot spring environments and all surface geothermal features are *expected* to contain viable microorganisms.

The presence of bacteria in hot springs *such* as those in Yellowstone and Iceland has been documented (Walter et al., 1972; Konhauser and Ferris, 1996) and contributions on the biofacies in sinter deposits of New Zealand are also available (c.f. Jones et al., 1997a,b). The discovery of viable bacteria in silica deposits in Iceland led to the conclusion that bacteria have evolved polysaccharide sheaths which prevent silicification of the bacteria wall and cytoplasm yet promote silica precipitation outside the cell thus *creating* biomediated sinter growth (Phoenix et al., 2000).

The present study was initiated to investigate the geochemical aspects of biomineralization using New Zealand geothermal areas as natural laboratories. It is not our aim to describe biofacies but to understand the chemical nature of the interactions between dissolved species and microbes. The initial objective is to conduct field experiments to determine the types of bio-mineralization and the rate of growth of this mineralization. This contribution presents some early results ftom three of the seven geothermal areas where experiments are currently underway.

2. METHOD

Seven *geothermal systems* were chosen for this study. These included Wairakei, Rotokawa, Waiotapu, Waikite, Ngatamariki, Orakei Korako, and Tokaanu. In each of these areas, glass microscope slides have been placed to allow bacterial growth and consequent bio-mineralization to form. Water samples were collected and analyzed for major components at the Wairakei Laboratory, IGNS. Table 1 lists the temperature, pH and location of slides in each area.

Table 1. Location, pH, and Temperature of Experiments*

System	Location	pH	T(°C)
Wairakei	Main Drain	8.5	49-66
	W59 Drain	8.2	83-86
	Kiriohineke stream	8.5	50-65
Rotokawa	North Springs	3.0	60-85
	Main upflow	3.8	82-90
	V-Notch	3.0	49
Waiotapu	Champagne Pool	5.5	71-75
Waikite	Artificial Terrace	7.6	55-100
Ngatamariki	Pool 3	7.2	83
Orakei Korako	Tim and Terry Geyser	7.4	76-91
Tokaanu	Old Bore	7.5	55-65

*Temperatures are variable. Approximate range is shown.

Samples of mineralizaiton were taken from each location. These were split and preserved in two ways. The first portion was preserved with 2.5% glutaraldehyde and retained for scanning electron microscopy (SEM) and transmission electron microscopy (TEM). This chemical is a preservative that prevents breakdown of organic material. The second portion was frozen without further treatment for later use in infrared studies.

3. RESULTS

3.1 Wairakei

Main Drain. Two plastic trays containing glass slides were placed in the Main Drain approximately 100 metres upstream from the drop structure to Waraikei stream (Fig. 1). This drain contains the combined wastewater from the western borefield. The chemistry of the water is fairly uniform throughout the drains with a pH ~8.5, 1900 ppm Cl^- and 570 ppm SiO_2. Under normal conditions, flow rate at the sample site is about I metre/second, however, this rate can increase during heavy rainfall. Temperature is normally uniform but can fluctuate dramatically if the station goes on bypass or there is a heavy rainfall. In March 2001, the temperature of the right drain was uniform at about 62°C, while that of the left drain had a strong gradient with a temperature of 62°C at the surface and progressing downwards tu a temperature of about 42°C at the bottom (~1.0 m).

Figure 1. Main Drain at Wairakei. Wastewater flows from left to right. Plastic tray containing glass slides hangs from bridge.

Mineralization in the drain consists of large, three-dimensional, fan-shaped accumulations attached to the concrete walls of the drain. The tips of the fans point downstream and their shape is partly hydrodynamic in origin (Fig. 2). The fans are normally white to pink in colour but after a heavy rainfall they turn dark brown due to trapping of suspended material. At the start of the experiment, the mineralization grew only in the right drain and in the top portion of the left drain indicating that temperature has some influence on its distribution. The cooler parts of the left drain were green in colour indicating the presence of thermophilic cyanobacteria.

SEM studies of the fans show they are composed of narrow fibres, ~2 μm in width and of unknown length, composed of amorphous silica. These fibres form a complex meshwork enclosing abundant void space. The fibres represent silica sheaths on, or replacements of, filamentous bacteria. This was confirmed by TEM that showed the presence of unmineralized filamentous bacteria (Fig. 3). Further evidence was found when underwater photographs were taken. The tips of the fans show fine filaments moving in the current that represent unmineralized bacteria. These fibres collapse when samples are removed from the water and thus are not visible.

Figure 2. Fan-shaped silica deposits on the concrete divider between the two channels of the main drain. Field of view approx. 1.5 metre. Water flows from bottom to top of picture.

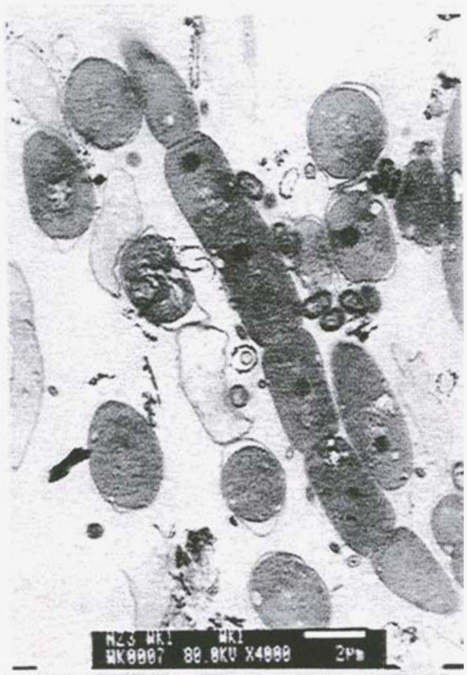

Figure 3. Transmission electron microscope photograph showing filamentous bacteria from Wairakei main drain. Scale bar is 2 μm.

Microbiologists at Hort Research successfully cultured these bacteria at 60°C. Bacterial cultures were pink in colour. This is attributed to the presence of a xanthene pigment that may help to protect the bacteria from ultraviolet light. The species of bacteria has not as yet been identified but they are thought to be autotrophs subsisting on dissolved CO_2 as their carbon source.

The original plan was to collect one glass slide on a monthly basis to determine biomineralization rates. However, the rate of silica growth is incredibly rapid and after one month the entire plastic tray was encased in amorphous silica. A second set of slides was placed in the drain and these were collected over about eight days. The weight of silica deposited on the slides was determined and an approximate growth rate of 10 g cm^{-2} yr^{-1} was estimated.

W59 Side Drain. This small drain was chosen because of its high temperature (~85°C) and close proximity to an operating bore (~20 m away). The flashed water is slightly more dilute (pH 8.21, 1450 ppm Cl^-, 390 ppm SiO_2) to that of the Main Drain. The W59 drain is lined with a thin, hard layer of silica that is dark gray in colour. A single plastic tray containing 6 slides was placed in the drain and these were collected on a monthly basis.

SEM examination of a specimen of amorphous silica showed an irregular agglomeration of rough anhedral grains. No other minerals were found and the explanation for the gray colouration is uncertain. Interestingly, careful searching revealed the presence of coccoid formed particles composed of amorphous silica (Fig. 4). These are interpreted to be the silicified remnants of bacteria. This is an example of the extreme resilience of some primitive forms of life. These bacteria are able to survive in fresh borewater at ~85°C that contains very little nutrients.

We were unable to measure the rate of growth of silica on the glass slides because they were unstable in the hot water and began to disintegrate after a couple of months. It is clear that the rate of growth is very slow.

Kiriohineke Stream, located on the south side of the Wairakei Borefield, has recently been cleaned out by NetCor for their tourist park scheme. The base of the stream is unconsolidated soil with a covering of leaves and branches. Small weirs, constructed of stones and branches, cross the stream along its length to slow water flow. Borewater (pH 8.3, 1900 ppm Cl^-, 580 ppm SiO_2) diverted from the Waraikei borefield passes through the stream. A thick layer of silica has deposited on stones and plant material.

Figure 4. Silicified coccoidal bacteria from W59 side drain.

The plastic tray and slides placed in the stream in March 2001 were rapidly encased in silica. After two months a layer approximately 1 cm in thickness covered the slides making their recovery difficult. The silica deposits were similar to those from the main drain, however, they lacked the oriented nature of the fibres and contain distinct green layers. These layers are attributed to the growth of cyanobacteria at times when the water temperature was lower. How these are preserved when temperature rises is uncertain. In general, SEM studies show textures similar to those found in the main drain with one interesting exception. Some samples show a distinct bimodal size distribution of filament size suggesting the presence of two species of filamentous bacteria (Fig. 4). At times when water temperature was lower, a filamentous cyanobacteria such as *Calothrix* could grow imparting a green coloration to the silica. Deeper portions of the silica fibre meshwork showed an increase in amorphous silica spheres. This indicates that the bacterially induced silica is promoting abiogenic silicification of the void spaces. Presumably, given sufficient time, the void space would be entirely filled with amorphous silica.

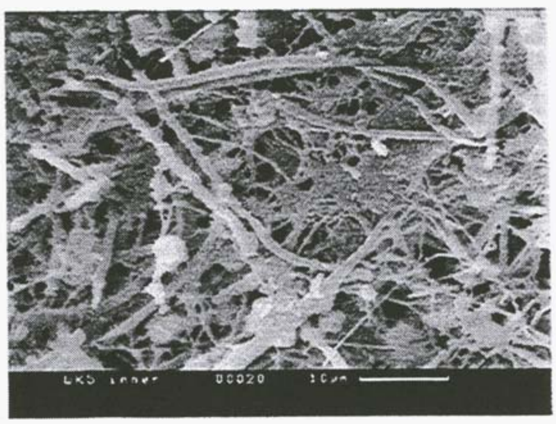

Figure 5. Silica casts of filamentous bacteria from Kiriohineke *Stream.* At least two different species of bacteria are interpreted to be present based on the bimodal width distribution.

3.2 Rotokawa

The North Springs at Rotokawa are two ebullient hot pools with temperatures greater than 85°C located on the northwest side of the sinter flat. Outflow from the springs (pH 2.7 - 3.2, 400 - 1200 ppm Cl^-, 600 - 1000 ppm SO_4^{2-}) flows as a fan-shaped, shallow sheet (<0.5 cm) with temperatures ranging from 60 to 85°C. The waters are turbid due to high concentration of suspended material composed principally of native sulphur, clays, and amorphous silica. This material is carried in the outflow and has built up a thick layer of fine mud in the outflow area. Microstromatolites populate this area as described by Jones et al. (2000). These structures start on pumice and wood fragments that originally protruded out of the water. As the mud thickens the microstromatolites grow upwards and outwards creating coral-shaped structures. Also present in the subsurface mud are yellow layers containing amorphous arsenic sulphide mineralization.

In order to study how these structures grow and the trace metals incorporated into them, a series of glass slides were inserted into the mud at regular distances from the pools in May 2001. Samples collected at monthly intervals show that no growth has occurred in the water. Above this a yellowish layer 1 - 2 mm in thickness composed of native sulphur is present and above this is a dark gray layer of hard silica (Fig. 6a). There is insufficient wave action to keep the entire slide wet and the growth of the silica layer is interpreted to form as a result of capillary action through the sulphur layer and up the slide. Irregular protuberances on the sides of the slides may represent the beginnings of spicules but, at present, there has been insufficient growth to determine rates. It is certain that growth rates are very slow. Another interesting possibility is that the microorganisms that form the spicules prefer not to grow on the sides of the glass slides but prefer more horizontal surfaces. The tops of the slides are approximately 2 cm above the water surface where temperatures drop to 45°C or lower, possibly discouraging thermophile growth.

The Main Upflow at Rotokawa is located in the southeast section of the sinter flat. It is a large, dark pool approximately 20 metres in length and 10 metres width. The water temperature is up to 90°C and chemistry is typical of acid sulphate pools (pH 3.8, 1540 ppm Cl^-, 420 ppm SO_4^{2-}, 336 ppm SiO_2). The south side of the pool is composed of complex biomediated sinter structures (Jones et al., 2000) that at present are not active. Only immediately adjacent to the water are active microstromatolites found entirely submersed in water. When collected these slides were covered with a thin layer of fine mud which had presumably settled out of the turbid water. This mud consists of fine sulphur, clays, and amorphous silica. SEM examination showed no obvious microorganisms, however, TEM studies did show a few non-filamentous bacteria. These results show that although bacterial activity is present to some degree in the hot waters, the activity of microorganisms just above the water surface is much greater.

Glass slides were place in the water adjacent to the edge of the pool in March 2001. These were

The V-notch is located at the southern most extremity of the sinter flat where the thermal waters flow into Lake Rotokawa. Water temperature is much lower than at other sites (49°C) although water chemistry is similar (pH 3.0, 1000 ppm Cl^-, 600 ppm SO_4^{2-}). Glass slides collected over the last several months show slow growth of a slimey lime green layer but no obvious silicification. At present, no SEM and TEM work has been done on these samples.

3.3 Waiotapu

Champagne Pool occupies a large explosion crater (~60 m diameter) in the Waiotapu thermal area. Water temperature is typically 75°C but can be as low as 70°C in shallow areas around the edge of the pool. The pool contains chloride-rich waters at near neutral pH (pH 5.5, 1926 ppm Cl^-, 430 ppm SiO_2). On the west and southwest margins of the pool, the sinter edge is up to 40 cm above the water's surface while at the northeast margin the water is dammed by a raised terrace of silica. The pool empties to the northeast forming the well-known Primrose Terrace. The geometry of the sinter suggests that the ground surface is slowly tilting downwards towards the northeast.

A complex series of biomediated silicification features are present around the margins of the pool (Jones et al., 1997). Figure 6b shows the east margin of the pool. The bottom is covered with an orange precipitate, identified as amorphous antimony sulphide by Hedenquist (1986). Immediately adjacent to the water is a rim of native sulphur that overhangs the water surface. This is followed by a series of conical microstromatolites up to 3 cm in height. Towards the top of the sinter, these microstromatolites are covered with a greenish layer suggesting that cyanobacteria are present. The microstromatolites also form islands in the pool where the undulating bottom has come close enough to the surface to allow native sulphur to accumulate creating a "raft" that is slightly above the surface. These rafts then allow the growth of the microstromatolites (Fig. 6c and 6d). SEM examination of a small microstromatolite spine shows that their bases are composed of subhedral

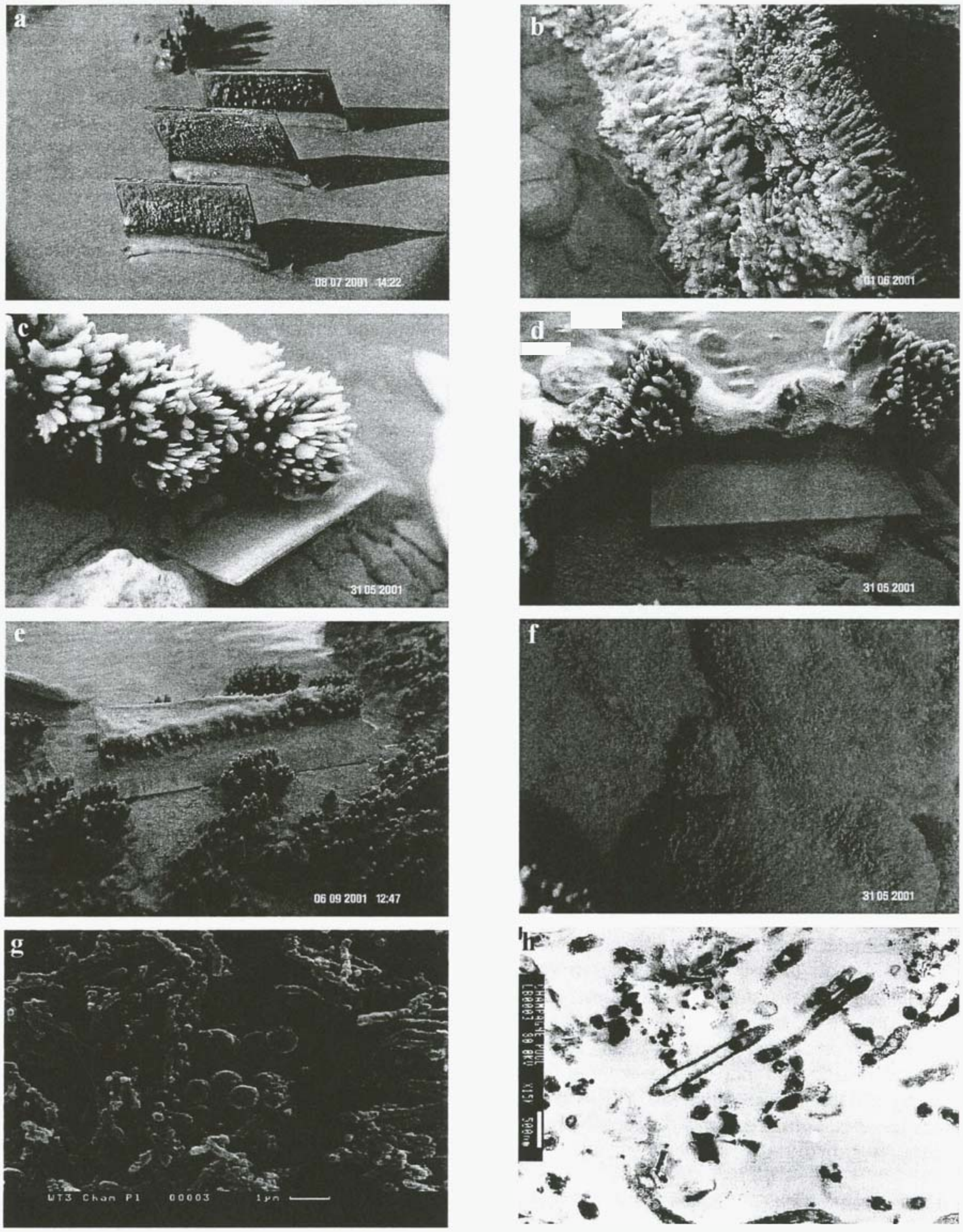

Figure 6. (a) Three glass slides inserted in mud near one of the north springs, Rotokawa. Water temperature is 74°C and air temperature at top of slide ~45°C. Water depth is approximately 0.5 cm. No mineralization occurs in water. A thin sulphur layer occurs at water surface and dark gray silica mineralization grows above. Slide dimensions 25 x 75 mm. (b) Northwest margin of Champagne Pool, Waiotapu showing orange precipitate in water, yellow native sulphur layer, conical microstromatolites and greenish cyanobacteria. Field of view 0.5 m. (c) Glass slide protruding from Champagne Pool next to islands of microstromatolites. Note sulphur layer and cloudy silica mineralization on slide. (d) Glass slide wholly immersed in Champagne Pool. Slide is covered with orange precipitate but no sulphur or silica mineralization. Note sulphur layer around microstromatolites. (e) Glass slide partially immersed in Champagne Pool outlet. Microstromatolites on slide have grown over a five month period. (f) Bottom of Champagne Pool. Orange precipitate is attached to bottom by fine filaments that move in the current. Field of view 20 cm. (g) SEM photograph of orange precipitate from Champagne Pool. Note the filamentous shape of the sulphur and antimony-rich precipitates. Spheres are amorphous silica beads. Scale bar is 1 µm. (h) TEM photograph of Champagne Pool orange precipitate. Dark rims are coatings of amorphous antimony sulphide and sulphur on filamentous bacteria. Scale bar is 500 nm.

crystalline masses of fine sulphur crystals. A porous mixture of filamentanous organisms and sulphur is built upon the sulphur rafts. The conical portion of the spine is composed of alternating layers of organism-free silica and bacterial-rich silicified layers.

Glass slides were placed in three positions along the edge of the pool in March 2001. These slides were not fastened to plastic trays and, as a result, many of the slides fell into the pool due to wind or wave action. Slides that were entirely immersed in water showed no accumulation of yellow native sulphur but became covered with a layer of orange precipitate (Fig. 6d). This precipitate did not appear to be attached to the slide and came off when the slide was removed. Slides that partially protruded from the water surface accumulated a layer of native sulphur at the water surface above which they became cloudy due to the precipitation of amorphous silica (Fig. 6c). This probably forms by capillary action through the sulphur layer. An estimation of spicule growth rate of 0.03 mm day^{-1} was made using a single slide which remained in place for five months (Fig. 5e). This is a maximum rate since it appears that the initial sulphur layer grows much more rapidly than the spicules themselves.

Except for a few slides, most of the initial set from March 2001 fell into the pool. Also, most were located in drainage channels on the northeast side of the pool where the water is shallow but turbulent. A second set of slides was placed in July 2001. These were secured in a plastic holder weighted with lead and placed in the main pool. The tips of these slides protrude 2 – 5 mm above the surface of the water. On our visit in September 2001, the slides showed growth of excellent spicules about 1 mm in height (-0.02 mm day^{-1}) at a regular spacing along the top of the slide. We will continue to collect these samples on a bimonthly basis to measure growth rates and metal contents.

Hedenquist (1986) noted the metal-rich composition of the orange precipitate in Champagne Pool. In order to examine the possibility that bacteria were involved with this mineralization, samples of the orange precipitate were analyzed by SEM and TEM. Figure 6g shows that it is composed of filamentous chains of an antimony-rich precipitate. Other minerals present were amorphous silica and kaolinite. The unusual texture of the precipitate suggests a bacterial origin. This is supported by TEM work (Fig. 6h) where the entire sample appeared to be composed of bacteria sheathed in a dark material representing the antimony-rich precipitate. X-ray fluorescence analysis of a dried sample of the orange material showed that it is composed of sulphur (70%), SiO_2 (13%), Sb (1.1%), As (0.6%) and Al (0.6%). In addition, measurable amounts Ca, Ti, Fe, and Se were found. X-ray diffraction analysis gave strong peaks only for native sulphur. This is to be expected as the antimony sulphide impurities in the sulphur are expected to be amorphous. It appears that thermophilic bacteria are thriving in the hot waters of Champagne Pool. It is possible that this bacteria metabolises reduced sulphur to form large amounts of native sulphur. Concurrently, antimony and arsenic are combining with sulphide and native sulphur to form amorphous arsenic and antimony sulphides which attach to the bacteria's cell walls along with the native sulphur. However, it is possible that the mineralization is a passive response to the presence ofthe bacterid surfaces. In either case, the bacterial casts will have an extensive reactive surface area and thus effectively scavenge other trace metals from Champagne Pool.

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