The growth of siliceous sinter deposits around high-temperature eruptive hot springs

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ABSTRACT

Siliceous hot spring deposits (sinter) are of interest as they are indicative of hydrothermal resources at depth and may provide evidence for early life on Earth and possibly Mars. Numeric models of concurrent evaporation and opal-A precipitation around high temperature (>73 °C), eruptive hot spring vents such as geysers show that silica is most efficiently precipitated by complete evaporation owing to very sluggish growth kinetics for silica precipitation from supersaturated hydrothermal water. Where evaporation is complete between geyser events, areas of initially deeper water precipitate more silica that, over time, fill in topographic lows to produce a smooth surface. In contrast, incomplete evaporation, in which water is left in low areas prior to being washed away by the next geyser event (or equivalently where there is continuous surface flow in topographic low areas), tends to enhance the growth of minor topographic highs and leads to an increase in surface roughness such as seen in the development of "knobby" geyserite sinter texture around vents.

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1. Introduction

Terrestrial siliceous hot spring deposits, referred to as sinter, are common in geothermal regions where deep alkali chloride reservoir water discharges at the surface and deposits silica. The amount of silica present in hot spring water is not accounted for by the solubility of amorphous silica, which is the silica phase that precipitates at the surface to form sinters, but is controlled by the solubility of quartz at depth (Fournier and Rowe, 1966). Therefore, the silica concentration of boiling water discharged at the surface can be used to estimate the temperature of a geothermal reservoir at depth, based on the water being in equilibrium with quartz prior to its ascent and discharge, as long as the water is cooled by steam formation and not by conduction, convection, separation of abundant, non-aqueous gases or by mixing with dilute, cooler near-surface water (Fournier and Rowe, 1966). In addition, sinters are important as they host unusual thermophilic biota that may provide clues to ancient life on Earth (e.g., Corliss et al., 1981) and possibly Mars (e.g., Walter and Des Marais, 1993).

Walter (1976a, 1976b) and Cady and Farmer (1996) suggested that sinters could be subdivided into a number of "sinter facies" in which sinter morphology is controlled mainly by temperature, cyanobacterial growth (particularly important at temperatures up to 73 °C), and hot spring hydrodynamics (still or boiling, waves, splashing and the like). At temperatures below 73 °C, a variety of thermophilic bacteria can grow in lush multicolored mats that become silicified over time and which can be the dominate feature of the outflow system. Silicified

microbes can constitute up to half of a sinter deposit (Bartley, 1996; Cady and Farmer, 1996; Konhauser et al., 2001). Above 73 °C, however, the hot spring deposits are composed mainly of amorphous silica (opal-A). While there have been a number of studies showing the presence of biofilms in the high temperature hydrothermal waters and a possible role for a biogenic origin (e.g., Jones and Renaut, 2003; Handley et al., 2005), their role in silica precipitation and sinter morphology is uncertain (e.g., Jones et al., 1997; Braunstein and Lowe, 2001). It is this largely abiologic growth of high temperature sinters that is the main focus of this work.

Braunstein and Lowe (2001) have distinguished six types of high temperature hot springs and geysers in the Yellowstone area based on activity and eruption style for which each develops its own characteristic high temperature sinter morphology. They also noted that sinter deposition occurs in three main environments: 1) Continuously wet areas, 2) periodically wetted splash zones and 3) subareal regions of the rim and outflow area that are wetted mainly by overflow that dry quickly. Braunstein and Lowe (2001) and Lowe and Braunstein (2003) suggest that, while high temperature hot springs may have a biofilm that can influence the rates of silica deposition, the morphology and macrostructures of high-temperature sinters are largely controlled by surface wetting, evaporation and drying. In addition, Mountain et al. (2003) found that the precipitation of subaqueous silica sinter (e.g., in pools) can be predicted from the silica saturation index. This implies that, although microorganisms may be present, they cannot induce subaqueous precipitation where the geothermal waters are not saturated in silica. In contrast, however, Tobler et al. (2008) found high sinter precipitation rates in waters undersaturated in silica, which they suggest may be due to the observed biofilms. Mountain et al. (2003) also note that the fastest rates of sinter growth occurred

in areas where hydrodynamic effects (wave action and splashing) were dominant and where temperature gradients were steep. In contrast, in quieter environments it is capillary rise and diffusion as the dominant mechanisms for subareal sinter growth. Once a surface is wetted and undergoes cooling and evaporation, rapid nucleation of silica occurs on all available surfaces, including on microorganisms.

If it is generally true that high temperature sinters are largely a function of hydrodynamics and drying, then the geomorphology of the sinters should be amenable to modeling based on the interaction of wetting, advective flow (both surface flow and capillary pull) and diffusive mass transport, evaporation, and silica precipitation. Although the papers noted above and many other have looked at the growth of sinters and a good qualitative picture of sinter formation is emerging, fully quantitative models that can enhance one's understanding of abiologic sinter growth appear to be lacking. This is potentially important because one must be able to separate features that can arise from purely abiologic processes if one wishes to infer biologic processes to ancient sinters, particularly if microfossils have been destroyed over time. Also, quantitative models can allow one to explore sinter morphologies in environments not commonly observed on Earth, as for example in the much drier and colder Martian atmosphere. We report here a first-order quantitative model of sinter growth.

2. Precipitation and evaporation in sinter formation

There has been considerable work over the past few decades on the kinetics of silica precipitation in both simple laboratory SiO_2-H_2O systems and in natural hot springs of varying temperature, salinity, SiO_2 concentration, pH and biologic activity (e.g., Bohlmann et al., 1980; Rimstidt and Barnes, 1980; Weres et al., 1982); Carroll et al., 1998; Conrad et al., 2007). In the following we have adopted the formulation of Rimstidt and Barnes (1980) as it has been used in hydrothermal circulation models (e.g., Takeno et al., 2000) and it applies to the simple SiO_2-H_2O system.

As noted by Rimstidt and Barnes, the rates of silica precipitation from waters below 100 °C can be very low even though the solution concentrations can be much higher that the saturation values. For dilute, low salinity fluids for which the activity of water and the activity coefficient of aqueous silica can both be taken as 1.0, the precipitation rate kinetic equation 55 of Rimstidt and Barnes (in cgs units) for the change in the molar concentration of SiO_2, C, with time is given by (symbols and units are as defined in Table 1):

$$Q = \frac{\partial C}{\partial t} = k\left(\frac{A}{M}\right)\left(1 - \left(\frac{C}{K}\right)\right) \qquad (1)$$

Table 1
List of symbols.

A	Surface precipitation area (cm^2)
C	Concentration of aqueous SiO_2 in the hydrothermal water (mol)
D	Mass diffusion coefficient for aqueous SiO_2 (cm^2/s)
E	Evaporation rate, (cm/s)
K	Aqueous silica concentration in equilibrium with amorphous silica (mol)
M	Mass of hydrothermal water (g)
Q	Rate of change of aqueous silica concentration due to precipitation (mol/s)
T	Temperature (K)
f	Fraction of water remaining as evaporation proceeds (dimensionless)
k	Reaction rate constant (s^{-1})
t	Time (s)
z	Distance (cm)
δ	Thickness of opal-A layer (cm)
Δ	Thickness of evaporated water layer (cm)
ρ	Density of water (g/cm^3)
Φ	Liquid volume fraction relative to initial nominal water film thickness (dimensionless)

For which

k	rate constant,
Log k	$-0.369 - 000789\ T - 3438.0/T$.

Note that the form of Eq. (1) states that there is a greater change in solution concentration (more silica is precipitated) if there is more surface area over which the solution can precipitate, all else being equal. However, because the amount of precipitated silica is proportional to area, the thickness of the deposited silica in any time interval is essentially a function of supersaturation, all else remaining constant.

For example, at 368 K (95 °C), log k = −10.0 or k = 1.0×10^{-10} s^{-1}. Amorphous silica (opal-A) saturation concentration is given by the following equation (Gunnarsson and Arnórsson, 2000):

$$Log\,K = -8.476 - 485.24/T - 2.268 \times 10^{-6}T^2 + 3.068\,log\,(T) \qquad (2)$$

At 368 K (95 °C), K = 0.005892 m or 354 ppm SiO_2: at this temperature any hydrothermal water with SiO_2 concentrations higher than this will be supersaturated with regards to amorphous silica. However the rate Eq. (1) suggests this will be very slow, particularly in the absence of a biocatalyst. For example, 1 L of strongly oversaturated solution with C_0 = 800 ppm SiO_2 at 95 °C will, over the course of an entire year, precipitate a layer of opal-A only 9.6×10^{-9} cm thick over an area of 1 cm^2. The high initial silica concentration in this example is about twice as high as is found in most natural hot spring waters and illustrates the low precipitation rate of silica even in strongly saturated solutions.

In contrast, the thickness of opal-A, δ, precipitated as a function of the thickness of the water layer evaporated, Δ, where the initial silica concentration in the water is C_0 (in ppm SiO_2) is given by:

$$\delta = 6.874\times^{-7}\Delta C_0 \qquad (3)$$

Thus, the complete evaporation of the same 1 L of water with the same 800 ppm initial silica concentration as used above, if all concentrated in 1 cm^2 (equivalent of evaporation of a column of water 10 m high and 1 cm^2 in cross sectional area), would produce a layer 0.55 cm thick, or $5.73*10^7$ thicker than by precipitation from the supersaturated solution over the course of an entire year. In other words, evaporation to dryness is 7–8 orders of magnitude more effective for precipitation of silica than is precipitation from a supersaturated solution. Even accounting for the fact that the silica precipitation rate in natural hot springs is about three orders of magnitude higher than predicted by the Rimstidt and Barnes (1980) (e.g., Carroll et al., 1998), evaporation would still be 4–5 orders of magnitude more efficient than precipitation in silica deposition.

The importance of evaporation is supported by the field observations noted above that silica precipitation is most efficient in energetic systems where hydrothermal waters can splash and dry. Relative to the volume of flow, channeled water flowing over sinter fields should not deposit much silica. It is only when the water occasionally overtop or splash out of the channel and dry completely will the surroundings accumulate a significant volume of silica. In this regards the cycles of overtopping/splashing and subsequent drying are grossly similar to levee formation when rivers flood and deposit their sediment load in the surrounding floodplain but otherwise may not have much active deposition.

2.1. Evaporation rate

Although evaporation appears to be fundamental to silica precipitation, it is difficult to find measurement of evaporation rates in hot spring systems (c.f., White et al., 1956 and Day and Seely, 1988, for two exceptions). Equations for evaporation of relatively low temperature open