THE RELATIONSHIP OF ENVIRONMENTAL CONDITIONS AND PHYSICO-CHEMISTRY OF THERMAL WATER AND THE NATURE OF THEIR SILICEOUS SINTER DEPOSITS AT EL TATIO, CHILE

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ABSTRACT

Siliceous sinter forms by evaporation and cooling to temperatures <100 °C of near-neutral, alkali-chloride silica-rich thermal waters. Their importance resides in their capacity to record environmental conditions and their relationship to the presence of a geothermal field at depth.

Sinter textures are controlled by environmental and hydrodynamic conditions whereas their initial mineralogy and chemistry is controlled by the chemical composition of thermal waters. For siliceous sinters to form the discharging hot spring water is oversaturated with respect to amorphous silica. Therefore, the extreme climatic conditions and the particular water geochemistry that occurs at El Tatio geothermal field is reflected in the characteristics of the siliceous sinter deposits.

Here we present preliminary results of a study undertaken at El Tatio, designed to determine the effects of thermal water geochemistry and of environmental conditions present during the sinter formation process.

1. INTRODUCTION

Siliceous sinter deposits are hot spring rocks formed by cooling of alkali-chloride, near-neutral and silica-saturated thermal waters (e.g. Jones *et al*., 2000; Rodgers *et al*., 2004; Guidry and Chafetz, 2003; Mountain *et al*., 2003). Sinter deposits infer the presence of high temperature hydrothermal reservoir at depth (Fournier and Rowe, 1966) and therefore are commonly used in geothermal and ore exploration. Sinter textures and morphology are influenced by the environmental conditions, the biological communities that thrive in the thermal waters and the hydrological conditions of the water flow (e.g. Cady and Farmer, 1996, Campbell *et al*., 2001, Lowe *et al*., 2001, Jones *et al*., 2002; Lynne and Campbell, 2003 and Handley *et al*, 2005).

The Andean Central Volcanic Zone is currently under exploration for hydrothermal deposits and energy resources, yet the characteristics of siliceous sinter deposits formed under the particular environmental conditions of this location have been understudied. It is of vital importance to understand the origin of the unique textures and mineralogy that occur in siliceous sinter deposits formed at high altitude, to successfully use these deposits as a tool for geothermal exploration.

Previous studies of the siliceous sinter deposits at the El Tatio geothermal field focused on the genesis of siliceous oncoids around geyser vents and hot pools, and sinter mineralogical variability related to diagenesis (Jones and Renaut, 1997; García-Valles *et al*., 2008; Fernández-Turiel *et al*. 2005). However, the effects on sinter architecture of the particular environmental conditions, such as high evaporation rate, high atmospheric temperature variability (reaching -30°C at night; Fernández-Turiel *et al*. 2005). and a lower boiling point temperature (~86°C at 4200 m above sea level), have not been determined.

In this work, we report new textural, mineralogical and geochemical data of the high-altitude siliceous sinter deposits from the El Tatio geothermal field. The main objective of this work is to determine the relationship between environmental conditions and physico-chemical characteristics of the thermal fluids with the chemical composition, mineralogy and textures of siliceous sinter deposits at the El Tatio geothermal field.

1.1 Site of study

El Tatio geothermal field (22°20'S and 68°W) is located in the altiplano of north Chile, 95 km east of the town of Calama, in the El Loa Province, Antofagasta Region, northern Chile. It presents numerous thermal features, including fumaroles, geysers, springs, hot and boiling pools and sinter deposits covering an area of more than 100 km^2 at 4270 meters above mean sea level.

The first investigations at El Tatio focused on evaluating the energy potential and are almost exclusively on fluid geochemistry (Cusicanqui *et al*, 1975, Lahsen and Trujillo, 1976; Giggenbach, 1978). More recently, other studies have addressed the issue of the source and genesis of the thermal waters (Tassi *et al*., 2005; Cortecci *et al*., 2005) and the characterization of geothermal features present at the site (Glennon and Pfaff, 2003).

El Tatio thermal waters are characterized by their near neutral pH, high content in chlorine (~8000 mg/l) and sodium (~4000 mg/l), they show high silica (up to ~220 mg/l) and arsenic content (up to ~30 mg/l), and low sulphur content (up to ~70 mg/l) (Landrum *et al.* 2005; Cortecci *et al*., 2005).

According to previous studies, siliceous sinter deposits at El Tatio are mainly composed of opal-A, with a minor occurrence of opal-A/CT and opal-CT (Fernández-Turiel et al., 2005; García-Valles *et al*., 2008). Their chemical composition shows variable concentrations of Cl, Na, Ca, S, As, Sb and B (from 5 to 20 wt%; Fernández-Turiel et al., 2005, Landrum *et al*., 2009). Mineralogical studies reveal the common occurrence of opal, halite, sylvite and realgar, and rare accessory minerals such as sassolite [H_3BO_3],

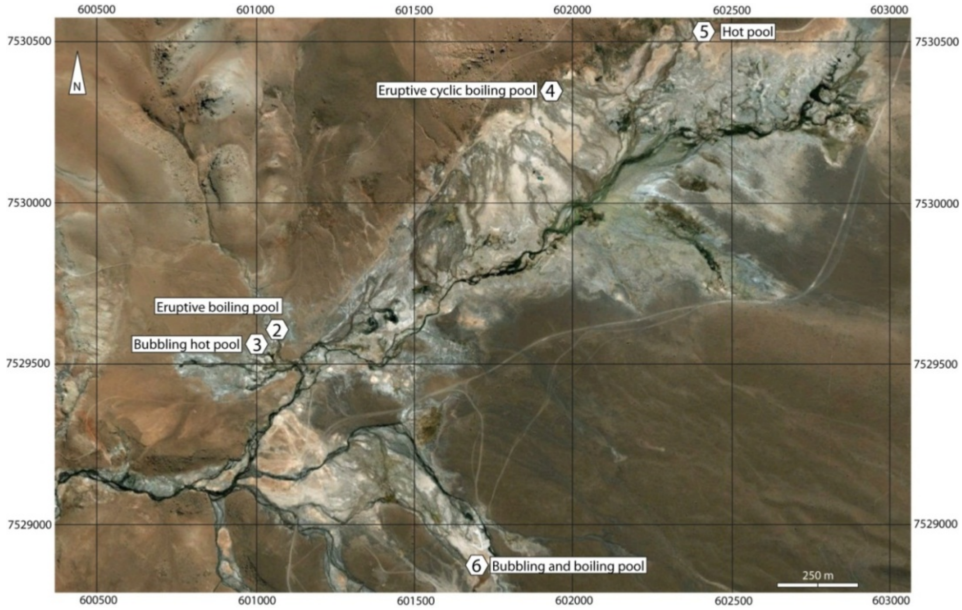

Figure 1: Sampling sites location at El Tatio Geothermal Field. Samples were taken from sinter deposits distributed along a NE valley that forms the Salado river.

teruggite [$Ca_4MgAs_2B_{12}O_{22}(OH)_{12}\cdot 12(H_2O)$] and nobleite [$CaB_6O_{10}\cdot 4H_2O$] (Rodgers *et al*., 2002; García-Valles *et al.,* 2008). In addition, a variety of biological communities of cyanobacteria (*Leptolyngbya* and *Calothrix*) and diatoms thrive in the hot springs that form sinter deposits, whose existence is extremely dependent on specific thermal waters physico-chemical conditions (Fernández-Turiel *et al*., 2005).

The climate in this area is characterized by low precipitation (<100 mm/year). Rainfall is particularly seasonal, because this area is under the influence of the South American Summer Monsoon, with rains occurring from November to March (Zhou and Lau, 1998) and particularly focused form December to March (Fernández-Turiel *et al*., 2005).The mean annual temperature ranges from 8 to 11 °C. Daily temperature variation reaches 35 °C. In winter the temperature can fall to -30 °C (Fernández-Turiel *et al*., 2005).

1.2 Methods

Five sampling sites were selected at the El Tatio Geothermal Field (Figure 1). Sites correspond to sodium-chloride pools that differ in their hydrodynamic characteristics, and the textures and coloration of their associated siliceous sinter deposit.

We characterize the mineralogy, chemistry and textures of El Tatio sinters trough Scanning Electron Microscopy (SEM) and FEG-SEM, Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) and petrography. We also characterize the hydrodynamics of the associated thermal waters through field measurements and their chemistry through laboratory examination (ICP-OES and Ionic Chromatography (IC).

2. RESULTS

2.1 Sampling sites characteristics

The water from the selected sites are near neutral pH (6.5 to 7.5) and their temperature ranges from 76.9 to 87.6°C. Sites 2 and 6 are eruptive pools, site 4 is an eruptive cyclic boiling pool, site 3 is quiescent and bubbling with a few eruptive events, and site 5 is a non-bubbling, non-boiling pool.

2.2 Mineralogy of sinter deposits

SEM observation of sinter samples reveals that they are mainly composed of opal-A silica. The opal-A morphology varies from smooth, well-rounded to bumpy; the sizes of smooth, well rounded spheres ranges between 0.2 to 3 µm, whereas the size of bumpy spheres reaches 6.5 µm. Opal-A spheres can occur randomly coalesced forming porous silica layers, evenly coalesced forming well defined layers, or clustered forming bumpy spheres (Figure 2).

However, other phases, different from opal-A, are minor constituents of El Tatio sinters. Accessory minerals are dominated by halite and gypsum. XRD analyses of sinter samples confirm the occurrence of halite in sites 2, 5 and 6, showing diffraction peaks at 32.2°2θ and 47.14° 2θ, nevertheless, gypsum peaks were not identified in the XRD traces.

Other minerals occur as infilling of micro-cavities or fractures within the sinter deposit, such as needle-like Si-Ca-As crystals, tetrahedral Ca-As crystals and lamellar As-Ca crystals. (Figure 3). The identification of all these minerals have not been possible, except for the tetrahedral crystals, which correspond to cahnite ($Ca_2B[OH]_4[AsO_4]$), a calcium and arsenic borate. The presence of cahnite is confirmed by the 25.05 and 33.97°2ϴ peaks in the XRD traces of one sample from site 3.

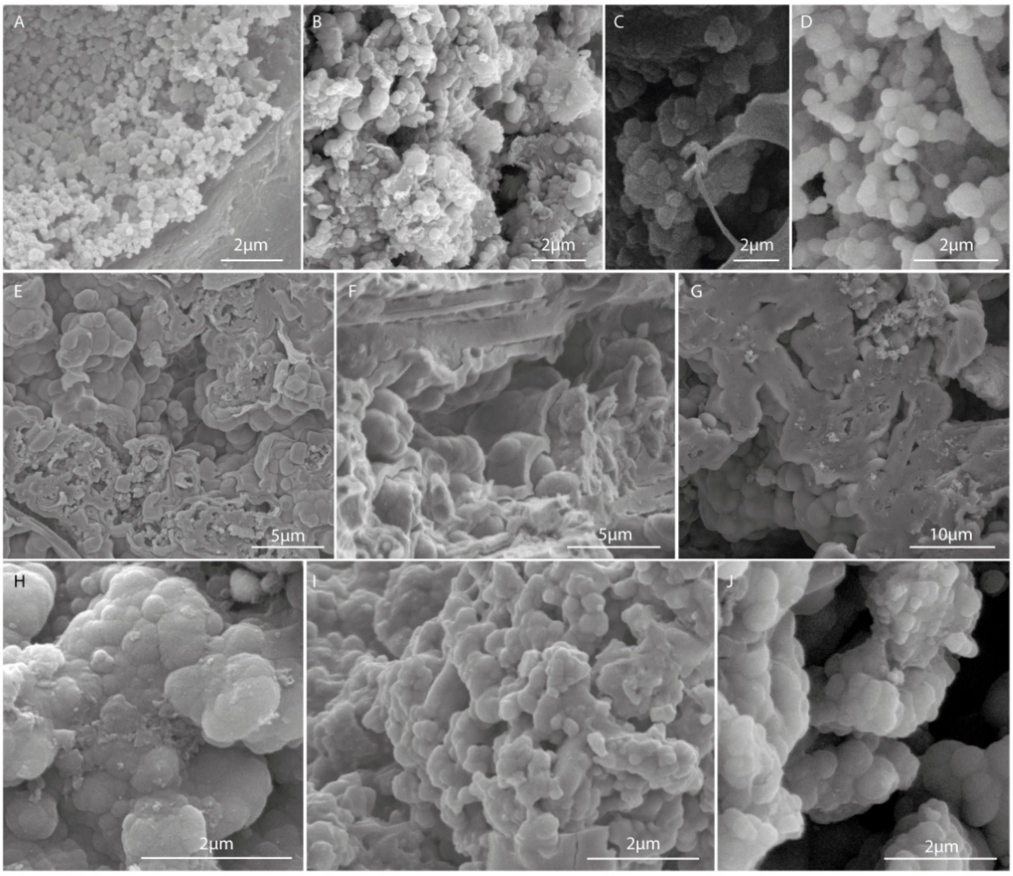

Figure 2. SEM images of silica phase morphology of El Tatio sinter samples: individual and coalesced opal-A spheres. A: Individual smooth opal-A nano-spheres, site 3. B: Individual opal-A nano- and micro-spheres with aggregates of bladed crystals, site 6. C-D: Individual smooth opal-A nano-spheres, site 2 and 5 respectively. E-J: Amalgamated or coalesced smooth opal-A micro-spheres, sites 2 (E-F), 6 (G), 3(H-I) and 5 (J).

XRD analysis of the sinter samples revealed opal-A to be the dominant silica phase at El Tatio FWHM values vary between 7.8 and 12.5 °2θ and the apex positions vary between 22.2 and 23.9 °2θ.

2.3 Textural characterization of sinter deposits

Sinter micro-textures identified through SEM observations include micro-columns and ridges (Figure 4A) formed by stacking opal-A spheres; layers formed by broken silica platelets (Figure 4B) that occur predominantly on sinter surfaces although some deeper horizons; massive laminated silica layers with variable thickness (Figure 4C); silicified microbial filaments (Figure 4D), which can be encrusted by low diameter opal-A spheres or replaced by them; lithic rich horizons which are commonly covered by a silica coating and where the presence of microbial filaments is common (Figure 4E); and porous silica layers formed by coalesced opal-A spheres and void space (Figure 4F).

Silicified microbes are 0.8 to 10 µm diameter occur in mid to high temperature areas, >1 µm diameter filamentous microbes are identified in the surface of a sinter spicule.

2.3 Chemical characterization of sinter deposits

The chemical composition of the sinter samples is dominated by silica as expected, but high concentrations of iron, sodium, chloride and calcium are also present. The silica content of sinter samples varies between 41 wt% and 85 wt% SiO_2. Iron content is also high in some samples (up to 3.2 wt% Fe_2O3). Detailed chemistry of the El Tatio sinter samples is shown in Table 1.

2.4 Thermal waters characterization

Thermal waters at El Tatio geothermal field are classified as sodium-chloride waters based on the Piper classification (Piper, 1953). All samples show high concentrations of dissolved silica (147-285 mg/l SiO_2), calcium (156-306 mg/l) and potassium (192-848 mg/l). Arsenic content is high in all samples (>17 mg/l), but the highest value occurs at sites 4 and 5 (31 mg/l). Sulfur content is higher at site 3 (377 mg/l), intermediate at site 2 (104 mg/l) and site 6 (145 mg/l), and low at sites 4 and 5 (<90 mg/l).

Table 1. Chemical composition of El Tatio sinter samples

		DL	M2.1	M2.3	M3B	M3R	M3.2	M4.2	M5	M6.4
SiO_2	wt%	0.01	64.15	59.58	41.08	8.10	70.09	73.25	85.04	77.63
Al_2O_3	wt%	0.01	0.62	5.85	0.76	0.81	3.86	0.97	0.67	1.98
$Fe_2O_3^{(T)}$	wt%	0.01	0.87	2.88	3.16	18.75	1.53	0.44	0.23	1.73
MnO	wt%	0.001	0.2	0.146	1.093	0.811	0.184	0.013	0.006	0.043
MgO	wt%	0.01	0.22	0.79	1.64	0.24	0.63	0.08	0.06	0.27
CaO	wt%	0.01	3.46	2.83	7.26	8.59	3.72	0.38	0.56	2.07
Na_2O	wt%	0.01	2.17	3.36	0.55	0.70	1.6	0.72	0.96	0.79
K_2O	wt%	0.01	0.54	1.12	0.31	0.49	0.91	0.5	0.43	0.39
Cl	wt%	0.01	1.54	2.67	0.2	0.71	0.48	0.47	0.56	0.14
Total S	wt%	0.01	0.11	0.06	0.07	0.08	0.13	0.04	0.02	0.05
B	ppm	2	8440	3820	4330	717	5790	2040	2180	1890
As	ppm	5	> 2000	315	> 2000	> 2000	694	177	334	> 2000

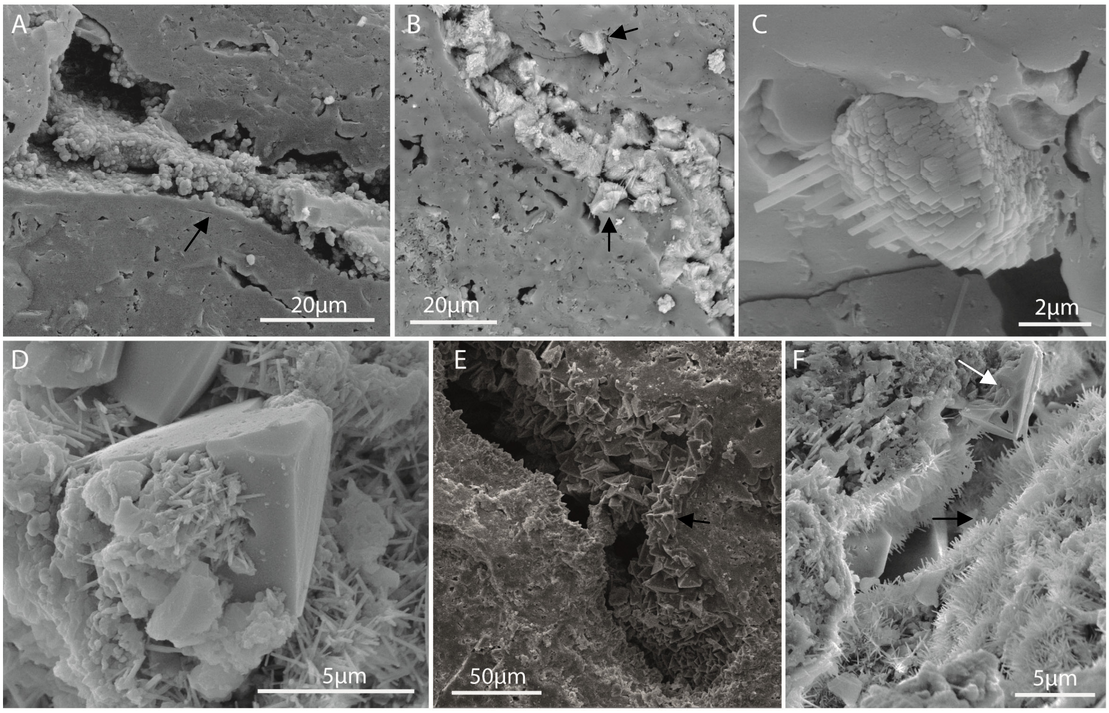

Figure 3: SEM images show opal-A and other minerals of sample from site 6. A: Secondary infilling of a cavity by smooth opal-A nano-spheres (arrow). B: Lamellar As-Ca crystals infilling avoid in massive silica horizon (arrows). C: Detail of one lamellar As-Ca crystal. D: Detail of tetrahedral Ca-As crystal and needle-like Si-As-Ca crystals. E: Tetrahedral crystals formed at the walls of a cavity (arrow). F: Needle-like crystals (white arrow) and tetrahedral crystals (black arrow) formed at the walls of a cavity.

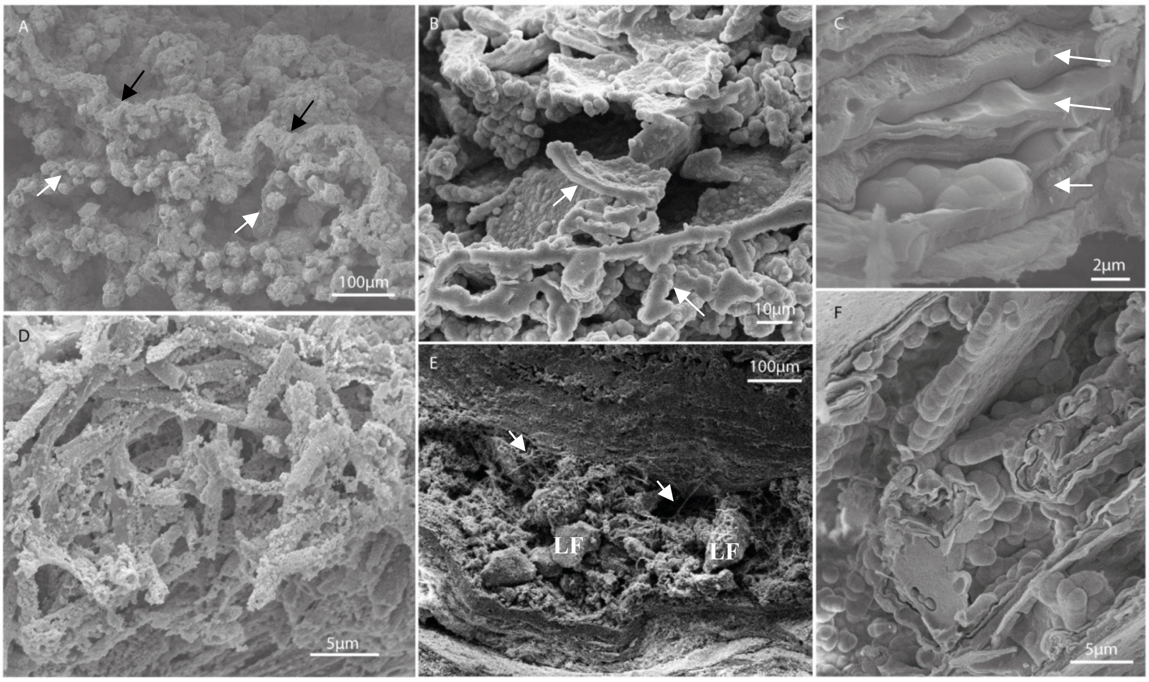

Figure 4: El Tatio sinter micro-textures under SEM. A: Micro-columns (white arrows) and ridges (black arrows) from the surface of a sample at site 4. B: Silica platelets (white arrows) found at the surface of samples from site 2. C: Massive silica layers formed by coalesced opal-A spheres in sample from site 3. D: Mid-temperature microbial filaments encrusted by nanometer sized, opal-A spheres from sinter at site 3. E: Lithic fragments (LF)- and microbial filament-rich horizon (arrows) between two massive silica layers from a sample from site 4. F: Porous silica layers from sample from site 2.

3. DISCUSSIONS

The study of thermal water and associated sinter deposits at the El Tatio Geothermal Field in northern Chile provides new insights into the characteristics of siliceous sinter deposits formed in an Andean setting. El Tatio's hot spring water is dominated by high concentrations of silica, chlorine, arsenic and boron. The environmental conditions are characterized by the high altitude, high evaporation rates and high thermal oscillation. These characteristics provided an ideal setting for the study of the relationship between environmental conditions and physico-chemical characteristics of high altitude discharging hot springs and their associated sinter deposits.

El Tatio sinters mainly consist of micro- and nano-scale opal-A spheres, and show a very low degree of structural order. FWHM values range from 7.8 to 12.5 and this parameter might be increased by the incorporation of cations in the silica structure, revealed by SEM-EDS analysis of smooth opal-A spheres.

The occurrence of highly soluble minerals such as cahnite, halite and gypsum is related to the sinter formation process through evaporation to dryness and to the high content of Na, Cl, Ca and S in the thermal waters. The occurrence of arsenic borates has been previously reported at El Tatio (García-Valles *et al.* 2008, Rodgers *et al.* 2002), although their origin in geothermal fields has not been studied.

El Tatio sinters show a relatively high content of iron and aluminium. The iron content is possibly associated to the occurrence of hydrous ferric oxides, as have been reported by Landrum *et al*. (2009) and Alsina *et al.* (2008, 2013), yet they were not observed in this study, while the aluminium content is attributed to lithic material blown into the sinter deposit.

Regarding trace elements, arsenic and boron show the highest content, and are related to cahnite or other arsenic borates such as teruggite and nobleite, reported by García-Valles *et al*. (2008) and Rodgers *et al*. (2002). Chemical composition of thermal waters plays an important role in El Tatio sinter chemistry because sinter formation is mainly sub-aerial and driven by evaporation to dryness.

Distinctive macro- and micro-textures identified in El Tatio sinters are related in some cases to ambient temperatures, while others are linked exclusively to water temperature and hydrodynamics.

Silica platelet formation is attributed to freezing-unfreezing events that occur daily at El Tatio, as sub-zero temperature is common at night. Freezing would lead to an increase in the volume of interstitial water remaining in newly formed silica layers, which can cause the breakdown silica layer originating the silica platelets. As day temperature usually raises enough to allow thawing to take place, silica platelets dislocate, producing the observed texture, unless they are re-cemented by silica precipitation, which would lead to the formation of a massive layer with no remains of the platelets. Iler (1979) report similar silica morphology, silica flakes, which are similarly formed by freezing conditions. Nevertheless, these silica flakes are considerably smaller (20 – 30 Å in diameter; Iler, 1979) than the silica platelets reported in this study.

The co-existence of spicular texture with >1 µm diameter microbial filaments is an interesting finding, because geyserite is usually related to high temperature near-vent settings, where the water temperature is too high to support life, or at least high enough that only high-temperature <1 µm diameter microbes can tolerate (Cassie, 1989; Cady and Farmer, 1996). Nevertheless, boiling temperature is lower at high altitude, allowing the co-existence a boiling-related texture and mid-temperature microbes. Thus, at El Tatio and other high altitude geothermal fields, the interpretation of near-vent settings should be done based on sinter textures.

3. CONCLUSIONS

The integrative study of siliceous sinter deposits at active geothermal fields, that includes mineralogical and textural determinations, along with thermal water characterization, provides new insights about the nature of siliceous sinter deposits in the Andean context.

The results of this study reveal that the origin of the particular mineralogy and textures of El Tatio sinters is related to the specific geochemistry of the thermal waters (high in arsenic and boron) and the high altitude conditions; which are reflected in a lower boiling point and freezing-unfreezing- daily cycles.

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