MORPHOLOGICAL AND CHEMICAL PROPERTIES OF SILICEOUS DEPOSITS AT STEEP CONE SPRING, YELLOWSTONE NATIONAL PARK

Y. MOTOMURA[1], Y. NAKAGAKI[2], E. IZAWA[2] & K. WATANABE[2]

[1]Department of Earth and Planetary Sciences, Kyushu University, Fukuoka, Japan
[2]Department of Earth Resource Engineering, Kyushu University, Fukuoka, Japan

SUMMARY - Steep Cone Spring, Yellowstone National Park, has a small sinter mound of 7 m high and 60 m wide. Microstructure, mineralogy and chemical compositions of siliceous deposits collected from five locations of the mound have been examined. Siliceous deposits are essentially composed of sub-micron to micron size spherules of non-crystalline silica (opal-A). There are variations in silicified microbial structures and chemical compositions of amorphous silica along the flow channel on the mound. In the high-temperature (>73°C) vent areas, especially in the boiling pool (94°C, pH = 8.3), microbial microstructures composed of filamentous silica and framboidal pyrite are present. In the intermediate- and low-temperature areas (73-25°C), where macroscopic cyanobacterial mats predominate, accumulation of amorphous silica spherules on surfaces of microbes are common and various microbial structures are well preserved in silica matrix. The concentration of SiO_2 is low (88-97 wt %) in vent areas and increases to distal terrace areas (91-98 wt %). In contrast, Al_2O_3 (–5.3 wt %), CaO (–0.3 wt %), Na_2O (–2.3 wt %) and K_2O (–0.9 wt %) show higher concentrations in vent areas than those of distal areas. Some pool rim geyserite have exceptionally high concentrations of FeO (–1 1.9 wt %) and TiO_2 (–1.0 wt %). These characteristic morphological and chemical zoning patterns may apply to ancient siliceous deposits.

1. INTRODUCTION

Recent morphological and mineralogical investigations of modem siliceous deposits forming in high temperature (>73°C) hot springs and geysers revealed various kinds of microbial fabrics preserved in amorphous silica matrix (Cady and Farmet, 1996; Jones *et al.,* 1997a, b; Campbell *et al.*, 2001; Herdianita and Browne 2001; Inagaki *et al.*, 2001; Jones *et al.,* 2001a). Recent microbiological surveys also confirmed the existence of thermophilic or hyperthermophilic microorganisms in such extreme geothermal environments (Inagaki *et al.,* 2001; Blank *et al.,* 2002). In addition, microbiological and geochemical investigations revealed that microorganisms are likely to promote the formation of siliceous deposits (Inagaki *et al.,* 1998; Jones *et al,* 200 lb).

While chemical analyses of natural siliceous deposits have been reported (Fournier *et al.,* 1994, Jones *et al.*, 200 lb), mineralogical properties and spatial chemical variation around the vents are not fully described. In this study, morphological fabrics and mineralogical and chemical compositions of siliceous deposits in Steep Cone Spring of Yellowstone National Park were examined to elucidate the mode of microbial control on the formation of siliceous deposits and zonal distribution of elements in siliceous deposits around the vent.

2. STEEP CONE SPRING

Steep Cone Spring is situated in Sentinel Meadows, northern part of Lower Geyser Basin of Yellowstone National Park. It has a circular vent pool, 3 m wide, on the top of a 7 m high and 60 m wide siliceous sinter mound (Lowe *et al.*, 2001). The discharging water (pH = **8.3**) is boiling at 94°C, and presently flows down to south through a shallow outflow channel.

Dry parts of the mound are generally white, but wetted parts with hot water are orange and grayish colored due to bacterial mats. The boiling pool is encircled by a brown colored geyserite fringe, and the surrounding area is predominated by pale brownish sinter with digitate rim. Several meters apart from the pool edge, a beige colored biofilm is present indicating high-temperatures (>73°C) and hydrodynamically formed wavy structure is found in a narrow stream (10 cm wide) with a digitated edge.

The downstream area of the outflow channel (60-30°C) is occupied by an orange colored ***Phormidium*** mat, and columnar and streamer structures are common. Gray colored ***Calothrix*** sinter terrace extends into lower temperature (<30°C) area. Columnar structured laminated sinter is covered with ***Calothrix*** mat. As mentioned above, the Steep Cone outflow system has a large temperature range of 94°C to <30°C and produces wide petrographic and microbial variations of the sinter mound.

3. SAMPLES AND METHODS

In this study, samples were collected at five locations along the outflow channel (Figure 1). S-1 is collected from subaqueous inner wall of the pool (94°C), and is a thin-layered white to brownish colored siliceous deposit covered by silica spherules and black powdery particles. **S-2** is a brown spinous geyserite collected fkom the edge of the pool. **S-3** is a beige colored siliceous deposit collected from the bottom of high temperature **(74°C)** water channel **(4** m along the outflow channel from the pool edge). S-4 is a dark brown colored laminated siliceous deposit covered by a ***Phormidium*** mat **(53°C,** 25 m fi-om the pool). ***S-5*** is a laminated siliceous deposit collected from a dark grey *Calothrix* terrace **(29°C, 25** m from the pool).

Figure **1.** Boiling pool encircled by a geyserite fringe and surrounding sinter terraces at Steep Cone Spring. Arrows show locations of sampling sites (S-1-S-3). Diameter of the pool is approximately 3 m.

Powder X-ray diffraction (XRD) was performed with a Rigaku RINT2100 diffractometer using CuKα radiation to identify the mineral phases present and to determine the crystallinity of silica phases. Textural and morphological observations were undertaken with optical microscopy and scanning electron microscopy. Secondary and backscattered electron images were observed in detail with a **JCXA733** electron-probe microanalyzer (EPMA).

Bulk chemical analyses were performed with a Rigaku **RIX3** 100 X-ray fluorescence spectrometer (XRF). Gold (Au) was analyzed using inductivity coupled plasma mass spectrometry (ICP-MS) with a Yokogawa PMS2000 mass spectrometer. Qualitative and quantitative spot analyses of the samples were performed **by EPMA** with accelerating voltages of 20 kV and 15 kV with 0.1 μA electron-probe current. In the case of amorphous silica analysis, electron beam spot sizes were broadened to 10 to **20** μm for prevent thermal damage of the sample.

4. RESULTS AND DISCUSSION

Optical microscopy: Microscopic observation showed abundant and ubiquitous distribution of isotropic non-crystalline silica spherules throughout the thin-sectioned samples. Several grains of quartz and plagioclase were found in some thin sections. Their fragmental shapes suggest a detrital origin.

X-ray diffraction analysis: Most of X-ray powder diffraction patterns of the samples showed very broad bands, typical of opal-A, centered at about [redacted] **20 (CuKα),** although a few samples showed additional weak lines of opal-CT or quartz. The widths at half-maximum intensity of the bands of opal-A, ranging **7-8° 20,** correspond to those of modem fresh opal-A (Herdianita *et al.,* 2000) and no apparent decrease was recognized between the samples. Thus from the XRD experiments, it is revealed that these siliceous deposits are mostly composed of non-crystalline silica (opal-A).

Scanning electron microscopy: Secondary and backscattered electron images of the siliceous deposits were observed by EPMA. Figure 2 shows representative backscattered electron images of the samples. The samples are essentially composed of fine-grained amorphous silica spherules and show different microstructures according to their spatial distribution.

Figures **2A** and 2B are surface images of an inner wall sample from the boiling pool **(S-1).** The surface of an wavy laminated amorphous silica is covered by network structures of rod-like to filamentous amorphous silica and spinous pyrite (Fig. **2A). A** small knob of amorphous silica is also covered by aggregates of framboidal pyrite crystals (Fig. **2B).** Although microbial **DNA** could not be detected in the extract prepared from this sample (Inagaki *et al.,* 2001), filamentous to rod-like shapes of amorphous silica and spinous shapes of pyrite seem to suggest the shapes of endogenous thermophilic to hyperthermophilic microbes living in the pool. Framboidal pyrite also suggests bio-mediated mineralization.

Figures 2C, 2D and 2E are cross sections of geyserite **(S-2).** Thin amorphous silica layers show a convex-upward lamination and cross-lamination textures with small lenticular voids (Figure 2C). Sometimes stacked, convex-upward laminae form columnar stromatolite-like microstructures (Figure **2D)** and some laminae are rich in Fe, Al, Ti, Ca, Na and K **(S-2s** in Table 2). Some voids are filled with abiogenic tiny silica beads (Fig. 2E). There is no apparent microbial structure in the sample.

Figure 2F is a cross section of a beige colored siliceous deposit **(S-3)** collected from a high-temperature area. Porous aggregates of silica spherules are connected with fine silica filaments.

Figure **2G** represents a cross section of a siliceous deposit (S-4) collected fkom the bottom of the

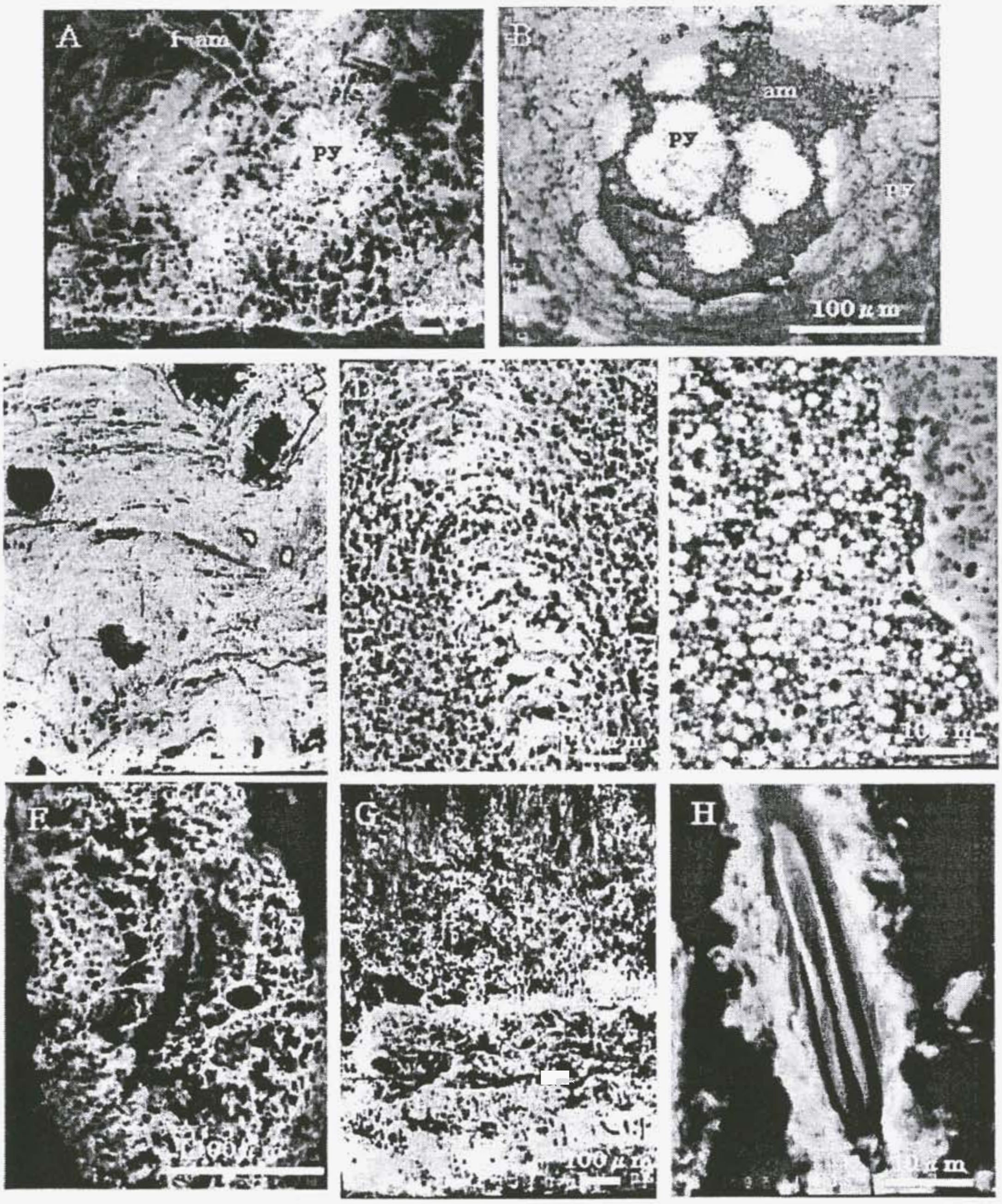

Figure 2 Backscattered electron images of sinter samples. A and B. Microbial structures preserved on the surface of the subaqueous inner wall (S-1) from boiling pool, am = amorphous silica, f-am = filamentous amorphous silica, py = framboidal to spinous pyrite. C, D and E. Cross sections of nonbiologically formed geyserite *(S-2)* showing convex-upward lamination (C), columnar stromatolite-like microstructure, in which bright layers have high concentrations of Fe, Al, Ti, Ca, Na and K (D), and sedimentary infilling structure of silica beads in small void (E). F. Cross section of beige colored siliceous deposit (S-3) showing porous aggregation of silica spherules and filamentous silica. G: Cross section of laminated siliceous deposit (S-4) covered with ***Phormidium*** mat showing intimate association of microbes (dark to black filaments) and silica spherules (gray). H. A silicified remnant of hollow microbe found in siliceous deposit *(S-5)* from distal low-temperature *Calothrix* area.

Phormidium mat. Horizontal compact silica layers alternate with porous columnar silica layers. Upward-erect hollow filamentous microbes ***(Phormidium)*** are embedded in aggregates of silica spherules.

Figure 2H shows a silicified remnant of a hollow microbe found in a siliceous deposit *(S-5)* collected fiom a distal low-temperature *Calothrix* area *(S-5)*.

As mentioned above, the silica precipitates generally as a minute amorphous spherule. There are significant microbial controls on the mode of silica aggregation at Steep Cone Spring, except for the case of subaerial formation of geyserite. In the boiling pool, silica covers filamentous or rod-shaped microbes and forms a silicified network structure. These silicified networks serve as good nucleation sites for successive mineral precipitation.

In the high-temperature (>73°C) area of outflow system, where only thin biofilms exist, nonbiologically precipitated aggregates of amorphous silica are common and minor amounts of microbial filaments with silica encrustation occur. Inagaki *et al.* (1998) suggested that the extremely thermophilic bacterium *Thermus* spp. may affect aggregation of silica *in vitro.* The genus *Thermus* is a predominant microbial component in the Steep Cone outflow system (Inagaki *et al.* 2001), and a part of silica deposition in high-temperature areas seems to be promoted microbiologically.

In the areas of lower temperatures (<73°C), where macroscopic cyanobacterial mats predominate, amorphous silica spherules easily attach to the surfaces of abundant microbes. Hence, microbial colonies act passively but greatly as templates of silica precipitation and make the main framework of the siliceous mound.

Although biotic silica deposition is suggested at high-temperature areas in this hot spring system, accumulation and preservation of silica within the environment of microorganisms have a passive role.

Table 1 Chemical composition of siliceous deposits (XRF analysis)

	S-1	s-2	s-3	S-4	s-5
SiO_2 (%)	75.30	71.86	83.45	92.94	93.58
TiO_2	0.30	0.02	0.01	0.00	0.00
Al_2O_3	9.81	6.27	3.16	0.18	0.18
Fe_2O_3	0.25	0.21	0.07	0.01	0.02
MnO	0.03	0.01	0.01	0.00	0.01
MgO	0.02	0.01	0.01	0.00	0.01
CaO	0.64	0.42	0.15	0.08	0.08
Na_2O	3.93	2.60	1.42	0.56	0.68
K_2O	1.58	0.93	0.51	0.10	0.12
P_2O_5	0.00	0.00	0.02	0.00	0.00
Total	91.62	82.15	88.81	93.87	94.68
S (ppm)	344	147	2040	103	75
Cl	400	150	840	200	180
Rb	510	321	115	38	38
Zr	36		-		
As	16		-		
Y	32	22	-		
Au (ppb)	-	106	19	5	23

- = below detection limits (ca. 10 ppm).
Sr, Ba, Zn, Hg and Nb were below detection limits.

XRF analysis: Bulk chemical compositions of the siliceous deposits analyzed by XRF are shown in Table 1. There are compositional variations between vent samples and distal terrace samples. The concentration of SiO_2 is low in vent areas and increases to distal areas. In contrast, Al_2O_3, Fe_2O_3, CaO, Na_2O and K_2O show higher concentrations in vent areas than those of distal areas. The concentrations of TiO_2, MnO, MgO and P_2O_5 are generally less than 0.1 wt %.

Although variations in S and Cl concentrations are not systematic, some trace and minor elements show spatial variations. The concentration of Au ranges from 5 to 106 ppb and is high in the vicinity of the vent pool and decreases outwards abruptly to a low level of 10 or less ppb. Rb concentration is also high in the vent areas.

EPMA analysis: In addition to bulk XRF analysis, spot analysis of amorphous silica grains was performed by EPMA. Results are given in Table 2. Consistent with the result of XRF analysis, the concentration of Al_2O_3 in amorphous silica is high (>1 wt %) in the vent area. In paticular, amorphous silica in geyserite (S-2g in Table 2) has high Al_2O_3 up to 5.3 wt %. The concentration decreases gradually from the pool rim to distal areas and is less than 1 wt % in areas of low temperature (<50°C). The concentrations of CaO, Na_2O and K_2O show positive correlation with that of Al_2O_3 These analytical data show that replacement of Si^{4+} with Al^{3+} in amorphous silica lattice and simultaneous compensation of charge imbalance by Ca^{2+}, Na^+ and K^+ are common in high-temperature areas.

The concentrations of FeO and TiO_2 in Steep Cone amorphous silica are generally low (<0.2 wt %). On the other hand, some laminae comprising stromatolite-like microstructures in geyserite (bright parts in Fig. 2D) have exceptionally high concentrations of FeO and TiO_2 (FeO: 2.6-11.9 wt %, TiO_2: 0.2-1.0 wt %) and there is a good correlation between FeO and TiO_2. The concentrations of Al_2O_3, CaO, Na_2O and K_2O are also high in these laminae (S-2s in Table 2). Although growth of geyserite is maintained nonbiologically by repeated splashing and evaporation of vent waters (Braunstein and Lowe, 2001), it is not clear that these stromatolite-like microstructures are biotic or abiotic in origin. Their formation process and especially the source of Ti are interesting and need further investigation. In ancient siliceous deposits, amorphous silica rich in Al, Fe, Ti, Ca, Na and K will be a good indicator of a fossil vent position.

5. CONCLUSIONS

Morphological and chemical properties of amorphous silica (opal-A) comprising siliceous deposits of Steep Cone Spring show spatial variations reflecting temperature structure and chemical structure of the mound.

In the high-temperature (>73°C) vent areas,

	s-2g						s-2s					
	2	3	4	5	6	7	8	9	10	11	12	15
SiO_2	87.0	89.2	90.0	86.1	83.5	77.2	83.2	86.7	82.9	83.1	78.5	78.2
TiO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.4	0.4	1.0	0.8
Al_2O_3	0.2	0.3	0.9	1.0	3.4	5.3	1.0	1.0	1.3	2.0	2.7	3.2
FeO	0.0	0.0	0.1	0.2	0.0	0.1	3.0	2.6	4.4	4.8	11.7	8.8
MnO	0.0	0.0	0.1	0.0	0.0	0.1	0.1	0.0	0.1	0.1	0.2	0.2
MgO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1
CaO	0.2	0.0	0.1	0.2	0.3	0.3	0.1	0.1	0.1	0.3	0.3	0.3
Na_2O	0.5	0.5	0.3	0.4	1.2	2.3	0.3	0.3	0.3	0.2	0.4	0.4
K_2O	0.1	0.0	0.2	0.2	0.6	0.9	0.3	0.3	0.5	0.6	0.7	1.0
Total	88.0	90.0	91.7	88.1	89.0	86.2	88.2	91.2	90.0	91.6	95.6	93.0

Table 2 continued

	s-4							s-5	
	16	17	18	19	20	21	22	23	24
SiO_2	90.6	90.7	93.8	96.2	97.5	91.2	96.6	93.4	93.6
TiO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
A1203	0.0	0.1	0.1	0.1	0.2	0.3	0.3	0.2	0.2
FeO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
MnO	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0
MgO	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0
CaO	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1
Na_2O	0.2	0.3	0.3	0.5	0.3	0.2	0.3	0.3	0.1
K20	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1
Total	91.0	91.3	94.4	97.0	98.3	92.0	97.6	94.1	94.2

especially in the boiling pool, microbially mediated microstructures composed of filamentous silica and framboidal pyrite are present.

In the low-temperature (<73°C) area, where macroscopic cyanobacterial mats predominate, sedimentary aggregation of amorphous silica spherules on surfaces of abundant microbes are common and microbial structures are well preserved in silica matrix.

The chemical composition varies between vent samples and distal terrace samples. The concentration of SiO_2 is low in vent areas and increase to distal areas. In contrast, the concentrations of Al_2O_3, Fe_2O_3, CaO, Na_2O and K_2O are higher in the vent areas than those of distal areas. Some stromatolite-like columnar parts in geyserite are exceptionally rich in Al, Fe, Ti, Ca, Na and K.

These morphological and chemical zonal patterns found in the siliceous deposits of Steep Cone Spring will apply to ancient siliceous deposits.

6. ACKNOWLEDGEMENTS

We thank the Research Office at Yellowstone National Park for permitting collection of the samples. We are grateful to Drs. D.R. Lowe and D. Braunstein at Stanford University for guiding us through Yellowstone National Park. This work was partly supported by a grant-in aid for international scientific research (joint research) No. 08044159, Japan.

7. REFERENCES

Blank, C.E., Cady, S.L. and Pace, N.R. (2002). Microbial composition of near-boiling silica depositing thermal springs throughout Yellowstone National Park. ***Appl. Environ. Microbiol.,*** Vol. 68, 5123-5135.

Braunstein, D. and Lowe, D.R. (2001). Relationship between spring and geyser activity and the deposition and morphology of high temperature (>73°C) siliceous sinter, Yellowstone National Park, Wyoming, U.S.A. ***J. Sediment. Res.,*** Vol. 71,747-763.

Cady, S.L. and Farmer, J.D. (1996). Fossilization processes in siliceous thermal springs: trends in preservation along thermal gradients. In: ***Evolution of hydrothermal ecosystems on Earth (and Mars?).*** Ciba Foundation Symposium 202, Wiley, Chickester, pp. 150-173.

Campbell, K. A., Sannazzaro, K., Rodgers, K.A.,Herdianita, N.R. and Browne, P.R.L. (2001). Sedimentary facies and mineralogy of the late Pleistocene Umukuri silica sinter, Taupo Volcanic Zone, New Zeland. ***J. Sediment. Res.,*** Vol. 71, 727-746.

Fournier, R.O., Kennedy, B.M. ,Aoki, M. and Thompson J.M,. (1994). Correlation of gold in siliceous sinters with $^3He/^4He$ in hot spring waters of Yellowstone National Park. *Geochim. Cosmochim. Acta,* Vol. 58, 5401-5419.

Herdianita, N.R., Browne, P.R.L., Rodgers, K.A. and Campbell, K.A. (2000). Mineralogical and textural changes accompanying ageing of silica sinter. *Mineralium Deposita,* Vol. 35, 48-62.

Inagaki, F., Motomura, Y., Doi, K., Taguchi, S., Izawa, E., Lowe, D.R. and Ogata, S. (2001). Silicified microbial community at Steep Cone hot spring, Yellowstone National Park. *Microb. Environ.,* Vol. 16, 125-130.

Inagaki, F., Yokoyama, T., Doi, K., Izawa, E. and Ogata, S. (1998). Bio-deposition of amorphous silica by an extremely thermophilic bacterium, *Thermus* spp. *Biosci. Biotechnol. Biochem.,* Vol. 62, 1271-1272.

Jones, B., Renaut, R. W. and Rosen, M.R. (1997). Biogenicity of silica precipitation around geysers and hot-spring vents, North Island, New Zealand. *J. Sediment. Res.,* Vol. 67, 88-104.

Jones, B., Renaut, R. W. and Rosen, M.R. (1998). Microbial biofaces in hot-spring sinters: a model based on Ohaaki Pool, North Island, New Zealand. *J. Sediment. Res.,* Vol. 68,413-434.

Jones, B., Rosen, M.R. and Renaut, R. W. (2001a). "Geyser eggs" from Te Whakarewarewatangaoteopetauaawahiao, North Island, New Zeland. *J. Sediment. Res.,* Vol. 71, 190-204.

Jones, B., Renaut, R.W. and Rosen, M.R. (2001b). Biogenicity of gold- and silver-bearing siliceous sinters forming in hot (75°C) anaerobic spring-waters of Champagne Pool, Waiotapu, North Island, New Zealand. *J. Geol. Soc. London,* Vol. 158, 895-911.

Lowe, D.R., Anderson, K.S. and Braunstein, D. (2001). The zonation and structuring of siliceous sinter around hot springs, Yellowstone National Park, and the role of thermophilic bacteria in its deposition. In: *Thermophiles: Biodiversity, Ecology, and Evolution,* Reisenbach *et al.* (Eds). Kluwer Academic/Plenum Publishers, New York, pp. 143-166.

Mckenzie, E.J., Brown, K.L., Cady, S.L. and Campbell, K.A.. (2001). Trace metal chemistry and silicification of microorganisms in geothermal sinter, Taupo Volcanic Zone, New Zealand. *Geothermics,* Vol. 30,483-502.