A COMPARISON OF THE MINERALOGY AND MORPHOLOGY OF TRAVERTINE FROM THE USA AND NZ

Kevin Channel, Bridget Lynne, and Sadiq Zarrouk

Faculty of Engineering Science, University of Auckland
Institute of Earth Science and Engineering, New Zealand

kevin_channel_geol@yahoo.com, b.lynne@auckland.ac.nz and s.zarrouk@auckland.ac.nz

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ABSTRACT

Travertine is a common geothermal surface feature that forms by the deposition of carbonate from discharging bicarbonate thermal water. Travertine samples from two sites: Silver Peak, Nevada, USA, and Waikite, New Zealand, were examined to contrast their mineralogy, morphology, and chemical composition.

These sites were chosen as they provided examples of travertine formed in different countries and in different geothermal settings. Travertine formed at Silver Peak is related to a deep-reaching heat-sweep system, Travertine at Waikite contains silica and is related to a flat terrain geothermal system where the heat source appears to be extensive, hot rhyolitic crustal rock.

X-ray Powder Diffraction (XRPD) determined differences in the travertine mineralogy of Silver Peak samples were calcite, whereas samples from Waikite consisted of calcite with some samples also containing silica (opal-A). Based on the XRPD trace samples from Waikite were slightly more crystalline than those from Silver Peak. The crystal size (> 100 μm) of Waikite’s samples is larger than Silver Peak’s samples (~ 100 μm) while some samples have no obvious crystal shape.

Different morphologies exist between the Silver Peak and Waikite calcite. Also calcite/silica samples from Waikite show that amorphous silica is deposited above the water level.

The depositional and hydrological conditions of these geothermal fields differs which influences the mineralogy, morphology, and chemical composition of their associated travertine deposits. Therefore, fine-scale examination of travertine enables us to better understand the hydrological setting (i.e. no hot intrusion Vs hot intrusion) and how the setting effects the formation of travertine.

1. INTRODUCTION

Travertine is a common geothermal surface feature that is formed by the deposition of carbonate from discharging bicarbonate thermal water. This study includes the macroscopic and microscopic aspects of travertine samples from two different sites: (1) Silver Peak, Nevada, USA, and (2) Waikite, Taupo Volcanic Zone (TVZ), New Zealand.

The aim of this project is to compare the mineralogical and morphological components of each sample and compare the two sites for similarities and/or differences. The sites were selected to represent different hydrologic and geothermal systems (Figures 1 to 2).
3. GEOLOGY OVERVIEW

3.1 Silver Peak, Nevada, USA

Clayton Valley is located in Esmeralda County, west central Nevada. The Clayton Valley playa floor is surrounded by alluvial fan slopes mountain ranges. Davis and Vine, (1979) summarises the geology.

Stratigraphically, Silver Peak consists of several rock formations from Pre-Tertiary to Tertiary (Figure 3):

Clayton Valley lies within the Basin and Range Province, a structural and physiographic region of generally linear mountain ranges and valleys (Davis and Vine, 1979). It lies within the Walker Lane structural corridor, which is dominated by right lateral wrench-faulting. This normal faulting is related to regional extension (Davis and Vine, 1979), and is coincident with basin and range faulting (Craig, 2003).

Silver Peaks, hot springs are found close to the edge of the playa. They have a maximum reported temperature of 118 °F (47.7 °C). Modern day site photographs of Silver Peak and its travertine geothermal manifestations can be seen in Figure 4.

3.2 Waikite, Taupo Volcanic Zone, New Zealand

Waikite is located within the Taupo Volcanic Zone (TVZ), New Zealand. The TVZ has long been recognised as an active arc/back-arc system related to the westward subduction of the Pacific beneath the Australian (Karig, 1970, in O’Brien, 2010).

The Taupo Fault Belt, a series of northeast trending normal faults in the centre of the TVZ are related to the intrusion of magma into shallow crust which also acts as the heat source for the TVZ (Wilson et al., 1995; Kissling and Weir, 2005). The fault zone creates zones of high fracture permeability which often host intense geothermal activity, especially where the fractures interact with NE-SW trending regional faults, (eg. Paeroa and Kaingaroa Faults).

Waikite geothermal field is located at the eastern side of the TVZ about 22 km south of Rotorua. Jones et al. (1996a) described hot springs near Waikite emerge 1.5 km below the Paeroa Fault Scarp next to Waikite Valley Road. Other springs (Waikite Scarp and Puakkohurea groups) are located in open ground 1-2 km to the northeast.

Manuroa hot spring located at Waikiti is a vigorously boiling spring that deposits carbonate along the rims of the discharge channel. It is this travertine that was collected for analyses in this study.
On February 7th, 2012, during the sample collection, the temperature of the Waikiti hot spring discharge channel was 86.6 °C, pH 7.68, with the fluid flow velocity of 4 m/s. Waikite samples collected in Manuroa discharge channel were found above the surface water are called “lily pads” shaped travertine (Figure 5) They are flat and sheet like masses rooted on boulders on a stream bed and shelfstone ledges that are attached to the banks, a term adopted from White (1976) in Jones et al. (1996).

Figure 5. Close up view of travertine from Waikite (lily pad shaped). Temperature of the water was 86.6 °C, pH 7.68, with the fluid flow velocity of 4 m/s.

4. HYDROGEOLOGY

4.1 The Hydrogeology of Silver Peak

The occurrence of the springs may be controlled by a major north-northeast trending fault along the west side of Clayton Valley (Alberst and Stewart, 1972).

The Paleozoic rocks in Clayton Valley contain much thinner sequences of carbonate rocks and probably do not form effective fractured aquifers as they do 150 km to the southeast at the Nevada Test Site (Winograd and Thordarson, 1975, in Davis et al., 1986). However, the upper Cenozoic rocks include alluvial sediments, bedded tuffs, and welded tuffs that act as aquifers. The chemical character of the ground water varies considerably within the basin, and three basic types can be identified (Davis et al., 1986): (1) cold, dilute ground water in the bedrock highlands; (2) thermal, saline ground water near the playa margin; and (3) cold, saline brines of the playa zone.

At Silver Peak, the thermal ground-water system obtains its heat from deep circulation (Davis et al., 1986). Circulation to at least 1 km depth would be necessary to acquire this heat from contact with rocks heated due to the natural geothermal gradient, and the basin structure would require at least 500 meters of this circulation into bedrock that is relatively impermeable except where fractured. Davis et al. (1986) also suggested that the Quaternary cinder cone and Pliocene volcanic north of the playa suggest the presence of a magma chamber that could increase the heat flux in excess of the normal geothermal gradient.
Stratigraphic impediments occur around much of the rest of the playa, isolating it from significant freshwater recharge and dilution (Zampiro, 2003).

4.2 The Hydrogeology of Waikite

The Waikite hot springs are associated with the NE-SW Paeroa Fault. Hot springs discharge from the boundary faults of the major graben (Wood, 1994). They flow from near the bottom of Paeroa Fault Scarp, from a step fault on the downthrown (NW) (Wood, 1994). This fault acts as the eastern boundary of the Taupo-Rotorua depression (Wood, 1994). Wood (1994) after Bibbly et al. (1994) suggested that based on the resistivity survey, these springs are an outflow from a deep hydrothermal system to the SE which also feed WaioTapu.

Jones et al. (1996) described that Waikite discharged as alkaline Na-Cl-HCO₃ waters that contain more bicarbonate than most thermal waters in the TVZ. The reservoir temperature based on empirical geothermometers are >150 °C and maybe even >200°C (Jones et al., 1996).

Waikite travertine is a product of dissolved CO₂ converted to HCO₃, resulting in a high ratio of HCO₃/Cl (Giggenbach et al., 1994 in Jones et al., 1996). The bicarbonate water is the ground water surrounding a deeper and higher temperature chloride water which feeds the WaioTapu system (Jones et al., 1996).

5. RESULTS

5.1 Travertine Hand Specimens

Six travertine samples from Silver Peak, three travertine samples from Waikite, display a variety of textures visible in the travertine hand specimens (Figure 6), such as: crystalline samples (SP 01 and WKT 05), nodule (SP 02), sugary like texture (SP 03), convex crust (SP 04), vuggy crystalline with disseminated black minerals (SP 05), layering calcite (SP 06), lily pad texture (WKT 01), and soft crust (WKT 04).

5.2 Travertine Mineralogy

The XRPD scanning results (Table 1) showed that all samples collected consist of: a) calcite only, or b) calcite and amorphous silica, or c) calcite, quartz, cristobalite, and feldspar. Six samples from Silver Peak consisted of calcite with the APEX positioned at 29.5-29.75 °2θ. Two samples from Waikite contain calcite with amorphous silica (WKT 01, and WKT 04), and three samples contain calcite and silica (WKT 02, WKT 03, and WKT 05).

The Silver Peak calcite samples showed higher maximum intensities (1200 to 2735 count/sec) compared to the Waikite samples (145 to 965 count/sec). There is a slight shift to a smaller APEX value in the Waikite samples (29.5 to 29.65 °2θ) when compare to the Silver Peak samples (29.5 to 29.75 °2θ). FWHM values for Silver Peak samples ranged from 0.2 to 0.3 °2θ while those from Waikite ranged from 0.15 to 0.25 °2θ. The FWHM values show that the samples from Waikite are more crystalline than Silver Peak.

XRF analyses (Table 2) showed that WKT 02 and WKT 03 have high content of SiO₂ (45.06 and 42.68 %), but the elevated SiO₂ content is due to the presence of quartz, feldspar, and cristobalite.

The APEX position and maximum intensity from the XRPD traces of Silver Peak travertine samples (29.5 to 29.75 °2θ) showed minimal difference to those from Waikite (29.5 to 29.65 °2θ). The maximum intensity for Silver Peak travertine samples (1200 to 2735 count/sec) are significantly higher than Waikite’s (145 to 965 count/sec). This is related to the calcite content in each sample, where according to the XRF data (Table 2), the Silver Peak samples have more CaCO₃ (79.84 to 96.89 wt%) compared to Waikite’s (10.40 to 16.61 wt%).

Two samples from Waikite also contain amorphous silica. The APEX position of amorphous silica in Waikite is between 21.75 to 22 °2θ. The maximum intensity of the Waikite amorphous silica is between 40 to 60 count/sec. Samples from Waikite reveal FWHM values of 5.2 to 5.5 °2θ.

Silica sinter transforms with time progressively, losing water in the process (Hochstein and Browne, 1999). According to the study of silica phase maturation in sinter at Opal Mound (USA) (Lyne et al., 2005), the FWHM values of opal-A are between 6 to 8 °2θ, opal-CT is approximately between 4 to 6 °2θ, opal-CT is between 2 to 4 °2θ, opal-CT is between 0.5 to 2 °2θ, and quartz is less than 0.5 °2θ. Based on that study, the samples in Waikite are opal-CT (FWHM values of 5.2 and 5.5 °2θ).

5.3 Travertine Morphology

5.3.1 Silver Peak

Hand specimen travertine sample SP 01 was white and crystalline (Figure 6). ESEM observations showed a unique irregular crystal morphology (Figure 7 a) with rhomb shaped crystals (~2 mm; Figure 7 b).

Hand specimen travertine sample SP 02 consisted of a grey coloured, rounded nodule of calcite (Figure 6). No calcite crystals were found in this sample. ESEM observations revealed that the surface of the sample has minimal topography (Figure 7 c) and displays a layered calcite surface (Figure 7 c). Minor pitting was observed possibly resulting from dissolution (Figure 7 c).

Hand specimen travertine sample SP 03 consisted of a yellowish crystalline sample (Figure 6). No obvious calcite crystals were found in this sample. ESEM revealed that some part of the sample did reveal a spiky surface texture possibly resulting from dissolution (Figure 7 d). Figure 7 e revealed the presence of an unknown rounded shaped crystal. The mineralogy of the mineral has to be determined using EDS which unfortunately was not done for this project.

Hand specimen travertine sample SP 04 consisted of a layered and convex calcite crust (Figure 6). No obvious calcite crystals were found in this sample. ESEM revealed that the sample has minimum surface topography (Figure 7 f). Figure 7 f revealed that this sample has overlapping mineral surfaces that might be secondary minerals. Based on the XRF analysis (Table 2), the overlapping mineral is most likely to be calcite. Hand specimen travertine sample SP 05 consisted of vuggy and crystalline calcite with disseminated black
fragments. Figure 7 g showed fine rhomb calcite crystals > 20 µm surrounded by a rough surface.

Hand specimen travertine sample SP 06 consisted of a highly porous but dense calcite sample (Figure 6). The presence of clay minerals (Figure 7 h) suggest the possibility of alteration. Figure 7 h shows the calcite crystal are > 20 µm.

<table>
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<th>Sample</th>
<th>Maximum Intensity</th>
<th>FWHM</th>
<th>Rock type</th>
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<td>Travertine</td>
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<tr>
<td>SP 02</td>
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<td>SP 04</td>
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<td>Travertine</td>
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<td>SP 06</td>
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<td>WKT 01</td>
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<td>Mixed travertine and sinter</td>
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<tr>
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</tr>
<tr>
<td>WKT 03</td>
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<tr>
<td>WKT 04</td>
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<td>Mixed travertine and sinter</td>
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<tr>
<td>WKT 05</td>
<td>200</td>
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Table 1. XRPD calculations (samples are calcite unless indicated otherwise).
Table 2. XRF analysis (unit in percentage weight wt%).

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<th>SP 04</th>
<th>SP 05</th>
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Figure 7. ESEM images of Silver Peak travertine samples. a: unique irregular crystal morphology (red arrow). b: Calcite crystal sized ~ 100 μm (red arrow). c: Layered surface of calcite (red arrow) and pitted surface (yellow arrow). d: Possible dissolved surface of sample with spiky texture. e: Increased magnification at the round shaped mineral (red arrow). f: Increased magnification view of the surface shows the sample is made of overlapping layers of calcite (red arrow). g: Rhomb shaped calcite crystal (>20 μm; red arrow). h: A calcite crystal > 20 μm (red arrow) and clay minerals (yellow arrow).
5.3.2 Waikite
Hand specimen travertine sample WKT 01 consisted of white lily pad shaped travertine (Figure 8 a and b). Besides calcite, this sample also consisted of amorphous silica (Table 1). A magnified view of the amorphous silica shows a layered texture (Figure 9). Fine rhomb shaped calcite crystals < 20 \( \mu m \) were observed (Figure 9 b). Slabbed hand specimen sample (Figure 8 b) shows that the samples consists of a polymix of rock fragments. Hand specimen sample of travertine WKT 04 consisted of friable, white, and crusty travertine (Figure 6). ESEM reveals that beside calcite, this sample also contains a mineral with smooth surface (Figure 9 c and d). No obvious calcite crystals were found in this sample. Figure 9 e revealed fractured surfaces of calcite. Figure 4.4 d shows the dissolved surface.

Figure 8. Lateral view and slabbed hand specimen of Waikite 01. a: Lateral view of lily pad shaped sample. Green box shows the location of microbial mat in the sample. b: Slabbed hand specimen sample of Waikite lily pad travertine. a: White crusty deposit above the yellow line formed above the water level. Deposit below yellow line was deposited below water line and clearly displays polymix of rock fragments.

Hand specimen sample of travertine WKT 04 consisted of friable, white, and crusty travertine (Figure 6). ESEM reveals that beside calcite, this sample also contains mineral with smooth surface (Figure 9 c and d). No obvious calcite crystals were found in this sample. Figure 9 c reveals fractured surfaces of calcite. Figure 9 d shows the dissolved surface.

Hand specimen sample of travertine WKT 05 consisted of a black travertine (Figure 6). This black colour may due to the high content of manganese (29.74 wt%; Table 2). Figure 9 e reveals images of rhomb calcite crystal size >100 \( \mu m \) surrounded by rough surfaces. Some smooth calcite crystal surfaces show clay minerals adhered to their surfaces (Figure 9 f).

Figure 9. ESEM images of Waikite travertine samples. a: Layered amorphous silica (yellow arrow). b: Rhomb shaped calcite crystals < 20 \( \mu m \) (red arrow). c: View on dissolved surface (yellow arrow). d: Various views of fractured surface of calcite. E: Rhomb calcite (> 100 \( \mu m \); red arrow). f: Smooth calcite crystal with irregular minerals adhered to the surface, (possibly clay shown by red arrows).
5. DISCUSSION

At Silver Peak the mineralogy of the surrounding rocks dictates the fluid chemistry of the discharging hot springs. Since the subsurface formations are rich in carbonates (limestone from Emigrant, Mule Spring, Deep Spring, and Wyman Formation or dolomite from Reed Dolomite Formation), the discharging thermal fluid is rich in bicarbonate which deposits carbonate to travertine at the surface. Low SiO₂ concentrations (46 mg/l) + high Ca + HCO₃ concentration (300 + 609 mg/l respect) support at this hypothesis. (Davis and Vine, 1979).

Waikite is located at the margin of high temperature upflow zone where the heat source is hot crustal rocks and magmatic gases. The deep reservoir fluid is alkali chloride silica-rich thermal water. Minimum dissolution of surrounding rocks influencing the fluid chemistry. The CaCO₃ is derived from interaction of dissolved CO₂ gas the shallow outflow margins of the geothermal reservoir and the dissolution of Ca from the local rocks.

In summary at Silver Peak, the high content of CaCO₃ is derived from dissolution of subsurface carbonate rocks while at Waikite, it is derived by the CO₂ reservoir gas on the margins of the system and deep fluid-rock interactions and dissolution of Ca rich minerals (e.g. feldspar).

At Waikite based on the high fluid temperature (86.6 °C), following the conditions described by Jones et al. (1996) aragonite should be deposited as travertine, not calcite. Jones et al. (1996) suggested that the presence of mucus caused the calcite to precipitated although other conditions favored aragonite precipitation. This suggestion by Jones et al. (1996) was based on the fact that there was a favored aragonite precipitation. This suggestion by Jones et al. (1996) suggested that the presence of mucus caused the calcite to precipitated although other conditions favored aragonite precipitation. This suggestion by Jones et al. (1996) was based on the fact that there was a considerable amount of mucus probably produced by thermophilic bacteria in the submerged calcite. Microbial mat, presumably cyanobacteria (Mountain et al., 2003), was observed on the submerged calcite at Waikite which may contribute to the mucus and calcite formation.

XRPD analysis at Waikite revealed that calcite formed above the water level together with amorphous silica (WKT 01). This suggests that there were changes in water level from time to time. When the water level was high, this sample was submerged below water table to deposit calcite, and at other times, the water level dropped, allowing amorphous silica to deposit together with the calcite. Alternatively, there were water level drops, and the already deposited calcite which is now above the water level were splashed by thermal fluid or precipitation of steam at the surface, resulting in deposition of amorphous silica. Mountain et al. (2003) documented subaqueous deposits of calcite and subaerial deposits of siliceous sinter at Waikite (At Waioatau siliceous sinter can develop both subaquously and subaerially).

Travertine starts as crystalline rocks and then mature, but stay crystalline throughout time. Sinters start as amorphous or non crystalline rocks then mature to crystalline rocks. Lynne et al. (2003 and 2005) documented a decrease in FWHM value accompanying silica phase maturation and aging of the sinter. Clearly this does not apply to the travertine in this study.

FWHM values measure the degree of crystallinity of Silver Peak travertine samples (0.2 to 0.3 °20) have slightly greater FWHM values than Waikite travertine samples (0.05 to 0.1 °20) suggesting Silver Peak samples are less crystalline than Waikite. However, during the sample collection in 2010, the Silver Peak hot springs were in dry condition while Waikite travertine is modern and actively depositing today, therefore waikite samples were temporally younger.

Using the FWHM values of travertines as a degree of measure of the amount of crystallinity (i.e. lower FWHM value = more crystalline) then we would expect the older Silver Peak travertine to be more crystalline (i.e. lower FWHM value) than those of Waikite. However, this is not the case.

Equilibrium constant in dissolution–precipitation of amorphous silica is controlled by aH₄SiO₄, which is the concentration of silicic acid, or polymeric acid, or silica colloids (Mountain et al., 2003). On the other hand, the equilibrium constant in dissolution–precipitation of calcite is not only controlled by one parameter but three (Mountain et al., 2003): i.e. pH (aH⁺), calcium (aCa²⁺), and bicarbonate activity (aHCO₃⁻). These might be the reason why FWHM values cannot be applied in calcite samples to determine calcite aging in this study.

The maximum intensity of the calcite peak located at 29.5 to 29.75 °20 may indicate calcite maturity. The temporally older samples of Silver Peak have high maximum intensities (1200 to 2735 count/sec) when compared to the modern and actively forming travertine at Waikite (145 to 965 count/sec).

Lynne et al. (2007) documented that silica in sinter is initially deposited as semi stable silica phase that through Ostwald ripening changes, and recrystallizes to a more stable and crystalline phase, and in the end, quartz forms, which is the most stable silica phase. Calcite is an already crystalline mineral and also the most stable phase, so it does not change in phases as there is no calcite mineral more stable than calcite. On the other hand, another carbonate that may be deposited as travertine is aragonite, which is a meta-stable and less stable than calcite. Ostwald ripening involves the "dissolving" and recrystallizing of smaller crystals to larger crystals so this process can occur with calcite itself or perhaps aragonite to calcite.

However, Waikite travertine has bigger calcite crystals compared to Silver Peak. The largest rhomb crystals at Waikite is shown by WKT 05 (> 100 µm). This is sample was taken from under the water and was manganese-rich. The biggest rhomb crystal observed in Silver Peak is in SP05 (> 20 µm). This show that calcite crystal size cannot be used to determine the age of travertine.

Methods to determine travertine maturation are suggested by Guo and Riding (1994). They suggest old travertine samples are compact and hard while the young are delicate and can be easily crushed. Applying this model, hard and crystalline samples from Silver Peak are more mature than Waikite samples which are crusty and light in weight. This is true since Silver Peak travertine had ceased flowing while Waikite travertine is still actively forming from bicarbonate water from the Manuroa hot spring.

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REFERENCES


