

Stanley Geothermal Feasibility Study

Task 3 Report: Temperature Logging and Chemical Geothermometer Analysis

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1. Introduction

Task 3 of this study is aimed at documenting the spatial distribution of temperature at depth by logging existing wells and quantifying possible aquifer temperatures by utilizing hydrochemical geothermometry.

2. Temperature Logging

We have logged 6 wells in the Stanley area. This has allowed us to create temperature profiles of these sites along with 2 wells previously described by Chapman (1986). Figure 1 shows the locations of these wells. Temperature logging was done by lowering a thermometer into the well and reading the temperature after 5 minutes, this allowed the thermometer to equilibrate with surrounding temperatures. The temperature was then measured every 25 feet for Wells 2 and 3, and every 50 feet for the Neider's Well. The results can be seen in table 1 and graphically in figure 2. The wells logged by Chapman (1986) are the same as wells 2 and 3 of this study.

Well Name	Source	Northing (UTM 11N)	Easting (UTM 11N)	Surface Temp (°C)	BHT (°C)	TD (m)	Gradient (°C/km)
#2	This Study	4898404	665241	14.22	46.48	91	387.12
#3	This Study	4898511	665277	38.75	44.02	53	115.94
Neider's	This Study	4897256	665821	6.34	20.1	212	69.86
G-1	Chapman (1986)	4898512	665278	35	43	65	130.0
G-2	Chapman (1986)	4898405	665242	16	40	91	293.33
City Well	This Study	4898104	664888	9.8	10	45	5.28
Ken Smith's	This Study	4898665	665779	8.6	13.7	38	168.3
Harrah's Capped	This Study	4898573	665333	18.9	20.1	8	198.0

Table 1. Results of temperature logging done on selected wells near the Stanley area.

Upon inspection of figure 2, it is apparent that there are very high temperature gradients in the Stanley area, at least in the wells that have been logged. Table 1 lists calculated gradients from logged wells for this study. The values calculated represent gradients measured for the wells and should not be used in interpreting a local geothermal gradient within bedrock.

In addition of being able to determine temperature gradients, it is also possible to determine zones of warm or cool water infiltration from temperature profiles. Well G-2 shows a warm water intrusion of 30 °C starting near 22 meters and returning to normal gradient temperatures at about 32 meters. There is also another warm water intrusion near 50 meters, with a maximum temperature 37 °C. A similar pattern is recognizable in Well 2. Well G-1 shows a very high gradient in the upper 20 meters but then

has a negative gradient from 20-63 meters. Neider's well has a steady gradient of 69.86 °C/km until a depth of 136 meters where the temperature levels out near 20 °C.

Locations of Selected Wells



Figure 1. Location of wells logged for thermal gradients. Well 2 of this study corresponds to Well G-2 of the study done by Chapman (1986) and Well 3 of this study corresponds to Well G-1 of Chapman (1986).

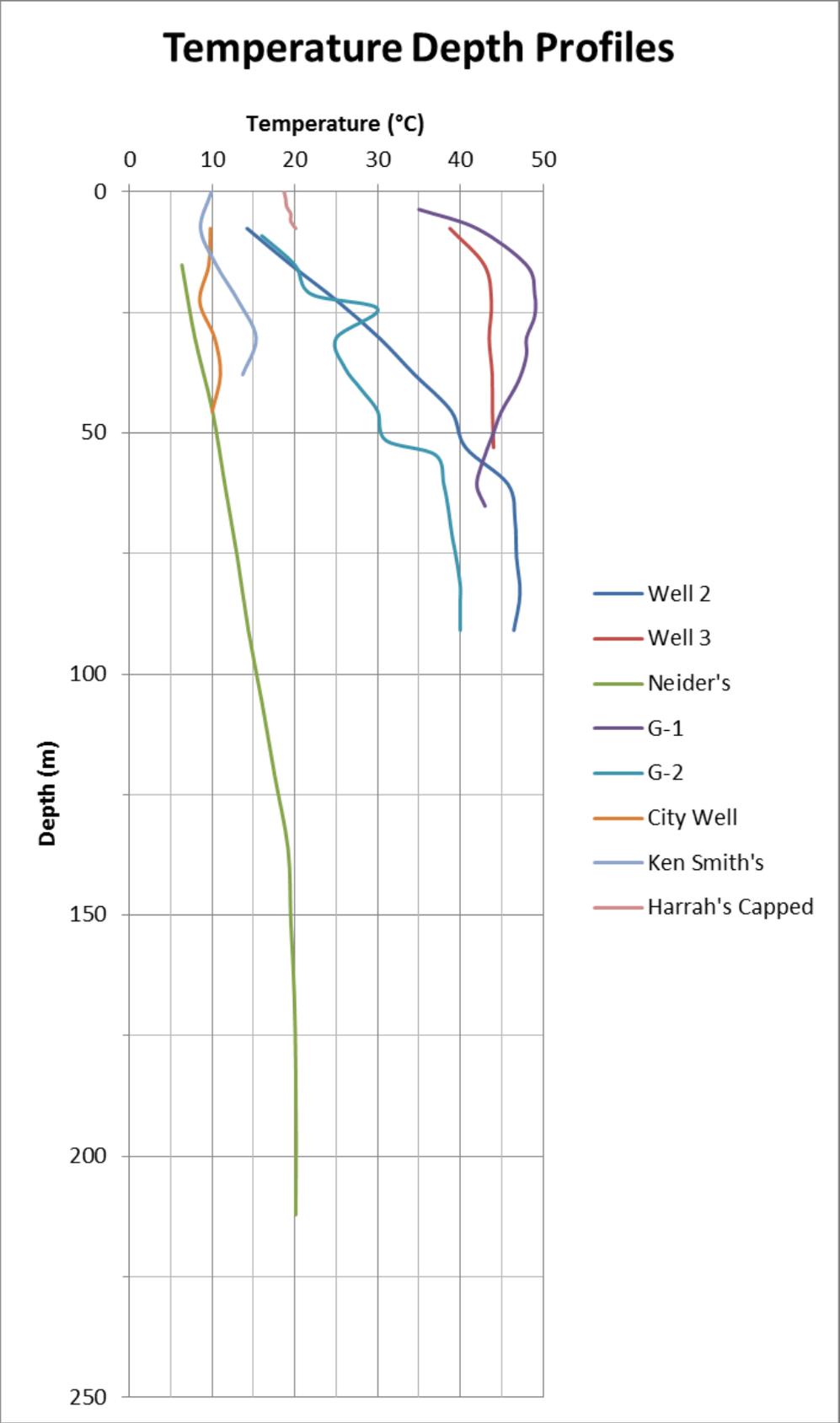


Figure 2. Thermal gradients measured for select wells in the Stanley area. Refer to figure 1 for locations. Note warm and cool water intrusions, this topic is discussed further in text.

3. Hydrochemistry

The thermal waters in the Stanley area have relatively high concentrations of sodium (Na) and bicarbonate (HCO_3), high concentrations of fluoride (F), and low concentrations of potassium (K) and magnesium (Mg). The thermal waters are also fairly high in pH, with values from 7.5-9. All of these results are consistent with those of Krahmer, (1995) where he reported waters of equal pH and major element concentrations. The high fluoride concentrations have been interpreted to be a product of interaction with fluoride rich micas (Krahmer, 1995; Young, 1985).

Water quality of the thermal water in the Stanley area is quite good with total dissolved solid (TDS) values ranging from 158 mg/l at the Stanley Hot Spring to 300 mg/l for Sunbeam Hot Springs. All of the hot springs along the Salmon River East of Stanley are elevated in TDS compared to the Stanley Hot Springs with values ranging from 226 mg/l - 300 mg/l. The cold water spring sample has a very low TDS value of 54 mg/l. The only parameter which exceeds drinking water quality standards is fluoride (F). Values of fluoride in the thermal spring water ranged from 10.9 mg/l at the Rocky Mountain Ranch spring to 17.9 mg/l at Elk Creek Hot Spring. High fluoride is common in geothermal waters and it has been documented that granitic rocks can contain as much as 100 times the fluoride as surrounding volcanic or sedimentary rocks. This allows more fluoride to be dissolved from the rock as the thermal water heats up and moves during deep circulation. Arsenic, Boron, Iron, Manganese and Magnesium were below detection limits in all of the samples. In an attempt to compensate for this, John Welhan of the Idaho Geological Survey performed a regression analysis for the elements Boron and Chlorine for this study based on Druschel's (1998) study of the geothermal system of the South Fork Payette River, west of Stanley (John Welhan written com., Nov., 2011). Refer to Appendix 1 for Welhan's summary of the regression analysis.

The thermal waters are dominantly sodium bicarbonate and sodium sulfate type waters with relatively high silica concentration. Calcium and chloride concentrations are low with calcium concentration less than 2 mg/l and chloride concentrations less than 7 mg/l. The low concentrations of Na, K, and Cl and high concentrations of silica are representative of granitic source rock in the Stanley area. Manganese (Mn) concentrations are low (less than 0.05 mg/l) indicating the thermal waters are not of a magmatic source. This along with the low TDS value indicate the thermal waters are of meteoric source and have somewhat short flow paths compared to other geothermal systems.

4. Chemical Geothermometers

Geothermometers are a useful tool that allows quantification of potential reservoir temperatures at depth to be estimated. This is done by measuring the concentration of chemical species such as calcium (Ca), magnesium (Mg), potassium (K), and silica (SiO_2). Samples were taken to Analytical Laboratories in Boise, Idaho for analysis, and table 2 lists the results of these analyses. Water quality samples were taken for six hot springs, one cold water spring and one well in the Stanley area. The hot springs ranged from the Sunbeam Hot Spring approximately 10 miles east of Stanley to the Rocky Mountain Ranch Hot Spring approximately 10 miles South of Stanley. The thermal well (Harrah's well 3) was a flowing well located approximately 1/4 mile north of Stanley on a low ridge between the Salmon River and Valley

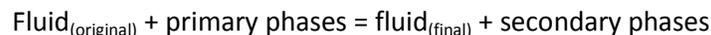
Creek. The cold water spring was located approximately 1/2 mile west of Stanley along State Highway 21 issuing from valley fill glacial material. Refer to figure 3 for sample locations.

There are several different geothermometers available, each has their own advantages and disadvantages. The reliability of each geothermometer depends on the local geologic environment, i.e. the rocks in which the fluid is interacting and the physical processes that affect the fluid in its rise to the surface. There are 6 major assumptions that must be made in order to use chemical geothermometers from hydrothermal solutions, they are (Young and Mitchel, 1973; White, 1970; Kraher, 1995):

“1.) The chemical reactions controlling the amount of a chemical constituent taken into solutions by hot water are temperature dependent; 2.) an adequate supply of these chemical constituents is present in the aquifer; 3.) chemical equilibrium has been established between the hot water and the specific aquifer minerals which supply the chemical constituents; 4.) hot water from the aquifer flows rapidly to the surface; 5.) the chemical composition of the hot water does not change as it ascends from the aquifer to the surface; 6.) there is no mixing or dilution of the reservoir fluid.”

It is not reasonable that all of these assumptions can be satisfied in every instance, but if kept in mind the use of geothermometers can still be a useful evaluation of reservoir temperatures (Young and Mitchel, 1973).

The concentration of major elements in solution is a function of temperature, time spent in contact with reservoir rocks, and the rocks in which they are interacting. As discussed in previous sections of this study, the main rock types in the Stanley area consist of granites, granodiorites, and rhyolites; all of which have minerals that contain K, Ca, Na, SiO₂, and minor amounts of Fe, Mg, and Al. As water interacts with these minerals, the minerals will break down form clay minerals; a general reaction for this is (Kraher, 1995):



The primary phases in this case consist of the minerals plagioclase feldspar, orthoclase/microcline feldspar, silica, and other aluminosilicate minerals. Secondary phases could include albite, quartz, sericite, opal-A, calcite, and fluorite (Kraher, 1995).

The three main geothermometers used in this study are the Na-K-Ca, quartz conductive cooling, and quartz adiabatic cooling geothermometers. These were chosen because of the dominant rock types near Stanley and because of the low observed surface temperatures of springs. An empirical approach to the derivation of the Na-K-Ca geothermometer was developed by Fournier and Truesdell (1973). They noticed that when molar concentrations Na, K, and Ca of thermal waters was plotted as the function $\log (\text{Na}/\text{K}) + \beta \log [(\text{Ca})^{1/2}/\text{Na}]$ vs the reciprocal of absolute temperature, the resulting graph would plot on a straight line (Fournier and Truesdell, 1973). This relationship allows for the quantitative analysis of the relationship between the molal concentrations of Na, K, and Ca in thermal waters and absolute temperature. There are several different species of silica present in most geothermal systems but the two chosen for this study (quartz adiabatic and conductive cooling) are the two most stable at

lower temperatures (Krahmer, 1995). The effect of pH on quartz solubility is paramount to correctly interpret calculated geothermometer temperatures (John Welhan written com., Nov., 2011). Quartz, chalcedogy, amorphous silica, and cristobalite are all polymorphs of the SiO_2 molecule and their concentration as a function of temperature can be seen in figure 4 (Ellis and Mahon, 1977; Krahmer, 1995).

Water Sample Locations

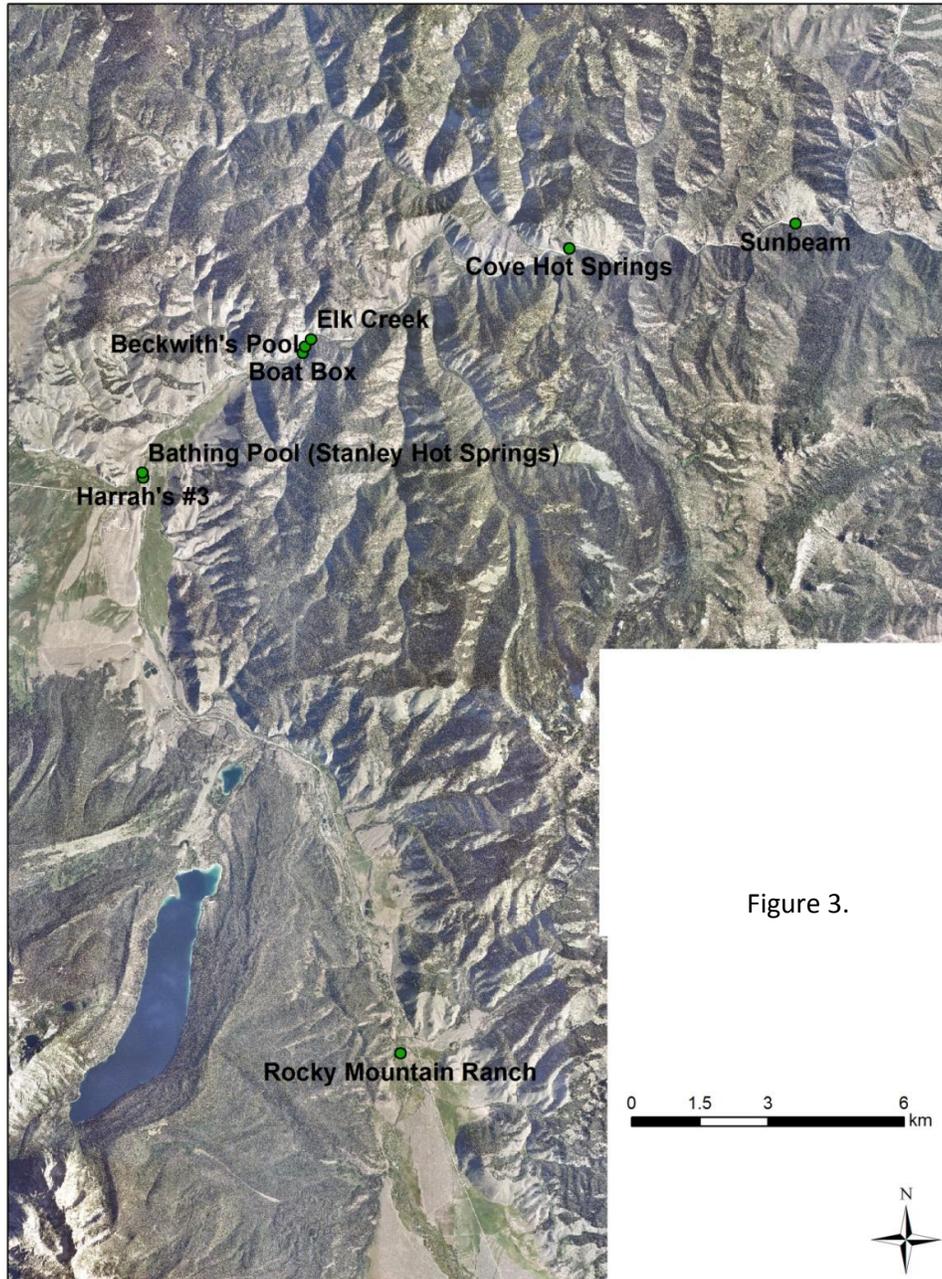


Figure 3.

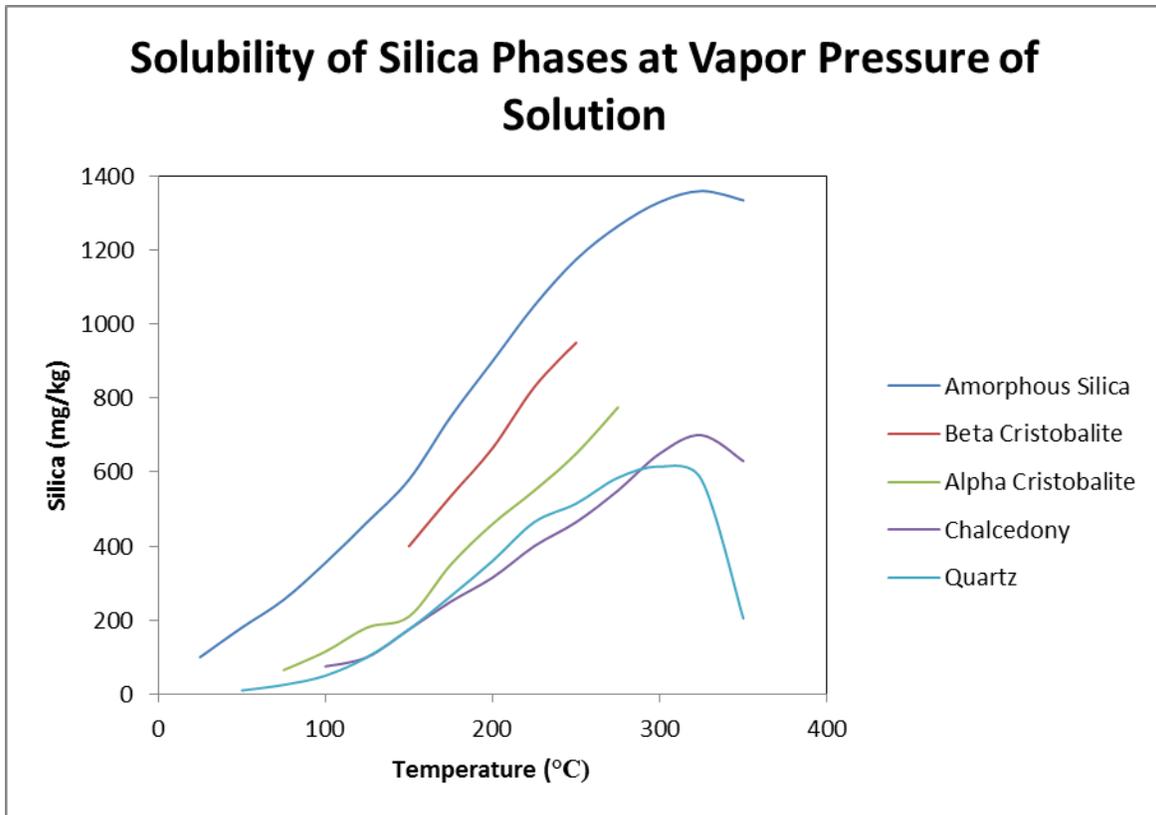


Figure 4. Solubility of polymorphs of SiO_2 as a function of temperature. Taken from Krahmer (1995) and modified from Fournier (1985).

The chemical species SO_4 , Cl, Mn, B, HCO_3 , and Li can be used to evaluate fluid transport pathways. If a sample of water has low Cl, Mn and HCO_3 concentrations and high SO_4 concentrations, it is usually diagnostic of interaction with a magmatic system. On the other hand if a sample of water has low Cl and SO_4 concentrations and high HCO_3 concentrations, the fluid is most likely groundwater being heated by a geothermal reservoir (Powell and Cumming, 2010). Figure 5 is a ternary diagram that shows the relationship between these chemical species for the Stanley area. If the chemical species B, Cl, and Li are plotted together on a ternary diagram (figure 6), one can make interpretations of fluid source and whether or not it has undergone fractionation due to boiling or mixed with a water that has boiled or waters that have been heated by steam (Powell and Cumming, 2010). Similarly, a ternary plot of Cl, F, and B (figure 7) is useful in distinguishing sources of water because, according to Powell and Cumming (2010), "in the absence of relatively rare fluorite with which to re-equilibrate, fluoride can be expected to be conservative." Due to the result our analysis of these elements being below analytical detection limits, these figures have been revised in John Welhan's report and can be found in Appendix 1. He determined that Stanley's thermal waters are evidence of a low lithium-high fluoride system that may have been diluted due to mixing with shallow waters (John Welhan written com., Nov., 2011).

Table 3 shows the values of calculated reservoir temperatures based on the chemical species described above. The highest temperatures obtained are from the quartz geothermometers. Sunbeam Hot Springs has the maximum calculated temperature of 130 °C while the lowest is the Rocky Mountain

Ranch at 106 °C. There appears to be an eastward increase in calculated temperature starting at Harrah’s well #3 with a calculated temperature of 110 °C moving northeastward to Sunbeam Hot Springs which have a calculated temperature of 130 °C. It is worth noting the two lowest temperatures both come from water samples taken from wells.

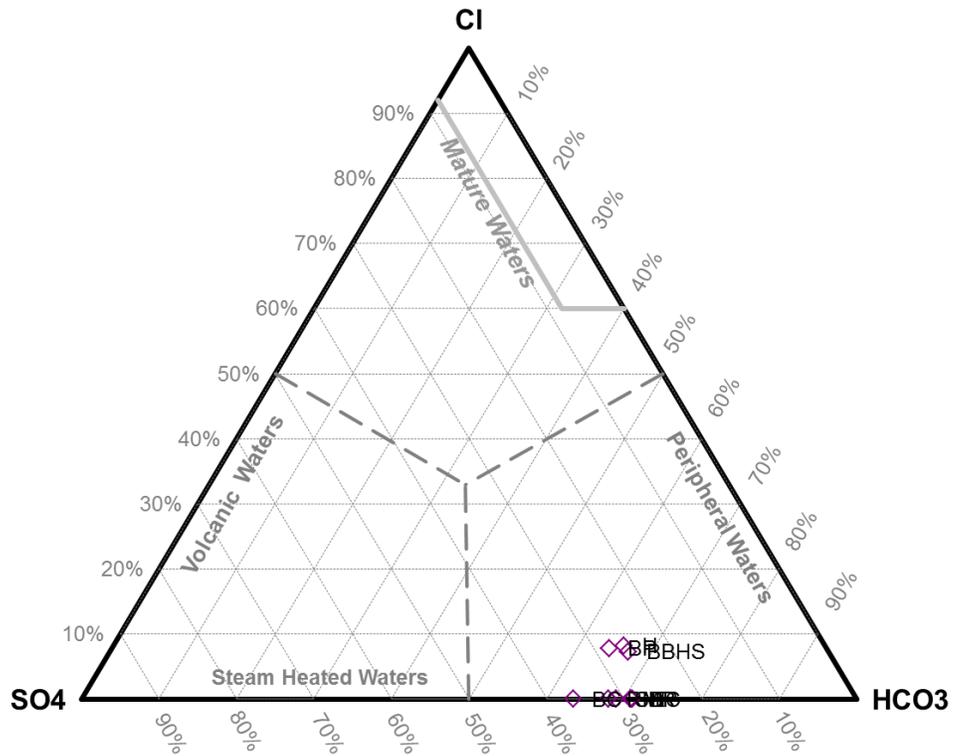


Figure 5. Cl-SO₄-HCO₃ ternary diagram. Shows waters in the Stanley area are Na-HCO₃ rich waters. Figure created in spreadsheet by Powell and Cumming (2010).

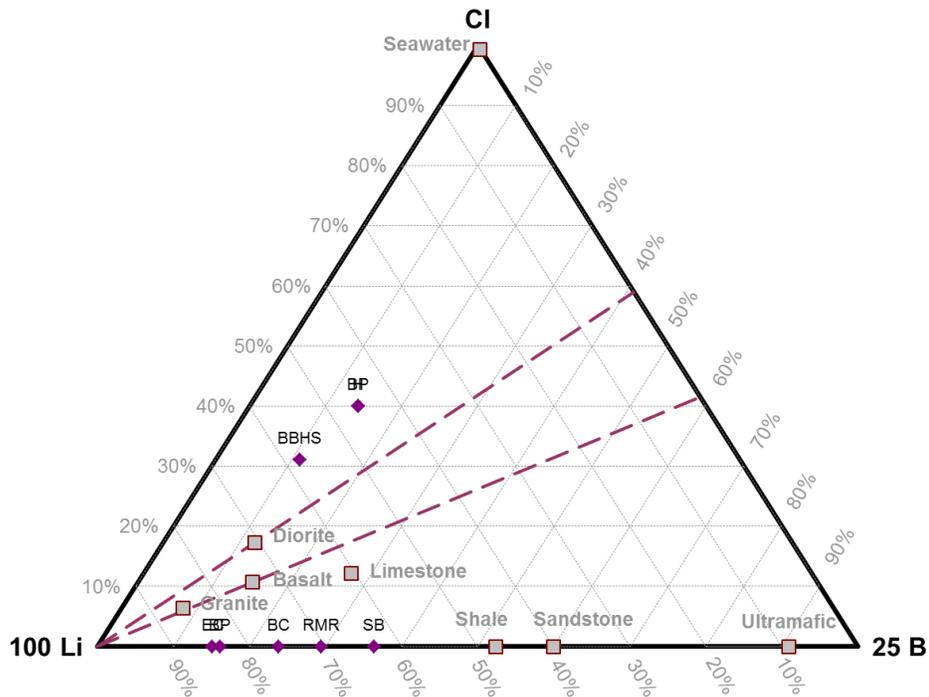


Figure 6. Li-Cl-B ternary diagram illustrating mixing behaviors of thermal waters. Only three samples were analyzed for chloride, but this diagram suggests that thermal waters in Stanley have undergone no or minimal amounts of boiling in their history. Figure created in spreadsheet by Powell and Cumming (2010).

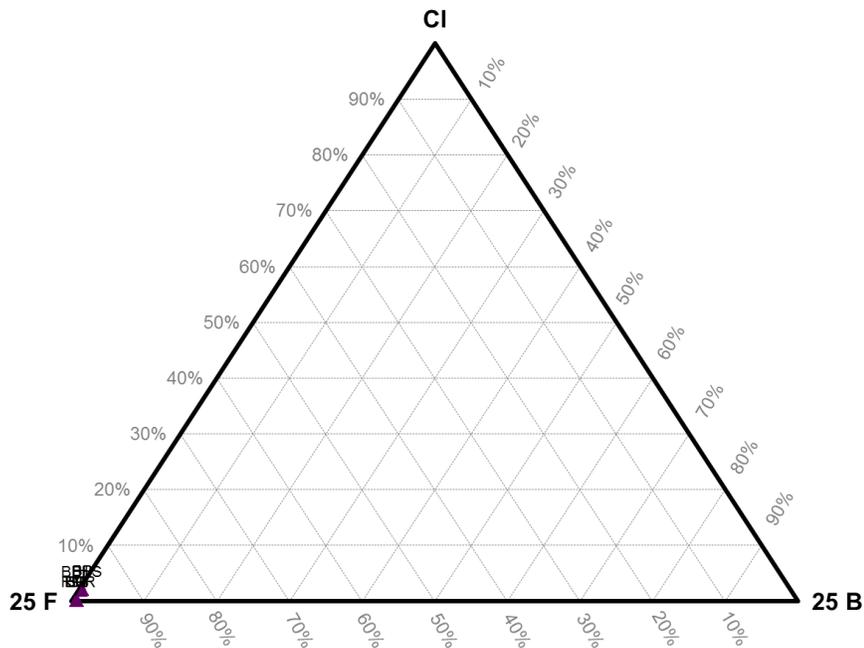


Figure 7. F-Cl-B ternary diagram. This figure illustrates the potential for mixing between different fluids. Though only three samples were analyzed for chloride, it is still apparent that the fluids have undergone minimal amounts of mixing, or since the concentration of fluoride is so high in all measured samples, it lessens the sensitivity of this technique. Figure created in spreadsheet by Powell and Cumming (2010).

Well/Spring	pH	Temp (C)	As	B	Ca	Fe	Li	Mg	Mn	K	SiO2	Na	HCO3	F	Cl	SO4	Cond. (µhmos)	TDS
Rocky Mountain Ranch (S)	7.5	43.8	<0.003	<0.10	2.69	<0.05	0.06	<0.50	<0.05	0.6	54.7	57.9	61.6	10.9	NA	29	276	188
Bathing Pool (Stanley H.S.) (S)	8	39.4	<0.003	<0.10	1.85	<0.05	0.08	<0.50	<0.05	0.7	62.1	64.5	57.3	14.5	7	25	297	158
Harrah's #3 (W)	7.5	NA	<0.003	<0.10	1.79	<0.05	0.08	<0.50	<0.05	<0.5	59.8	62.1	55.9	13.8	7	22	293	188
Boat Box (S)	8.2	57.2	<0.003	<0.10	1.5	<0.05	0.13	<0.50	<0.05	0.9	72.6	70.4	64.7	15.8	7	25	332	226
Beckwith's Pool (S)	8.5	57.2	<0.003	<0.10	1.49	<0.05	0.13	<0.50	<0.05	1	75.2	69.8	65.5	17	NA	27	337	248
Elk Creek (S)	8.25	51.6	<0.003	<0.10	1.49	<0.05	0.14	<0.50	<0.05	1	75.5	69.4	68.7	17.9	NA	28	337	254
Cove (S)	8.75	56.1	<0.003	<0.10	1.73	<0.05	0.08	<0.50	<0.05	1.4	85.4	71.7	65.9	14.3	NA	38	347	260
Sunbeam (S)	9	76.6	<0.003	0.16	1.44	<0.05	0.07	<0.50	<0.05	2.2	87.6	86.4	93.5	15.5	NA	42	417	300

Table 2. Results of chemical analysis of water samples collected. All concentrations are in mg/L. Refer to figure 1 for locations of samples. As mentioned in the text, As, B, Fe, Mg, and Mn were all below analytical detection limits.

Sample Name	Chalcedony cond	Quartz cond	Quartz adiabatic	Na-K-Ca	Na/K Fournier	Na/K Truesdell	Na/K (Giggenbach)
Rocky Mountain Ranch	76.44	106.41	106.21	47.45	77.82	27.92	99.05
Bathing Pool (Stanley H.S.)	83.09	112.50	111.49	59.82	79.86	30.06	101.06
Harrah's #3	81.09	110.67	109.91	50.53	67.07	16.74	88.44
Boat Box H.S.	89.92	118.72	116.86	72.58	87.30	37.91	108.37
Beckwith Pool	93.62	122.08	119.75	75.98	92.66	43.60	113.62
Elk Creek	93.84	122.28	119.92	75.92	92.94	43.90	113.89
Cove	100.96	128.73	125.43	84.07	108.07	60.20	128.65
Sunbeam	102.46	130.09	126.59	125.49	122.35	75.88	142.51

Table 3. Results of geothermometer analysis from concentration of select chemical species in degrees Celsius. Values were calculated in a spreadsheet by Powell and Cumming (2010).

5. References

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6. Appendix 1

**Preliminary Geothermometry Evaluation
of Hot Spring Data in the Stanley Area**

John Welhan

Idaho Geological Survey

November 17, 2011

Information Sources

The data considered in this analysis were obtained from two sources: 1) analyses of water samples collected by Roy Mink and Bob Beckwith on August 27-28, 2011 as part of their analysis of geothermal potential in the Stanley area (subsequently referred to as the Stanley Geothermal Study, or SGS); and 2) chemical analyses of hot spring waters reported by Druschel (1998). The latter data set represents a comprehensive suite of major and minor analytes and were found to be a more reliable data set from which to draw inferences. In contrast, analyses obtained from the August, 2011 sampling campaign lack information on some key analytes, leading to uncertainties in the geothermometry interpretation.

Data Confidence

Tables 1 and 2 compare the available water chemistry data from the SGS sampling campaign with some of Druschel's (1998) data. Charge balance errors for individual SGS analyses in Table 1 range from +9 to +15% (averaging +12%) and for the Druschel analyses, -4 to +9% (averaging -1%). As seen in Table 1, magnesium (Mg), chloride (Cl) and boron (B) were not analyzed or were analyzed with insufficient sensitivity in the SGS data, either or both of which could explain the high charge-balance errors associated with the SGS data.

Table 1 - Geochemical data from the Stanley Geothermal Study (R. Mink, written comm., 2011). All values are in mg/l except conductivity, which is in $\mu\text{mho/cm}$. Concentrations below the indicated detection limit are shown as negative values.

Sample ID	T, °C	pH	Li	Na	K	Ca	Mg	SiO ₂
Stanley Bathing Pool	n.m.	n.m.	0.08	64.5	0.7	1.9	-0.5	62.1
Harrah's Well #3	n.m.	n.m.	0.08	62.1	-0.5	1.8	-0.5	59.8
Boat Box Hot Spring	n.m.	n.m.	0.13	70.4	0.9	1.5	-0.5	72.6
Beckwith Hot Spring	n.m.	n.m.	0.13	69.8	1.0	1.5	-0.5	75.2
Elk Creek Hot Spring	n.m.	n.m.	0.14	69.4	1.0	1.5	-0.5	75.5
Cove Below Basin Creek	n.m.	n.m.	0.08	71.7	1.4	1.7	-0.5	85.4
Idaho Rocky Mtn. Ranch	n.m.	n.m.	0.06	57.9	0.6	2.7	-0.5	54.7
Sunbeam Hot Spring	n.m.	n.m.	0.07	86.4	2.2	1.4	-0.5	87.6

Sample ID	B	Cl	F	SO ₄	HCO ₃	CO ₃	Fe	Mn	Cond
Stanley Bathing Pool	-0.1	n.m.	14.5	25	57.3	n.m.	-0.05	-0.05	297
Harrah's Well #3	-0.1	n.m.	13.8	22	55.9	n.m.	-0.05	-0.05	293
Boat Box Hot Spring	-0.1	n.m.	15.8	25	64.7	n.m.	-0.05	-0.05	332
Beckwith Hot Spring	-0.1	n.m.	17.0	27	65.5	n.m.	-0.05	-0.05	337
Elk Creek Hot Spring	-0.1	n.m.	17.9	28	68.7	n.m.	-0.05	-0.05	337
Cove Below Basin Ck	-0.1	n.m.	14.3	38	65.9	n.m.	-0.05	-0.05	347
ID Rocky Mtn. Ranch	-0.1	n.m.	10.9	29	61.6	n.m.	-0.05	-0.05	276
Sunbeam Hot Spring	0.16	n.m.	15.5	42	93.5	n.m.	-0.05	-0.05	417

Table 2 - Geochemical data from the Stanley area, after Druschel (1998). All values are in mg/l except conductivity, which is in $\mu\text{mho}/\text{cm}$. See **Appendix I** for a map of Druschel's sampling locations.

Sample ID	T, °C	pH	Li	Na	K	Ca	Mg	SiO ₂
Iron Creek Hot Spring	59	9.19	0.084	52.2	1.4	1.4	0.012	88.2
Stanley Hot Spring	51	9.35	0.059	62.0	0.7	0.9	0.072	64.0
Elkhorn Creek Hot Spring	58	9.35	0.098	70.2	1.2	1.1	0.015	77.6
Basin Creek Hot Spring	61.5	9.25	0.057	62.2	1.7	0.9	0.010	97.8
Sunbeam Hot Spring	76	8.91	0.055	85.4	2.1	0.9	0.022	95.8
Robinson Bar Hot Spring	55	9.39	0.042	62.6	1.9	1.0	0.018	99.6
ID Rocky Mtn. Lodge	46.5	9.33	0.056	72.2	0.6	1.1	0.018	53.9
Easley Hot Spring	40.9	9.88	0.149	87.2	0.6	0.8	0.013	57.7

Sample ID	B	Cl	F	SO ₄	HCO ₃	CO ₃	Rb	Sr	Cond
Iron Creek Hot Spring	0.051	5.4	12	12.7	47.6	22.2	0.014	0.066	240
Stanley Hot Spring	0.048	7.2	15.6	15.4	61.0	15.6	0.005	0.078	270
Elkhorn Creek Hot Spring	0.071	8.9	17	16.4	67.1	17.4	0.009	0.083	310
Basin Creek Hot Spring	0.062	7.2	14.3	20.1	56.1	16.8	0.011	0.088	312
Sunbeam Hot Spring	0.203	13.6	15.2	30.6	103.7	17.4	0.015	0.098	382
Robinson Bar Hot Spring	0.148	11.2	10.2	31.6	65.9	13.2	0.012	0.107	305
ID Rocky Mtn. Lodge	0.050	6.2	11.1	27.3	73.2	5.3	0.004	0.050	400
Easley Hot Spring	0.290	6.2	13.9	42.4	73.2	4.2	0.006	0.099	420

Estimates of the Cl and B contents in most of the SGS samples were obtained by regressing B vs. Li and Cl vs. F data from the Druschel data set. On the assumption that all thermal waters in the Stanley area¹ have similar ratios of these elements, Cl and B concentrations in the SGS samples were then estimated from their Li and F contents. Magnesium concentrations were not estimated because actual concentrations are necessary for geothermometry purposes.

The B-Li and Cl-F regressions are shown in **Figure 1**. The Cl and B concentrations so estimated for the SGS samples reduced the average charge-balance error to +8%, still significantly greater than analytical errors associated with the Druschel (1998) data set. Overall, the chemical information in the SGS data set appears to be less reliable overall, so only the Druschel data were evaluated for their geothermometry information.

¹with the exception of Sunbeam, Robinson Bar and Easley H.S., which are spatially farthest removed

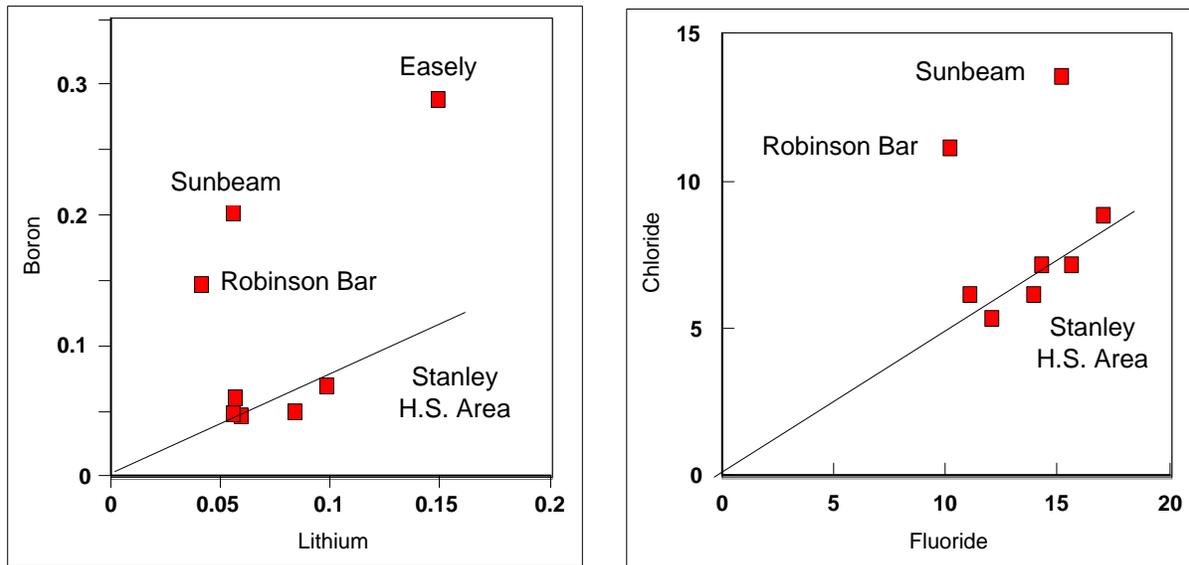


Figure 1 - Regression of Druschel's (1998) boron vs. lithium data (left) and chloride vs. fluoride data (right) for samples collected in the immediate Stanley area. The relatively tight groupings of these ionic ratios indicates that they are fairly uniform within the immediate Stanley area and can be used to estimate missing chloride and boron concentrations from lithium and fluoride concentrations, respectively.

Analysis of Water Compositions

The compositions of thermal waters were evaluated using the spreadsheet utilities published by Powell and Cumming (2010). **Figure 2** compares the major anion composition of Stanley Area hot springs based on both the SGS and Druschel data sets. Anion compositions of hot springs along the South Fork of the Payette River are also plotted for comparison. The Stanley Area and Payette River hot springs are chemically similar in almost all respects, with the exception of higher sulfate in the Payette waters. Anionic proportions in the Stanley waters are generally similar in the SGS and Druschel data sets.

With chloride concentrations estimated for the SGS data, Ternary plots of Cl-F-B and Cl-Li-B were constructed to evaluate trace-element abundances. **Figure 3** compares the reconstituted SGS Cl-Li-B data for the Stanley Area with the Druschel data for the Stanley and Payette areas; **Figure 4** compares the reconstituted SGS Cl-F-B proportions with Druschel's Stanley and Payette data. From the generally linear distribution of points within these ternary diagrams, it appears that Stanley's thermal waters reflect a single lithium- and fluoride-rich end member that is diluted to varying degrees by a lithium- and fluoride-poor (ground water?) source.

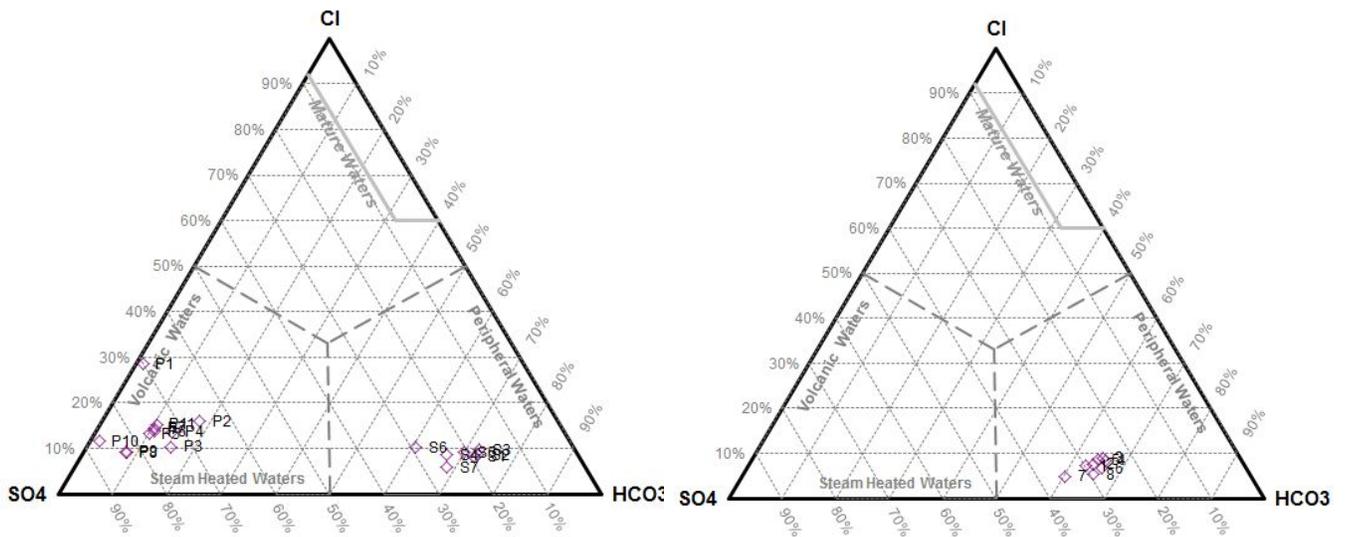


Figure 2 - Comparison of major anion compositions based on data of Druschel (left) and reconstituted chloride estimates for the SGS data (right) in the Stanley area. The ternary plot on the left includes anion compositions of hot springs along the South Fork of the Payette River ("P" labels). Stanley Area hot springs ("S" labels) are sodium-bicarbonate type waters with minor sulfate, whereas hot springs of the Payette River's South Fork are of a sodium-sulfate type with minor bicarbonate.

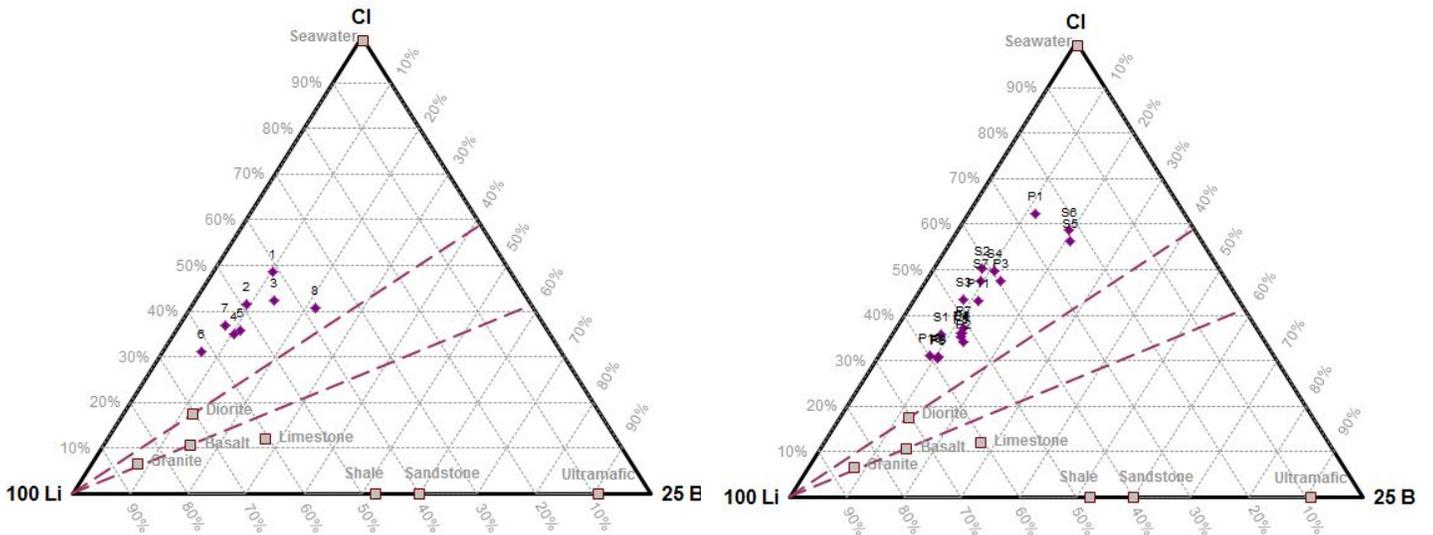


Figure 3 - Cl-Li-B ternary plots based on reconstituted SGS data (left) and Druschel's (1998) data (right). The latter also shows thermal waters of the Payette River's south fork (plotted with "P" labels) as well as thermal waters of the Stanley area ("S" labels).

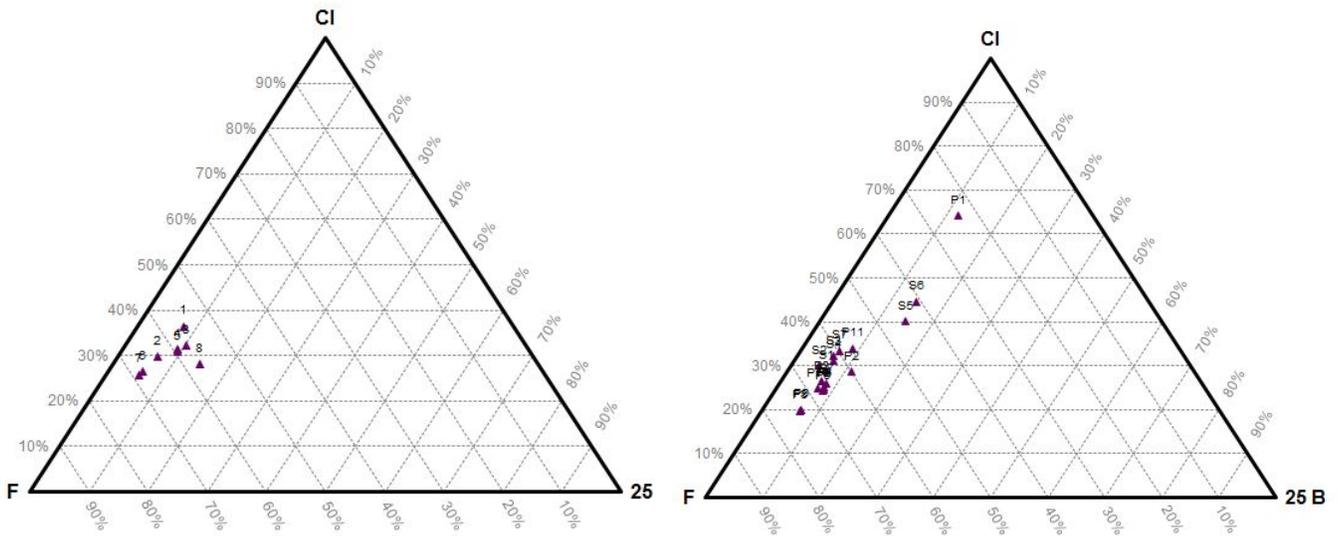


Figure 4 - Comparison of Cl-F-B ternary plots based on reconstituted SGS data (left) and Druschel's (1998) data (right). In the latter, thermal waters of the South Fork of the Payette River are plotted with "P" labels and Stanley waters, with "S" labels.

Geothermometry

Temperatures for a number of common geothermometers were computed using Powell and Cummings' (2007) spreadsheet. **Figure 5** summarizes the inferred geothermometer temperatures based only on Stanley hot spring data; **Figure 6** summarizes the temperatures inferred from all hot spring data in the Stanley and South Fork Payette River areas. There is generally good agreement among several of the most physically plausible geothermometers, suggesting that some confidence can be placed in these reservoir temperature estimates. Discordant temperatures were obtained for geothermometers that are either inappropriate and/or inapplicable in this low-temperature system. For example, the quartz geothermometers are not considered meaningful within this temperature range because of kinetic limitations (Fournier, 1973), and Truesdell's Na-K geothermometer is most commonly applied at $T > 200\text{ }^{\circ}\text{C}$.

Silica-Chalcedony Geothermometer

The most important question regarding the meaning of these temperatures is the effect of high pH on mineral solubility and equilibrium reactions. Ionization of silicic acid at high pH increases the solubility of silica, which necessitates corrections to the measured dissolved silica concentrations (e.g., Arnorsson, 1979). To illustrate this, consider a solution of low ionic strength at $100\text{ }^{\circ}\text{C}$; the concentration of dissolved silica in equilibrium with chalcedony at this temperature would be about 85 mg/l, similar to that measured in Stanley's thermal waters. At

normal pH, essentially all of this is in the form of H_4SiO_4 (silicic acid). However, silicic acid maintains equilibrium with its ionized forms via reactions like



which, at low H^+ -ion concentration (high pH), partition dissolved silica into ionized and unionized forms according to the prevailing temperature and pH. Such reactions are kinetically fast and are expected to rapidly adjust to the prevailing temperature and pH. At low ionic strength and $T = 100\text{ }^\circ\text{C}$, the first ionization constant (Busey and Mesmer, 1977) is

$$\frac{[H_3SiO_4^-][H^+]}{[H_4SiO_4]} = 7.9 \times 10^{-10}$$

At a pH of 9.5, the concentration of ionized silica, $[H_3SiO_4^-]$, is therefore 2.5 times higher than $[H_4SiO_4]$. The problem for geothermometry is that only H_4SiO_4 concentrations are considered in solubility and equilibrium reactions with mineralized phases. If the temperature and total dissolved silica content ($[H_3SiO_4^-] + [H_4SiO_4]$) did not change during ascent, then a water sample collected at the surface would contain 3.5 times as much silica than was actually in solubility equilibrium with minerals (chalcedony or aluminosilicates) in the reservoir. The concentration of H_4SiO_4 in solubility equilibrium with chalcedony at $100\text{ }^\circ\text{C}$ is 85 mg/l, so the total dissolved silica concentration at a pH of 9.5 would be 298 mg/l. Clearly, this is not the case in the Stanley - Payette hot spring system.

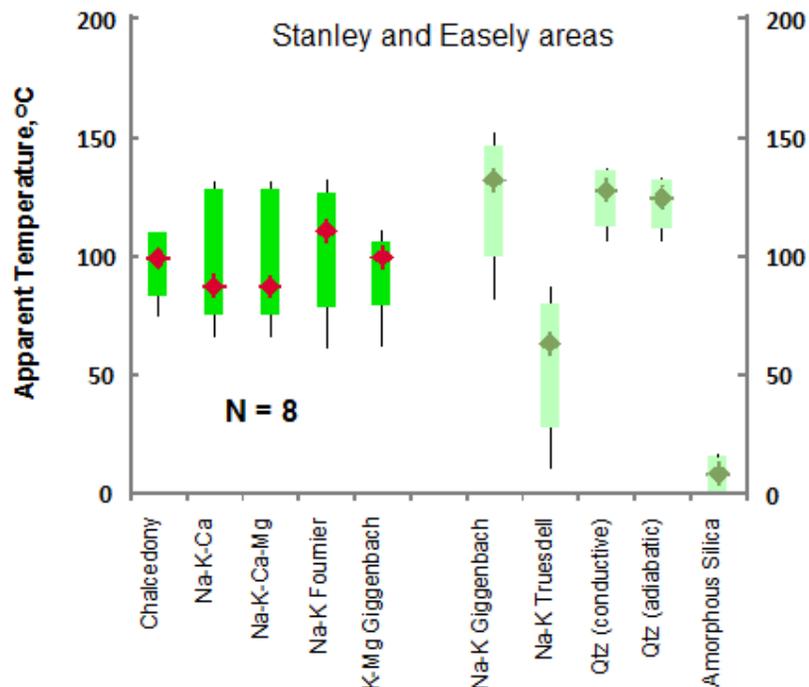


Figure 5 - Summary of calculated temperatures for various common geothermometers, based on Druschel's (1998) data for the Stanley area, including Easley Hot Springs. Median temperatures for each geothermometer are shown as diamonds; interquartile ranges (25th to 75th percentiles), as filled boxes; and max/minimum temperature ranges as vertical lines. Congruent geothermometers (dark green boxes) are grouped on the left and incongruent geothermometers (light green boxes), on the right. Median temperatures of congruent geothermometers range from about 85 to 115 °C and average 100 °C.

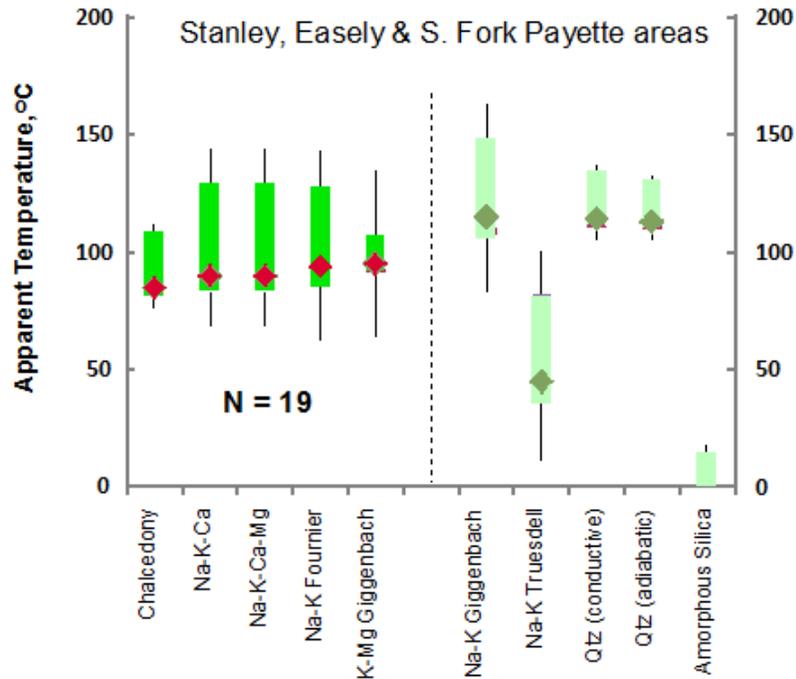


Figure 6 - Summary of geothermometry results for the Stanley area and South Fork of the Payette River, based on Druschel's (1998) chemistry data. Median temperatures for each geothermometer are shown as diamonds; interquartile ranges (25th to 75th percentiles), as filled boxes; and max/minimum temperature ranges as vertical lines. Congruent geothermometers (dark green boxes) are grouped on the left and incongruent geothermometers (light green boxes), on the right. Median temperatures of the congruent geothermometers range from about 85 to 95 °C, although the results are consistently skewed to higher temperatures (average temperatures range from 92 to 102 °C).

The effect of cooling further complicates the interpretation. For example, cooling the above solution to 50 °C would redistribute dissolved silica equally between the ionized and unionized forms but would not change the total amount of silica in solution. During further cooling to 25 °C (for example, during storage of unacidified samples) the silicic acid ionization constant drops to 1.5×10^{-10} and the $[\text{Si ionized}] / [\text{Si un-ionized}]$ ratio drops to 0.47 (while leaving total dissolved silica unchanged). The inevitable result is supersaturation of H_4SiO_4 due to conversion of silica from the ionized to the un-ionized form whenever these high-pH, silica-rich waters cool. Therefore, all of the silica temperatures in Tables 1 and 2 should be considered apparent equilibrium temperatures.

One process that could counteract the effect of silica ionization and bring silica geothermometers in line with the cation geothermometers would be silica precipitation (probably as amorphous silica) in response to supersaturation. If silica precipitation were kinetically fast during cooling, it would act to reduce total silica in solution and thereby bring about apparent silica equilibrium within the temperature range of the cation geothermometers.

Cation Geothermometry

Silica ionization may also influence cation geothermometry in these high-pH waters, although the effect is expected to be minor in comparison to the silica geothermometers. The cation geothermometers are based on the temperature dependence of the partitioning of sodium and potassium between solution and mineral phases; they are all formulated as ratios of cation concentrations and therefore are much less sensitive to ionic strength and other solution-specific variables (such as silicic acid dissociation). As shown in Figure 6, the common cation geothermometers (Na-K-Mg-Ca; Na/K; K^2/Mg) display surprisingly concordant results. **Figure 7** shows the relationship between the Na/K and K^2/Mg geothermometers. The Na/K geothermometer is typically found to reflect thermodynamic equilibrium with alkali feldspars above 100 °C (Arnorrson, 1979) but deviates from equilibrium below this. Another common tendency is for the K^2/Mg geothermometer to reflect equilibrium at lower temperatures as fluids re-equilibrate during ascent from a high-T reservoir (Giggenbach, 1988).

The close correspondence between the silica-chalcedony and K^2/Mg geothermometers shown in **Figure 8** suggests that these geothermometers may be more reflective of actual temperatures than one might infer from the discussion of silicic acid ionization. The close concordance between these geothermometers and adherence to the chalcedony-based solubility temperatures lends credence to the hypothesis that ionization of silicic acid may be counteracted by cooling-

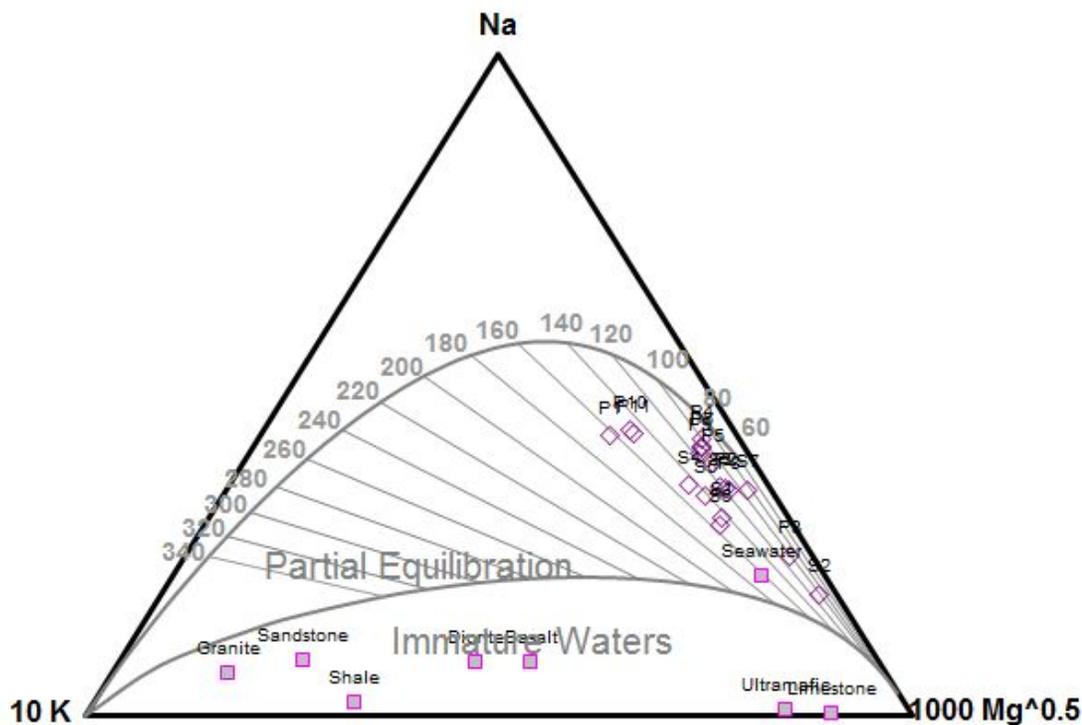


Figure 7 - Ternary ("Giggenbach") plot of Na, K and Mg concentrations in Stanley ("S") and South Fork Payette River ("P") thermal springs. Equilibrium temperatures for the Na/K geothermometer are shown in °C along the upper curved line; straight lines converging toward the Mg vertex indicate partial re-equilibration trajectories for the K^2/Mg geothermometer as fluids cooled during ascent from the high-T reservoir.

induced silica supersaturation so as to maintain dissolved silica concentrations closer to those expected in neutral-pH waters. Figure 8 also suggests that chemical re-equilibration of both geothermometers may be occurring during ascent (either due to mixing or conductive cooling), over a temperature range from 120 ° to almost 60 °C.

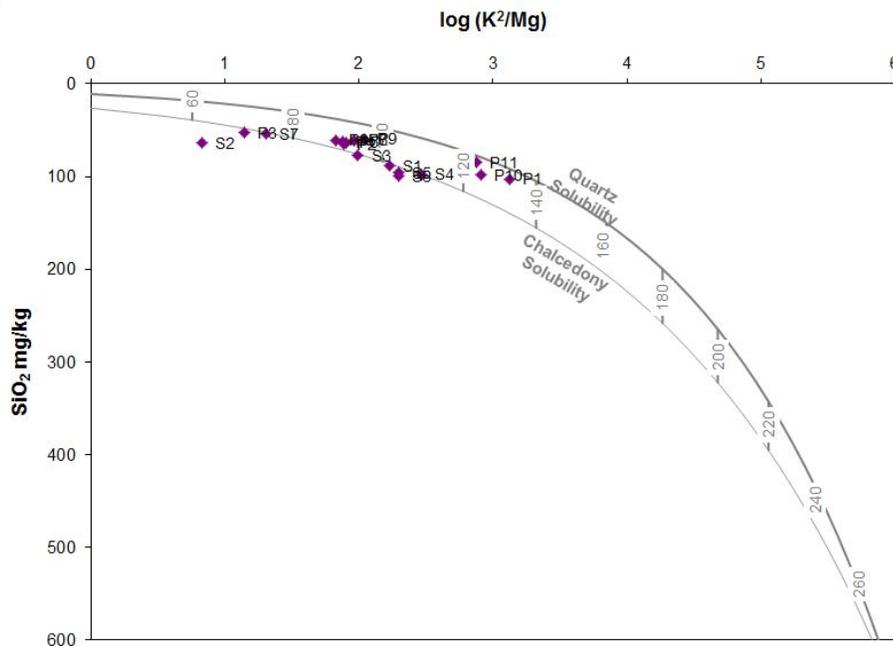


Figure 8 - Cross-plot of K^2/Mg and silica-chalcedony geothermometer results for Stanley ("S") and South Fork Payette River ("P") hot springs. The degree of concordance between the geothermometers and the apparent trajectory of sampled hot springs along the coupled geothermometer trend from 130 to 60 °C indicates that both geothermometers re-equilibrate during ascent from the reservoir.

Conclusions

The preceding analysis supports the hypothesis that Stanley's thermal waters originate from deep circulation along an elevated geothermal gradient and that thermal waters throughout the Stanley - Payette corridors reflect similar origins and geochemical processes (Druschel, 1998; Druschel and Rosenberg, 2000). A preliminary evaluation of concordant geothermometry indicators shows that several common geothermometers (silica-chalcedony; Na-K-Mg-Ca; Na/K; K^2/Mg) furnish reliable reservoir temperature estimates in the 85 to 115 °C range. Furthermore, the K^2/Mg cation geothermometer and the silica-chalcedony solubility geothermometer display remarkably consistent trends suggesting re-equilibration during ascent from a ca. 100 °C reservoir. Physical processes driving the chemical re-equilibration may be conductive cooling and/or mixing with cold ground water. However, a thorough analysis of the effects of silicic acid ionization, silica supersaturation and precipitation during ascent, and mixing under high pH conditions is necessary before substantial confidence can be placed in the interpreted reservoir temperatures.

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APPENDIX I

Map of Hot Spring Locations in the Stanley Area

