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MINERALOGICAL AND MICROBIAL CHARACTERISTICS OF AN ACID-DERIVED SILICEOUS SINTER FROM A THERMAL OUTFLOW AT PARARIKI STREAM, ROTOKAWA GEOTHERMAL FIELD, NEW ZEALAND

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SUMMARY – Unusual deposits of siliceous sinter form around hot (>75ºC) vents on a thermal outflow at Parariki Stream, in the Rotokawa geothermal field. The sinter forms subaerially on pumice clasts and pine cones from silica rich acid-sulphide-chloride waters (pH 2.3). The main mineral phase is noncrystalline opal-A silica with full width at half maximum intensity (FWHM) values of 1.34-1.42 ΔÅ (8.1º Δ2θ). Silica drapes the existing substrate topography and deposits as layers that can become substantially corroded. The deposits are formed predominantly by vitreous silica spheres that are <10 nm to 50 nm in diameter, and become progressively blurred and ill-defined by repeated episodes of dissolution and redeposition. Much of the sinter surface is covered by coccoidal microorganisms (1-1.5 µm in diameter) that connect to one another through extracellular polymeric substances (EPS), which together constitute a biofilm. These microbes are able to form isolated clumps of cell clusters that can become progressively encrusted by nanospheres of silica. Eventually, these encrustations are recolonised by a new succession of biofilm, forming vertically upright, pillar-like structures that constitute the spicular texture visible on outer surfaces of the sinter deposit. Care should be taken when examining *in situ* microbial compositions as preservational biases and post-collection fungal overgrowth can potentially affect interpretations of microbial composition, diversity and mineral-microbe interactions.

1. INTRODUCTION

Deposits of silica (SiO_2) are both common and visible surface manifestations of many geothermal systems. Many of these deposits comprise siliceous sinter, a chemical sediment deposited at the surface from near neutral alkali-chloride waters (pH 4-9) derived from reservoirs hotter than 175ºC (Fournier and Rowe, 1966). By contrast, siliceous deposits formed by acidic hot-spring waters largely have been described as silica residue, a product formed by the surface and near-surface leaching of, and reaction with, silicate country rock by acidified steam condensate (White et al., 1956; Rodgers et al., 2002).

To date, however, little is known of siliceous sinters deposited by acidic hot springs. Acid-sulphate-chloride hot spring waters (pH 1-5), like alkali-chloride waters, also originate from deep reservoirs, with silica, like chloride, ascending from depths where temperatures are hotter than 180˚C (White et al., 1956). Rapid cooling may therefore lead to the dissolved silica becoming oversaturated at vent temperatures (<100°C) causing noncrystalline silica to precipitate, and hence sinter to form (White et al., 1956).

Comparison of modern acid-related sinter with sinter formed from alkali-chloride waters might allow for the recognition of a specific fossil sinter deposit where there is no longer any evidence of the nature of its depositing waters (Rodgers et al., 2004).

Numerous microorganisms occur in hot spring settings. Some are the most primitive forms of known modern life; hence thermophile diversity and ecology are the focus of many studies concerning the origin of life and astrobiology (e.g., Farmer, 2000). Since the discovery by Walter et al. (1972) of modern bacterial stromatolites from Yellowstone that bear resemblance to their Precambrian counterparts, considerable attention also has been paid to the formation mechanisms of these organo-sedimentary structures.

This paper investigates both the abiotic and biotic components of sinter deposits in a thermal outflow where numerous high temperature vents (Fig. 1) collectively discharge acid-sulphate-chloride type waters into Parariki Stream, which drains Lake Rotokawa. The pH of the silica saturated spring water is 2.3, with temperatures ranging from 90º to 75ºC, depending on vent location. Sulphuric acid is the main acid forming constituent in these waters (Ellis and Wilson, 1961).

Previous water analysis by Teece (2000) has shown the dissolved silica in these waters to be almost entirely present in monomeric form, with concentrations of 568 ppm ± 90. Such relatively high silica values are a legacy of the >310°C temperatures encountered deep in the reservoir, with silica derived from depth, rather then leached from the surface country rock, as is the case in acid-sulphate areas (cf. Rodgers et al., 2002). For this reason, deposits forming directly from these silica-rich waters are interpreted as siliceous sinter, rather then silica residue.

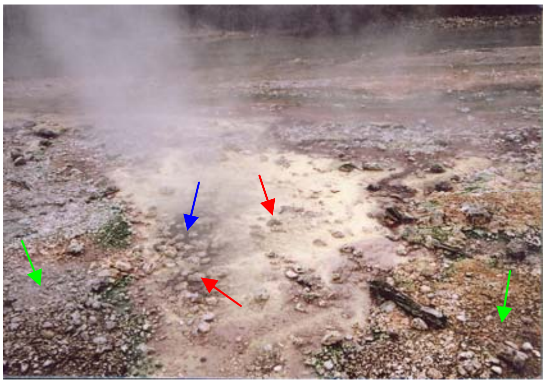


Figure 1. A large, sulphur-emitting vent (38 cm in width, 83ºC, blue arrow) typical of the high temperature areas around which sinter of this study deposits (red arrows). Note the considerable volume of rising steam. Other types of siliceous deposits are found further away (green arrows).

2. METHODS

Samples of sinter collected for scanning electron microscopy (SEM) were stored in 2.5% glutaraldehyde immediately upon field collection and prepared by sequential ethanol exchange and critical point drying. For comparison, sinter samples also were taken without glutaraldehyde treatment and air dried. Samples were mounted on aluminium stubs, sputter coated with platinum for six minutes, and subsequently examined with a Phillips SEM XL30S field emission gun.

X-ray powder diffractometry (XRPD) was used to identify the silica phases present and to investigate degree of lattice order-disorder. This analysis was made on a Phillips diffraction goniometer fitted with a graphite monochromator, with acquisition controlled by Sietronics (1993) VisXRD software. Determinative techniques followed those of Herdianita et al. (2000), allowing comparisons with previously published data on sinter from alkali-chloride waters. To check for consistency, XRPD was conducted on three individual siliceous deposits.

3. RESULTS

Sinter forms subaerially on substrates such as pumice and pine cones that provide sufficient relief above water level. The deposit is usually cup or ridge-shaped with minute microspicules visible on the outer side of the rim (Fig. 2). The occurrence and diameter of the rim is directly proportional to the width and height of the growth substrate above water level. A rim forms in a cup-shaped deposit, indicating the level to which the silica-rich waters were able to grow above the substrate. If silica is deposited throughout the substrate, no rim will form and a ridge shaped deposit forms. The sinter is massive, vitreous and light grey.

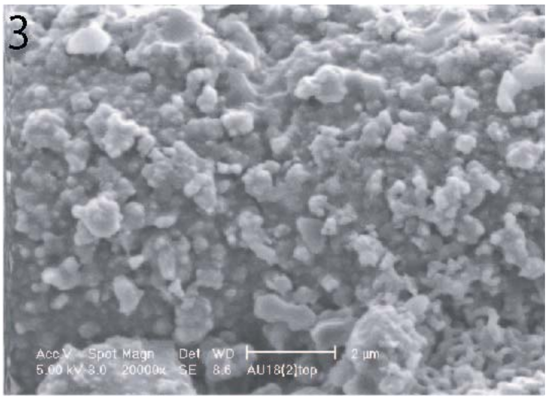
Neither splash nor spray occurs around the siliceous deposits. Glass slides placed diagonally above the water surface next to the sinter (~ 40 cm from vent orifice) grow silica that deposits in a sinuous form resembling minute wave wash, due to the ebullient discharge of the vents. Water washing onto the silica substrates also were recorded visually. Changes in water level were recorded during the winter season, after a period of high rainfall.

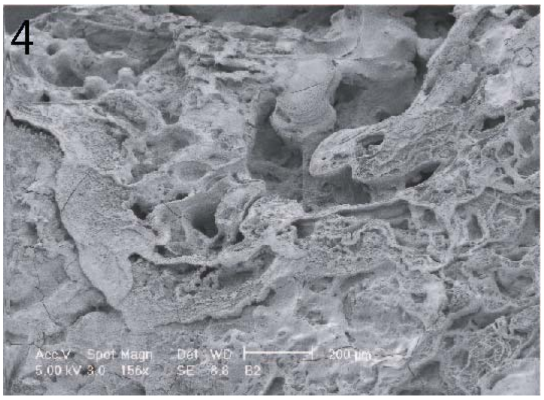
Results from the XRPD analysis show typical X-ray scattering bands of non-crystalline opal-A. The width at half maximum intensity (FWHM) of these bands ranges from 1.34-1.42 ΔÅ (8.1º Δ2θ).

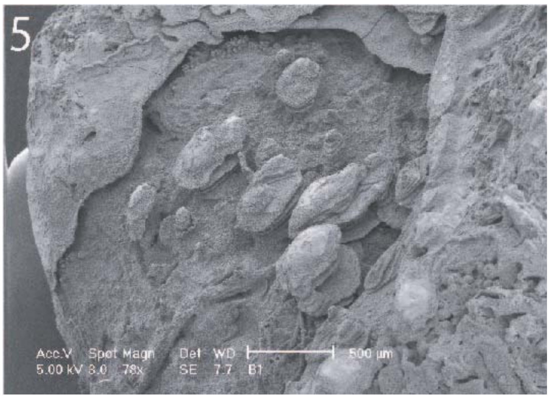
Silica deposits predominantly as vitreous spheres that are primarily <10 nm to 50 nm in diameter. However, spheres can reach a size of up to 500 nm in diameter through the aggregation of smaller spheres. Under SEM, two types of vitreous sphere shapes were observed: (1) freshly deposited round equidimensional spheres, or (2) faint, poorly defined spheres with interparticle "necks" (Fig. 3) (see also Iler, 1979, Fig. 5.14, p. 507). The letter superficially resembles the gelatinous "frog-spawn" described by Rodgers et al. (2002) in silica residue deposits.

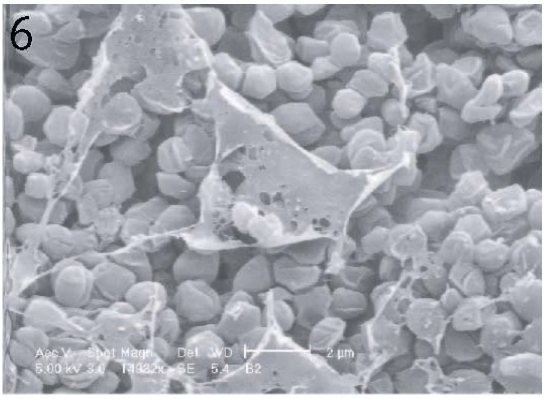
Figure 2. Cup-shaped siliceous sinter (grey rim) depositing on upper surface of pumice clast. Silica rim is 2 cm in height.

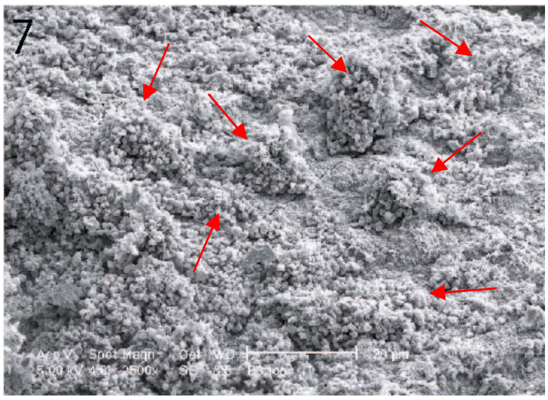
The opaline silica drapes existing surface topography, and is usually built up as layered sheets. In places, however, these sheets can become unevenly corroded, creating a highly irregular surface topography. Anastomosing ridges, nodules and associated cavities are common at these sites (Fig. 4). The ridges and nodules are usually covered by thin layers of smooth vitreous silica. A further succession of opal-A spheres can eventually deposit upon, and cover these residual features. With continuous pervasive corrosion, only remnant islands of the formerly flat siliceous layers are visible, so that they are often concentric, mirroring the topography of the underlying layers (Fig. 5).

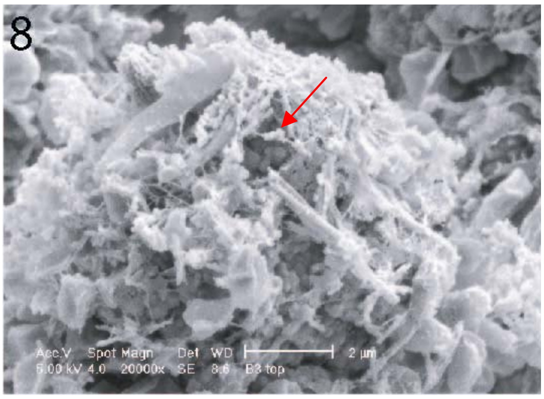


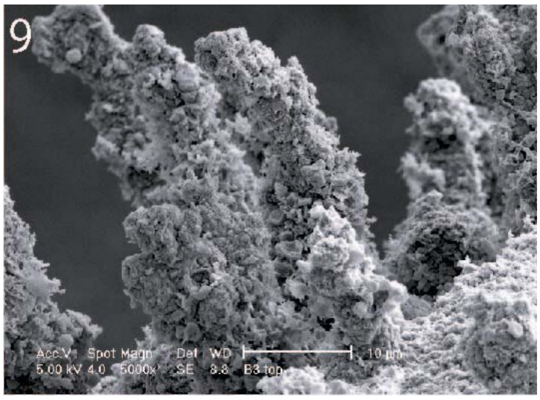












Figures 3-9: 3. Poorly defined silica spheres on a diatom affected by repeated episodes of dissolution and redeposition. 4. Numerous dissolution features occurring on sinter surface. 5. Remnant islands of formerly flat silica sheets. 6. Coccoidal microorganisms covering sinter surface and associated with sheets of EPS. 7. Isolated clumps of unsilicified cell clusters (arrows). 8. Recolonisation of a silicified clump of cell clusters. Strands of EPS are lightly silicified (arrow). 9. Vertically upright microspicules composed of biofilm and silica.

Large areas of the sinter surface are covered by coccoidal microorganisms (1-1.5µm in diameter) which, under SEM, appear to show a low diversity of morphotypes (Fig. 6). However, whether this translates into low biological diversity requires further investigation. The taxonomic nature of these organisms is currently under study using molecular phylogenetics. These microbes are connected to one another through extracellular bridges and/or a meshwork of extracellular polymeric substances (EPS). The whole microbe-EPS assemblage is known as a biofilm. While most of the microbial cells have a slightly deflated appearance, likely owing to critical point drying, no organic decay is evident on any of the biologic material. These microorganisms cover much of the sinter surface, except in areas which show extensive dissolution. In many places, isolated clumps of cell clusters occur (Fig. 7), which become progressively encrusted by nanospheres of silica. The siliceous covering eventually becomes recolonised by a new succession of biofilm (Fig. 8), forming microspicules of vertically upright pillar-like structures (Fig. 9).

In places, diatom tests are present on the sinter, which have been blown or washed from cooler environments onto its surface. The diatoms become pervasively coated by spheres of opal-A (Fig. 3) and eventually are incorporated into the sinter body.

In addition to noncrystalline silica, well-developed crystals of gypsum, barite and sulphur are present; they become covered by silica and hence incorporated into the sinter body. Gypsum is particularly ubiquitous on the uppermost portions of the deposit, which is in limited contact with water. Sulphur crystals, by contrast, form in the lower portions of the sinter, close to the air-water interface. Microbes can form leathery-like layers of EPS on the sulphur, over which spheres of silica will deposit. Silica spheres primarily deposit on the edges of EPS and diatoms.

No clay minerals were found anywhere on the sinter. This is in contrast to silica residue, which occurs with kaolinite, alunite, and alunogen (Rodgers et al., 2002).

Samples of the Parariki deposit that were taken without being fixed in glutaraldehyde, and stored in a moderately dry rock cabinet for two months, showed pervasive, unsilicified fungal overgrowth (seen under SEM). The fungi are interpreted to have grown after the samples were removed from their natural environment, as no fungal growth was observed on samples immediately treated with glutaraldehyde in the field and subsequently examined under SEM. In addition to secondary microbial overgrowth, samples that were not fixed in glutaraldehyde also showed a sharp reduction in the amount of microbes present on the sinter surface and a lack of associated EPS.

4. DISCUSSION

While acidophilic chemolithotrophic bacteria have been implicated in the formation of opaline silica (Fortin and Beveridge, 1997), the driving forces for the formation of siliceous sinter are largely attributed to abiotic mechanisms. The waters discharged from the high temperature vents at Parariki Stream are near saturation with respect to non-crystalline silica. However, the highly acid pH prohibits silica from precipitating subaqueously by inhibiting the tendency for monomeric silicic acid to deprotonate and, hence, polymerize and nucleate (Iler, 1979). Nevertheless, wet subaerial portions of a substrate become oversaturated with respect to non-crystalline silica owing to cooling and evaporation, thereby raising its precipitation rate (cf. Mountain et al., 2003). The silica supplied to the subaerial substrate is in monomeric form, but it polymerises and precipitates as the water evaporates. The ubiquitous presence of gypsum, an evaporite mineral, attests to evaporation occurring. The low propensity for silicic acid to polymerise in acid environments is responsible for the small size of the spheres (Iler, 1979).

The lack of a well-developed sphere morphology seen in acid-derived sinters is attributed to repeated episodes of silica dissolution and redeposition, causing a blurring of silica particle morphologies (Rodgers et al., 2004). Changes in microchemical conditions, such as pH, Eh and available moisture balance, are common in an acid thermal environment and are responsible for the episodic nature of silica deposition (Rodgers et al., 2002).

No precise mechanisms or causative factors have so far been given for the dissolution of noncrystalline silica. In most cases, acidic steam condensate has been implicated behind the dissolution and etching of siliceous deposits close to vents or steaming ground in acidic environments (e.g. Rodgers et al., 2002; Jones and Renaut, 2003). Anastomosing ridges are a common surface texture in silica residue and are interpreted to be the remnants of dissolved surfaces (Rodgers et al., 2002).

Since the main sinter body of this study is building up over time, silica deposition must exceed its rate of dissolution. It is possible that diurnal variations exist, with silica depositing during the day when evaporation is higher, and dissolution occurring at night when cooler conditions allow steam to condense. In addition, the influence of other effects such as cloudiness, wind direction and seasonality are also likely to affect sinter growth (cf. Handley et al., 2003).

The FWHM values for the Parariki sinter are higher than those reported from low-temperature sinter aprons formed by nearly neutral alkali-chloride waters elsewhere in the Taupo Volcanic Zone (TVZ). Instead, these values are similar to those reported for silica residue from acid-sulphate areas (Rodgers et al., 2002). Similarly high FWHM values also have been noted for young sinter and sinter deposited in high temperature (>75ºC) settings (Rodgers et al., 2004). This pattern can be explained by noting that a larger Δd ($\Delta 2\theta$) value is indicative of greater disorder within the opal-A structure. Constant silica dissolution and redeposition from acidic waters, combined with an increase in kinetic energy afforded by the available heat, are likely causes for the resulting high entropy or disorder of this deposit.

Microspicule formation has been attributed to both biotic mechanisms, whereby microbes act as structural templates (e.g. Campbell et al., 2002; Handley et al., 2003), and abiotic mechanisms, through hydrodynamic factors such as splash and spray from ebullient hot springs and geysers, and oscillatory wave activity and capillary action through wicking and diffusion (e.g. Renaut et al., 1998; Lowe and Braunstein, 2003). In this study, we observed that microspicule formation is biotically mediated, through a dynamic interplay between biofilm growth and silica deposition.

Biofilms afford protection from numerous environmental extremes that are likely to be encountered in an acidic hot spring setting, such as UV exposure, metal toxicity, acidic conditions, dehydration and high salinity (Hall-Stoodley et al., 2004). The formation of biofilms and their subsequent development includes the transport of microbes to a surface and their initial attachment, followed by microcolony formation (Stoodley, 2002). In quiescent waters with the ideal nutrient conditions, the microcolonies often resemble pillar, mushroom or mound-like structures. These features increase the surface area available for nutrient uptake and are formed by clonal division, whereby daughter cells spread outwards and upwards from the attachment surface to form cell clusters (Stoodley et al., 2002). Such positive relief appears to lead to microspicule formation.

The mechanisms of microbial silicification are poorly understood and it is not known if biomineralisation is caused by the evaporation and cooling of waters oversaturated in silica, or if it is mediated biogenically through metabolic activity. It appears that the silicification of microbes and their associated EPS is passive, with cell walls acting as templates for the precipitation of silica by cooling and evaporation. Experimental and observational work has shown that nucleation of silica is promoted on the reactive sites of microbial cell walls. Silica has been shown to have affinity with functional groups on proteins and polysaccharides of microbial cell walls and EPS (e.g. Westall et al., 1995; Renaut et al., 1998; Farmer, 1999). Hydrogen bonding and subsequent dehydration reactions can result in siloxane bond formation between silicic acid and the functional groups, followed by abiotic, homogeneous silica polymerisation (cf. Urrutia and Beveridge, 1993; Asada and Tazaki, 2001). This alternation among biofilm formation, silicification and subsequent recolonisation implies that the spicules on the sinter body from this study are stromatolitic in nature.

It seems that silicification of the microbes occurs early, even while they are still alive (c.f. Schultze-Lam et al., 1995; Renault et al., 1998). The cells show no sign of having perished as silica deposition outpaces the rate of decay (cf. Cady and Farmer, 1996).

The tendency of silica to deposit on the margins of diatoms and EPS is likely due to the higher energy encountered at these surfaces (Banfield and Hamers, 1997). Atoms on edges have lower coordination and strongly asymmetric bonding configurations, thereby allowing preferential deposition of silica (Banfield and Hamers, 1997).

Care must be taken when characterising *in situ* microbial compositions, as secondary overgrowth of microorganisms, especially fungi, from outside the native environment is a very likely possibility. Furthermore, the presence or absence of microbes and their relationship to the mineral substrate is key in evaluating whether certain sinter textures are abiotic or biotic in nature. It is therefore recommended to use cryo-SEM, environmental SEM (ESEM) or to treat samples with a biological fixative such as glutaraldehyde and critical point drying before examining the samples under SEM.

5. ACKNOWLEDGMENTS

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