Identification of blind geothermal resources in Surprise Valley, CA, using publicly available groundwater well water quality data

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Abstract

Geothermal resource exploration is generally limited to areas with surface expressions of thermal activity (fumaroles and hot springs), or relies on expensive geophysical exploration techniques. In this study, the hidden subsurface distribution of geothermal fluids has been identified using a free and publicly available water quality dataset from agricultural and domestic water wells in Surprise Valley, northeastern California. Thermally evolved waters in Surprise Valley have element ratios that vary in response to Ca carbonate and Mg silicate mineral precipitation, and have elevated total dissolved solids (TDS). The arid climate in Surprise Valley leads to surface water evaporation in a closed basin, producing high TDS Na-Cl-CO₃-SO₄ brines in three ephemeral alkali lakes and in shallow groundwater under elevated soil CO₂ conditions. Evaporated fluids in Surprise Valley follow a chemical divide that leads to Ca carbonate and Mg silicate mineral precipitation. Plots of dissolved element ratios can be used to distinguish groundwater affected by evaporation from water affected by thermal water-rock interaction, however it is challenging to select components for plotting that best illustrate different fluid evolution mechanisms. Here, we use a principal component analysis of centered log-ratio transformed data, coupled with geochemical models of fluid evaporation and thermal mixing pathways, to identify components to plot that distinguish between groundwater samples influenced by evaporation from those influenced by thermal processes. We find that groundwater samples with a thermal signature come from wells that define a coherent, linear geographical distribution that closely matches the location of known and inferred faults. Modification of the general approach employed here provides promise for identifying blind geothermal resources in other locations, by applying low-cost geochemical modeling and statistical techniques to areas where large groundwater quality geochemical datasets are available.

1. Introduction

Surprise Valley is an endorheic basin located in the northeastern corner of California, bordered by Nevada to the east and Oregon to the North (Figure 1). The climate is semi-arid with cold winters and hot dry summers. The valley is bounded by the Warner Mountains to the west and the Hays Canyon Range and Larkspur Hills to the east. Hydrogen isotope (δD) and oxygen isotope ($\delta^{18}O$) measurements of precipitation in Surprise Valley show that surface water originates from eastward-moving air masses sourced in the northern Pacific that subsequently undergo Rayleigh distillation and incorporate evaporated terrestrial water (Ingraham and Taylor, 1986). Surprise Valley precipitation principally falls in the form of winter snowfall in the Warner Mountains and to lesser degree in the Hays Canyon Range, the latter receiving significantly less precipitation due to the lower elevation and location in the rain shadow of the Warner Range (Ingraham and Taylor, 1989).

Water is distributed to the floor of Surprise Valley through seasonal and perennial creek drainages that are mainly located on the eastern slope of the Warner Mountains, and to a lesser extent on the western slope of the Hays Canyon Range (Clawson et al., 1986). Base flow in Surprise Valley creeks is controlled by groundwater reserves in the Warner Mountains and Hays Canyon Range that are recharged from snowmelt. Thus, creeks attain peak flow during spring snowmelt and during sporadic precipitation events (Ingraham and Taylor, 1989). Clawson et al. (1986) provide a detailed description of groundwater resources in Surprise Valley, which we summarize in the following paragraph. Warner Mountains creeks are the principal source of groundwater recharge in Surprise Valley. Principal aquifer formations in Surprise Valley include lake deposits formed from the Pleistocene Lake Surprise that covered the valley floor, and alluvial fan deposits at the base of the Warner Mountains. There are over 120 groundwater wells in Surprise Valley that are used for domestic, agricultural, and industrial purposes. Groundwater persists in unconfined aquifers that are prone to subsurface evaporation in the arid environment, and in confined aquifers that manifest as artesian wells. Surprise Valley groundwater quality data has been monitored and compiled by the California Department of Water Resources (CADWR)

since 1958. In addition to groundwater, the CADWR geochemical database includes aqueous geochemical data for thermal springs and alkali lake waters.

Three ephemeral closed-basin lakes (Upper, Middle, and Lower Alkali Lakes) fill annually during peak creek flow in Surprise Valley. Due to the semi-arid climate, evaporation exceeds precipitation during the summer months, forming an Na-Cl-(SO₄)-(CO₃) brine (Eugster and Hardie, 1978). While surface water in the alkali lakes evaporates to dryness each year, saline brine persists in the shallow subsurface. This subsurface brine was extracted from wells on the east shore of Middle Alkali Lake by the Surprise Valley Salt Works until 1943 for salt (NaCl) production by solar evaporation (Ver Planck and Heizer, 1958). Ingraham and Taylor (1989) used δD data to suggest that evaporated lake brine does not significantly mix or interact with groundwater, however their study was limited in scope to just three groundwater samples.

Thermal springs are located in four main areas in Surprise Valley: Eagleville at the southern end, Lake City on the western side, Seyferth/Leonards/Surprise Valley Hot Springs Resort on the eastern side, and Fort Bidwell at the northern end of the valley (Figure 1). There are also scattered warm springs throughout the valley, for which limited fluid geochemical data are available. There are no data on the longevity of various springs or duration of geothermal activity in Surprise Valley, although archaeological data suggests the thermal springs have been active and visited by humans for at least 5000-6000 years (O'Connell, 1975). Commercial direct use of hot springs began in the 1950's at the Surprise Valley Hot Springs Resort. Notoriety and interest in the geothermal energy potential of Surprise Valley was sparked following a dramatic mud volcano eruption at Lake City during March 1951 (White, 1955). A deep (~1500 m) geothermal exploration well (Phipps 2) was subsequently drilled near Lake City in the 1970's, and produced the hottest water found thus far in Surprise Valley at a temperature of ~170°C. Following drilling of Phipps 2, geothermal exploration activities waned until about 2001, when several temperature gradient wells and core holes (Holes OH-1 and LCSH-5) were drilled near Lake City (Benoit et al., 2004; Benoit et al., 2005a; Benoit et al., 2005b) and later at Fort Bidwell (LaFleur et al., 2010). Since then, a number of structural and geophysical studies have been conducted in Surprise Valley to better understand the geology of this area, the relationship between structures and hydrothermal activity, and to further assess the potential for geothermal energy development in the valley (Glen et al., 2008; Kell-Hills et al., 2009; Egger et al., 2010; Egger and Miller, 2011; Glen et al., 2013; Egger et al., 2014).

Hydrologic connections between hot spring areas and the broader subsurface distribution of thermal waters in Surprise Valley is currently unknown. The mapping work of Hedel (1981) assumed hydrological connections between thermal manifestations in Surprise Valley, particularly Lake City and the Surprise Valley/Seyferth/Leonards springs. Subsequent geophysical and geochemical studies established little evidence for hydrologic connectivity along this structure (Cantwell and Fowler, 2014; Egger et al., 2014). The majority of geochemical studies of Surprise Valley geothermal waters focused on establishing maximum subsurface temperatures using traditional geothermometry methods (Duffield and Fournier, 1974; Reed, 1975; Sladek et al., 2004). Cantwell and Fowler (2014) and Fowler et al. (2015) compiled Surprise Valley aqueous geochemical and stable isotope analyses from the literature to evaluate recharge sources and dilution processes affecting the various hot springs. Cantwell and Fowler (2014) suggested that Seyferth/Leonards/Surprise Valley Hot Springs have a distinct recharge source from the east, while hot springs at Fort Bidwell and Lake City are recharged from the Warner Mountains in the west. Fowler et al. (2015) used geochemical modeling techniques to identify that Fort Bidwell springs have geochemical characteristics and maximum temperatures similar to Phipps 2 fluids, but are heavily diluted (~60%) by cold groundwater. Eagleville waters bear geochemical similarities to Seyferth/Leonards/Surprise Valley Hot Springs, but are also heavily diluted by cold groundwater.

Distinguishing the various fluid maturation processes that influence Surprise Valley groundwater compositions presents a challenge. Evaporative and thermally influenced fluids share several geochemical features, making it difficult to back out fluid evolution histories based on traditional methods of chemical data analysis alone. Evaporation and thermal water-rock interaction leads to elevated concentrations of dissolved constituents, and both processes also lead to Ca carbonate and Mg silicate mineral supersaturation. The absolute concentrations of dissolved constituents are typically much higher in evaporated waters than thermally evolved water, and there are subtle differences in the specifics of the mineral precipitation and dissolution reactions that lead to subtle differences in ratios of major dissolved constituent ratios. However, these distinctions between thermal and evaporated waters are not obvious when there is only partial evaporation or mixing of the evolved fluid products with unevolved waters.

In this contribution, we provide a broader assessment of the subsurface distribution of thermal and evaporated waters affected by groundwater dilution in Surprise Valley by evaluating a large, publicly available, fluid geochemical dataset. We use a combination of principal component analysis (PCA), modeling of evaporation and thermal mixing pathways, considering the geographical distribution of groundwater types. Principal component analysis (PCA) is a statistical technique that provides a means to identify multiple distinct fluid evolution trends in large aqueous geochemical data sets (e.g Otero et al., 2005). The use of statistical techniques requires consideration of the compositional nature of geochemical data, and the data must be transformed accordingly for results to be meaningful (Aitchison, 1982). Results are displayed on a biplot (a PCA graphical technique), which is used to identify the dissolved constituents for plotting on traditional graphs that best illustrate compositional variation in the dataset. We show that PCA provides an effective means to inform plots that can be used to distinguish Surprise Valley groundwater samples affected by different evaporation and mixing processes. In order to effectively interpret the PCA results, knowledge of fluid geochemical evolution pathways is required. We achieve this by using geochemical modeling software to investigate specific thermal mixing and evaporation pathways. When the combined PCA and geochemical modeling results are considered in a geographic context, they provide insights into the subsurface distribution and hydrological controls on the flow of thermal fluids.

Surprise Valley provides an ideal location to test geochemical methods for identifying blind geothermal resources because of the numerous fluid types, fluid evolution mechanisms, constraints on fluid endmember compositions, and the large database of fluid geochemical analyses. Our approach has promise for identifying the ‘blind’ geochemical signature of geothermal waters in other locations where large groundwater geochemical datasets are available, such as geothermal prospects in agricultural areas of the Basin and Range where waters are strongly influenced by evaporation. This approach could be easily modified for other locations where evaporation is less important than other fluid evolution processes, such as the Salton Trough and the Snake River Plain.

2. Geologic Background

The Warner Mountains form the western edge of Surprise valley, and are composed of a succession of Eocene to Pliocene intact and reworked andesitic lahar deposits, andesitic lava flows, rhyolitic ash-flow tuffs and domes, and basaltic lava flows (Duffield and Weldon, 1976; Duffield and McKee, 1986). Rocks in the Hays Canyon Range and Larkspur Hills to the east of the valley include Pliocene to late Miocene basalt flows (Carmichael et al., 2006). The most prominent structural features are the roughly north-south trending and basin-bounding Surprise Valley Fault at the base of the Warner Mountains, and the Hays Canyon Fault in the east (Figure 1). The Surprise Valley Fault has accommodated the most offset, estimated at approximately 8 km of dip-slip motion since the mid-Miocene (Egger and Miller, 2011).

Valley fill includes volcanoclastics and lava flows of various compositions, moraine and alluvial fan deposits, and dune sands (Clawson et al., 1986). The uppermost basin fill is composed of interlayered alluvium, sand dunes and lake deposits (Clawson et al., 1986). Lake deposits and wave cut shorelines above the valley floor formed from a contiguous water body present in the Pleistocene termed 'Lake Surprise', that had a highstand approximately 176 m above the current valley floor (Ibarra et al., 2014). Seismic surveys have not been successful at determining the total Surprise Valley basin depth (Lerch et al., 2010), however drilling indicates at least 2100 m of alluvial and lacustrine sediments are present (Duffield and Fournier, 1974).

Water-rock interaction owing to geothermal activity in the subsurface has resulted in localized alteration of volcanic rocks as observed in drill core samples. Rigby and Zebal (1981) provided a cursory description of alteration minerals present in the Phipps-2 drill core, reporting the presence of quartz, calcite, and hydrous clay minerals. Moore and Segall, (2005) completed a detailed X-ray diffraction study of alteration mineral compositions in Lake City drill holes OH-1 and LCSH-5, and describe rocks dominated by Mg-chlorite alteration and accompanied with calcite, silica, smectite, illite, and laumontite mineralization. There have been no direct studies on the composition of actively forming evaporite minerals, however a study by Hardie and Eugster (1978) determined Middle Alkali Lake brine follows a chemical divide that results in the precipitation of calcium carbonate, magnesium silicate, and the formation of a Na-Cl-(SO₄)-(CO₃) brine.

Figure 1: Map of Surprise Valley showing locations of creek sampling stations, groundwater wells, alkali lake sampling stations and thermal springs.

3. Methods

Groundwater and creek chemical composition data were obtained from (Clawson et al., 1986), which is also available for download in electronic form (CADWR, 2014). This dataset was refined by excluding samples with absolute charge balance differences greater than 5%, and samples with incomplete analyses that did not include B, SiO₂, Na, K, Ca, Mg, Cl, SO₄, HCO₃, or F. All concentrations were converted to molal units, and total carbonate as CaCO₃ was recalculated to total carbonate expressed as bicarbonate, the dominant aqueous species at the pH of these waters. A value equivalent to the method detection limit was used for analytes reported below the specified limit for plotting purposes. The dataset included 190 samples after refinement, and was used for plotting purposes (Appendix 1).

We calculated groundwater evaporation pathways based on the work of Garrels and Mackenzie (1967) who traced evaporation pathways of Sierra Nevada springs that form saline brines in eastern California and Nevada. We achieved this by running multicomponent equilibrium reaction path simulations, using Geochemists' Workbench version 5.0.2. with the Pitzer ion activity model (thermo_pitzer.dat). The method (e.g., Bethke, 2008) consists of numerically removing H₂O from solutions of interest to simulate evaporative concentration accompanied by mineral precipitation. When doing so, however, precipitation is not allowed for minerals that are computed to form on thermodynamic grounds, but that are not expected to precipitate based on either slow rates of precipitation or poor thermodynamic data. In our case this included suppressing the precipitation of talc, dolomite, antigorite, tremolite, and all silica polymorphs other than amorphous silica. The evaporation model was completed by removing -999.99 grams of H₂O from 1000 initial grams of H₂O, reflecting a concentration factor (CF) of 10⁶ (CF = initial liquid weight/final liquid weight) at a temperature of 20°C. Creek water evaporation to alkali lake compositions was modeled using a water sample from Mill Creek (Appendix 1) and calculated assuming atmospheric P_{CO_2} (10^{-3.5} bar). Soil vadose evaporation was modeled using groundwater sample 40N16E11G001 – 8/1959 (Appendix 1), and assuming an order of magnitude higher P_{CO_2} (10^{-2.5} bar). Eugster and Hardie (1978) suggested that soil vadose P_{CO_2} is commonly an order of magnitude higher than atmospheric P_{CO_2} , therefore our use of a soil P_{CO_2} value of 10^{-2.5} bar represents a maximum. Mixing between groundwater and thermal water was modeled using an unevolved groundwater sample (40N16E11G001 – 8/1959) and a thermal spring sample collected from the Surprise Valley Resort hot spring (42N17E06P001). Mixing was evaluated at temperatures ranging from the measured 92°C spring temperature to 150°C. Different temperatures within this range had no noticeable effect on the mineral precipitation sequence predicted by the hot spring – groundwater mixing model.

Compositional data are closed data (e.g. a constant sum constraint where parts sum to 1 or 100%) and carry only relative information, thus the direct application of multivariate statistical methods can lead to spurious results (Pearson, 1896; Aitchison, 1982; Aitchison, 1986). The underlying assumption in applying multivariate statistics to non-compositional “open” data is that the difference between 1 and 2 is considered the same as the difference between 10 and 11 (Aitchison, 1982; Aitchison, 1986). Failure of this assumption applied to compositional data is particularly apparent when evaporation is considered, when the difference between 1 ppm and 2 ppm is the same as the difference between 10 ppm and 20 ppm (e.g. components double in concentration as half the water is lost to evaporation). Another problem with compositional “closed” data is that component values cannot vary independently. For example, if SiO₂ precipitated in veins in a rock with an initial composition of 50% SiO₂, 30% CaO and 20% MgO by weight resulting in 70% SiO₂ by weight, the concentration of CaO and MgO must decrease to satisfy the constant sum (100%) constraint. The closed nature of aqueous geochemical data stems from the inherent inclusion of H₂O as a component in the expression of concentrations (e.g. mg component per mass or volume of solute). Thus, if an aqueous component increases in

concentration, the mass or volume of H₂O must change along with values for other dissolved constituents. Ignoring the compositional nature of geochemical data can produce misleading results.

A centered log-ratio transformation must be applied to compositional data to remove closure restraints and “open” the data in order for multivariate statistical analysis to yield meaningful results (Aitchison, 1982; Aitchison, 1986). The specifics of pitfalls and approaches for applying multivariate statistics (in particular PCA) to compositional data is not the focus of this study, and detailed discussions specifically relating to aqueous geochemical data are provided elsewhere (e.g. Aitchison, 1982; Singh et al., 2004; Otero et al., 2005; van den Boogaart and Tolosana-Delgado, 2013). In this study, a PCA and associated statistics were computed using “Compositions”, a package installed in the software “R” for the statistical analysis of compositional data (van den Boogaart and Tolosana-Delgado, 2008; van den Boogaart and Tolosana-Delgado, 2013). For the purposes of PCA analysis, the groundwater dataset was further refined by eliminating samples with analyte values below the detection limit. The dataset used for the PCA included 113 samples (Appendix 2). Ten variables (B, SiO₂, Na, K, Ca, Mg, Cl, SO₄, HCO₃, and F) were considered, and data were transformed using a centered log-ratio (clr) transformation (Aitchison, 1986). The clr transformation is based on dividing each sample by the geometric mean and taking the logarithm. This method can fail for data containing extreme outliers, because it spoils estimation of the principal components (Filzmoser et al., 2009). For this reason, the PCA was completed for groundwater samples only, and extreme endmember fluids (thermal spring and alkali lake fluid data) were excluded from the analysis. Exclusion of the thermal spring and alkali lake data from the PCA is also necessary for applying the method presented here to truly “blind” geothermal areas where no thermal spring data are available. Thermal spring and alkali lake fluid data (Appendix 3) were however included on plots informed by the outcome of the PCA analysis to identify fluid evolution trends predicted. The thermal spring and alkali lake fluid data were compiled from multiple sources (Livingstone, 1963; Duffield and Fournier, 1974; Reed, 1975; Bliss, 1983; Clawson et al., 1986; Sladek et al., 2004).

4. Results

3.1 Geochemical Modeling Results

Figure 2 is a simplified chemical divide diagram, based on that of Eugster and Hardie (1978), that shows the mineral precipitation and brine evolution pathway predicted for evaporation of Surprise Valley surface and groundwater by our evaporation models. The geochemical modeling results show Surprise Valley waters follow the same chemical divide, regardless of P_{CO_2} . The predicted evaporation mineral sequence (Table 1) and resulting brine is consistent with the chemical divide pathway proposed for Middle Alkali Lake in Surprise Valley by Eugster and Hardie (1978), which leads to the precipitation of calcite, sepiolite, and the formation of a Na-Cl-CO₃-SO₄ brine.

The calculated evaporation pathways are indicated on a Piper representation (Figure 3). While evaporation under different P_{CO_2} assumptions ultimately leads to similar brine compositions (in terms of component proportions), mineral supersaturation occurs at different concentration factors (Table 1) leading to differences in absolute concentrations of dissolved species. Differences in the two models are a reflection of pH differences resulting from different P_{CO_2} constraints, and differences in the initial sample compositions used in the evaporation models. For example, calcite is closer to saturation in the groundwater sample (40N16E11G001 – 8/1959) than the Mill Creek sample when identical P_{CO_2} values are used as the initial constraint.

Table 1: Evaporation model results

Minerals Precipitated by Evaporation	Mill Creek $P_{CO_2} = 10^{-3.5}$ $pH_{initial} = 8.2$		40N16E11G001-8/1959 $P_{CO_2} = 10^{-2.5}$ $pH_{initial} = 7.6$	
	CF	pH	CF	pH
Calcite ($CaCO_3$)	1.26	8.30	1.28	7.68
Sepiolite ($Mg_4Si_6O_{15}(OH)$)	1.47	8.31	2.67	7.80
Amorphous Silica (SiO_2)	5.29	8.34	41.67	8.53
Fluorite (CaF_2)	3333.33	10.00	5000	9.67
Gaylussite ($Na_2Ca(CO_3)_2 \cdot 5H_2O$)	1.0E+05	10.03	5000	9.67
Borax ($Na_2B_4O_5(OH)_4 \cdot 8H_2O$)	1.0E+05	10.03	1.0E+04	9.59
Mirabilite ($Na_2SO_4 \cdot 10H_2O$)	--	--	1.0E+06	9.48
Arcanite (K_2SO_4)	--	--	1.0E+06	9.48

CF = Concentration Factor (CF = initial liquid weight/final liquid weight) at a temperature of 20°C

Figure 2: Simplified chemical divide schematic (modified after Eugster and Hardie, 1978) illustrating results of evaporation models of Surprise Valley creek and groundwater samples (see text for details). The chemical divide schematic predicts that surface creek water evaporation at atmospheric P_{CO_2} ($10^{-3.5}$ bar) follows a chemical divide pathway that is controlled by calcite and subsequent sepiolite precipitation, resulting in formation of a Na-Cl-SO₄-CO₃ brine (grey boxes). Evaporation of groundwater under elevated P_{CO_2} ($10^{-2.5}$ bar) follows an identical pathway, however mineral precipitation is suppressed owing to the pH effects until a higher concentration factor is achieved.

Figure 3: A Piper diagram of Surprise Valley groundwater samples illustrates that many groundwater samples have evolved compositions away from unevolved creek water compositions towards either alkali lake or thermal spring compositions. Arrows indicate three potential fluid evolution scenarios calculated by geochemical modeling (see 'Methods' section for details). Groundwater samples that fall on a mixing line with thermal waters could be equally explained by interaction with a groundwater evaporated under elevated P_{CO_2} conditions, or mixing with evaporated alkali lake waters. While the Piper diagram is useful for demonstrating a large number of samples have evolved compositions, the specific process (mixing or evaporation) cannot be determined.

3.2 PCA Results

PCA results are included graphically as Figure 4. A compositional biplot of clr-transformed data for components 1 and 2 captures 73% of variance in the dataset of, indicated by the cumulative variance histogram (scree plot) on Figure 4. Results for relative loadings (values >2.0) calculated using the “compositions” software suggests the variance in component 1 is best captured by ratios of conservative cations in water (Na and B) to cations that are most readily incorporated into hydrothermal or evaporite minerals (Ca and Mg). Component 2 variance is best captured by anion ratios SO_4 and Cl to HCO_3 and F.

Figure 4: PCA results for groundwater data provided in Appendix 2 after centered log-ratio transformation. The PCA was calculated for groundwater data only; known thermal spring and alkali lake waters were excluded from the analysis. Results calculated using “Compositions”, a statistical package run in R (van den Boogaart and Tolosana-Delgado, 2008). Data in the compositional biplot (left) represent scores (symbols) and loadings (arrows) and are color-coded according to the Na/Ca ratio plotted against the SO_4/HCO_3 ratio (Figure 6).

5. Discussion

Evaporation modeling is consistent with previous studies of Surprise Valley brines (e.g. Eugster and Hardie, 1978) that predict calcite, Mg-clay (sepiolite), and amorphous silica precipitation at relatively low concentration factors (<5.29). While the evaporation model predicts precipitation of fluorite, gaylussite, borax, mirabilite, and arcanite at extreme evaporation, it is conceivable that these concentration factors are not achieved in Surprise Valley, as evidenced by the persistence of a saline brine in the shallow subsurface. Specific mineral compositions and evaporation systematics are almost certainly more complex than predicted by these simple evaporation models, and the specific predicted evaporite minerals are of secondary importance to the outcome of this study. The relevant outcome of the modeling is to demonstrate that evaporated brines lose Ca, Mg, and SiO_2 relative to other dissolved constituents in the initial groundwater to achieve measured alkali lake brine compositions. Much like evaporated brines, thermal fluids at Surprise Valley also lose Mg, Ca and SiO_2 relative to the other dissolved constituents. Geothermal water-rock interaction in the subsurface of Surprise Valley leads

to extensive replacement of primary rock minerals with Mg-chlorite and precipitation of calcite and silica in veins (Rigby and Zebal, 1981; Moore and Segall, 2005).

The similarities in molar ratios of components in thermally and evaporatively evolved groundwater are illustrated using a Piper diagram (Figure 3). The fluid evolution pathways for calculated evaporative processes are difficult to distinguish from groundwater – hot spring mixing pathways (Figure 3). Mixing of unevolved groundwater with any of the thermal water compositions on Figure 3 provides a mechanism that could explain almost every groundwater composition plotted. Alternatively, mixing between unevolved and evaporated alkali lake water could also explain almost every evolved groundwater composition plotted on Figure 3. Evaporation at any P_{CO_2} value between $10^{-2.5}$ and $10^{-3.5}$ could also explain most groundwater compositions plotted on Figure 3. A technique other than plotting a standard geochemical diagram is required to distinguish the influence of thermal mixing and evaporative processes.

The PCA result (Figure 4) alone is not sufficient to draw meaningful conclusions about the relationship of groundwater compositions to specific geochemical processes, but is very powerful for informing how to construct plots that best present this information. An X-Y plot of dissolved component ratios is an effective method to distinguish different fluid evolution pathways, but selecting which ratios to plot is daunting. For an X-Y plot considering $n = 10$ elements, where each axis represents a ratio of two elements ratio ($r = 2$) there are 90 ratio permutations that must be considered for each axis alone (e.g. $n!/[(n-r)!]$ permutations). The compositional PCA technique provides a means to identify element ratios that best describe the compositional variability in a given geochemical dataset. However, as we show in the following discussion, PCA results must be carefully considered in the context of data quality and knowledge of geochemical processes.

van den Boogaart and Tolosana-Delgado (2013) describe the interpretation of compositional biplots as is summarized in the following paragraph. In a biplot of data that has not been log-ratio transformed, the length of an arrow is proportional to variance and the cosine of the angle between arrows is the correlation coefficient of the variables. A biplot of clr-transformed data describes clr variance, and cannot be directly related back to all of the original components. The interpretation of a biplot obtained using clr transformed data differs from a biplot obtained using non-compositional data, and relationships between arrows (also termed “rays”) should be investigated rather than interpreting individual arrows. If two arrow heads are close together, the variance may be proportional. The cosine of the angle between arrows approximates the correlation coefficient. Arrows with uncorrelated log ratios are at 90° from each other, perfectly positively correlated arrows are parallel, and perfectly negatively correlated arrows are at 180° .

The biplot presented in Figure 4 suggests component 1 represents a process whereby Ca and Mg define a common link, B, Na and F define a second common link, and that variation between these two links is inversely correlated. Component 2 appears to represent a process whereby SO_4 and Cl define a common link, and SiO_2 and HCO_3 define a second common link, and that variation of these two links is inversely related. The short length of the K arrow suggests it does not represent much of the variation displayed in the biplot. Also, the arrow groups described above for components 1 and 2 are nearly orthogonal, suggesting the data represented by these arrows may be plotted to very effectively distinguish the geochemical processes represented by components 1 and 2.

The relationships between component-1 arrows shown on the x-axis of the compositional biplot in Figure 4 are consistent with results of the evaporation models. Evaporated water is continuously depleted in Mg and Ca owing to calcite and sepiolite precipitation, leading to an inverse relationship with Na, F and B that behave

conservatively for the most of the evaporation pathway. The model predicts that Na, F and B concentrations only cease acting conservatively at near complete evaporation, when the Na-bearing minerals gaylussite and mirabilite, F-bearing mineral fluorite, and B-bearing mineral borax form. Based on the persistence of saline brine in the shallow subsurface, it is not clear if this extent of evaporation is ever fully achieved at Surprise Valley. Interpretation of component 2 is more complicated. The geochemical process represented by component 2 leads to an inverse correlation between SiO_2 and HCO_3 to SO_4 and Cl. An inverse relationship does not necessarily imply that SiO_2 and HCO_3 were depleted from the original fluid composition, and this relationship in the data could equally stem from overall gains of SiO_2 , HCO_3 , SO_4 and Cl with larger relative gains of SO_4 and Cl. This latter possibility is consistent with geothermal processes, where fluid SiO_2 and K generally increase with increasing temperatures and SO_4 and Cl have large increases relative to HCO_3 , particularly in geothermal waters that have equilibrated with volcanic rocks (Giggenbach and Goguel, 1989).

In clr-transformed data, the relative loadings of components provide a means to directly interpret the effects of the principal components (van den Boogaart and Tolosana-Delgado, 2013). The highest relative loadings (those presented on Figure 4) are useful indicators of the element ratios that best illustrate the maximum variance of each principal component. Element ratio plots informed by the highest relative loadings values results in clear distinctions between thermal and evaporated waters (Figure 5), supporting our interpretations of the processes represented by components 1 and 2. Known samples of thermal water and evaporated alkali lake samples are included on the plots in Figure 5 to evaluate the relative loadings results, however in a true blind geothermal area these constraints would not be available. In such a case, endmember evolved water compositions could easily be estimated using geochemical modeling tools, such as the evaporation pathway calculated in this study.

While the relative loading results from our compositional PCA provide a useful estimate of which combinations of elements describe the maximum variation in each principal component, this is only a guide and the results must be considered in greater detail. The relative loadings for component 1 indicate that the B/Mg ratio would be the most effective indicator of the variation represented by component 1. The metric variance of the B and Mg subcomposition relative to the total metric variance of the dataset can be quantified using the “components” R software package (van den Boogaart and Tolosana-Delgado, 2013), and results in the highest proportion (25.6%) of the total variance for any two components (Figure 4), suggesting B and Mg are important geochemical indicators for this dataset. An important consideration is that B is present in trace (<1 mg/L) concentrations in virtually all of the groundwater samples. B was (mostly) measured using Std Method 4500-B or C, which has a standard reporting limit of 0.1 mg/L and a modified detection of 0.05 mg/L (CADWR, 2014). Closer investigation of the dataset reveals that a large number (nearly half) of the groundwater samples have B values that fall within the 0.1 to 0.05 mg/L range, and these data likely have very large associated errors. Much of the metric variance represented by the B/Mg ratio reflects highly evaporated samples that contribute a high proportion of variability to the dataset. So while the B/Mg ratio is useful for distinguishing high TDS evaporated waters (Figure 5), it is not particularly useful for distinguishing subtle evaporation signatures in dilute groundwater samples.

Figure 5: Element ratio plots of Surprise Valley groundwater and creeks data contained in Appendix 1 (black symbols), and alkali lake (solid green triangles) and thermal spring data (solid red squares) contained in Appendix 3. Axis values are informed by the relative loading values for components 1 and 2 given in Figure 4. Points shown as “alkali-lake influenced” and “thermal water mixing” are cold groundwater samples, and are interpreted to be influenced by thermal and evaporative processes based on the Na/Ca versus SO_4/HCO_3 plot (see text for discussion).

The relative loadings also suggest that the Na/Mg ratio is useful for distinguishing thermal mixing from evaporative processes, and this is certainly the case for alkali lake and groundwaters that have undergone a significant degree of evaporation (Figure 5). The detection limit is 0.1 mg/L for Mg and 1 mg/L for Na, and the majority of groundwater samples have values several times the detection limits, so we can have reasonable confidence in the Mg and Na values. However, ratios that include Mg (Mg/B and Na/Mg) are biased towards waters that have undergone a significant degree of evaporation and have passed the sepiolite chemical divide,

and again are not particularly useful for distinguishing evaporation processes that have affected more dilute groundwater. The failure of B/Mg and Na/Mg ratios to predict evaporation signatures in dilute groundwater samples is evident on Figure 5, where highly evaporated alkali samples (green triangles) that have not passed the sepiolite divide overlap with dilute groundwater (black symbols) in terms of the B/Mg and Na/Mg ratios.

The B/Ca ratio provides a better estimate of evaporation, considering most Surprise Valley waters are at or near calcite saturation, so even low degrees of evaporation are reflected in element ratios with Ca as the denominator. Again, B is not a great measure for dilute groundwater samples, owing to poor precision in the very low B values of dilute groundwater samples, so the B/Ca ratio is potentially inadequate for distinguishing low degrees of evaporation. The Na/Ca ratio provides a more robust estimate of the degree of evaporation because 1) Na behaves conservatively until near complete evaporation, 2) Na is present at relatively high values relative to the method detection limit in dilute samples so precision is good, and 3) Large differences in the initial Na and Ca concentrations lead to magnified relative changes in concentration between these two components for small degrees of evaporation. For these reasons, we use the Na/Ca ratio to identify groundwater influenced by evaporation or mixing with alkali lake waters (Figure 6).

The relative loadings suggest that the SO_4/HCO_3 ratio is the best estimate for waters that have a thermal signature, and this is supported by the variation of this ratio for known thermal fluids (Figures 5 and 6). The relative loadings for component 2 (Figure 4) also suggest that F might be a useful thermal indicator, but like B this is a trace element present at very low concentrations in dilute waters with low analytical precision. Relative loadings also suggest that Cl could be used in ratios to distinguish thermal waters (Figure 4), however Cl varies similarly for both component 1 and component 2, so is of limited use for distinguishing between them. For these reasons, we use the SO_4/HCO_3 ratio to identify groundwater influenced by evaporation or mixing with alkali lake waters (Figure 6).

Plots of Na/Ca against SO_4/HCO_3 provide a tool to visually estimate which groundwater samples have been influenced by evaporation or mixing with alkali lake waters, and groundwater samples that have mixed with thermal waters (Figure 6). Using Figure 6, there are clearly some samples that are unambiguously affected by thermal or evaporative processes, however the cutoff between unevolved groundwater and thermal/evaporative water is somewhat arbitrary. We visually estimate this cutoff using breaks in the clustering of samples on Figure 6, and suggest samples with Na/Ca ratios ≥ 8 and $\text{SO}_4/\text{HCO}_3 < 0.1$ have an evaporative signature, and samples with $\text{SO}_4/\text{HCO}_3 \geq 0.1$ have a thermal signature. When the PCA results are color coded according to the results for Na/Ca and SO_4/HCO_3 ratios, the data break out into distinct groups of unevolved, evaporative, and thermally influenced groundwater samples (Figure 4), further supporting use of these ratios to identify geochemical processes that have affected the dataset. We further evaluate our predictions by considering the geographical distribution of wells from which these samples were collected.

In order to determine the three dimensional picture of groundwater geochemical distributions, well depths must be considered. The majority of wells ranged between 11 and 77 m deep, eight wells between 107 and 139 m, and one well was 335 m deep. There is no correlation between well depth and predicted mixing processes that have affected groundwater samples. While monitoring wells have distinct screened intervals and are used to obtain discrete samples from particular aquifers or water bearing zones, the wells used in this study are agricultural, industrial, and domestic production wells. These types of well are screened over large intervals and sample groundwater from multiple lateral recharge zones. Water affected by soil vadose evaporation, evaporated alkali lake waters, thermal waters could potentially mix before entering the well bore or mix within the well bore, therefore it is not possible to make predictions about subsurface zones affected by various groundwater

geochemical evolution processes and this study is necessarily restricted to a horizontally two-dimensional consideration of groundwater distributions (Figure 7).

The distribution of groundwater predicted to be influenced by evaporative processes is largely coincident with the edge of the alkali lakes. This would suggest that these samples are influenced by mixing with evaporated alkali lake brine that is known to persist in the subsurface (Ver Planck and Heizer, 1958), rather than being affected by soil vadose evaporation at elevated P_{CO_2} values. One evaporated sample is located adjacent to a hot well at Fort Bidwell and one is located adjacent to a thermal well at the Surprise Valley Resort. While these samples may be influenced by mixing with evaporated water, they also fall on a mixing line with thermal waters (Figure 6) and would be considered thermal if we marginally changed our selection criteria for thermal waters from SO_4/HCO_3 ratios ≥ 0.1 to SO_4/HCO_3 ratios ≥ 0.08 . In the interest of making conservative visual estimates, we stick with the higher value estimate and acknowledge that at very low concentrations the visual clustering selection method can yield conflicting results.

The distribution of thermally influenced groundwater forms two distinct linear arrays coincident with faults recently mapped or inferred by Egger et al. (2014), and lie between known hot spring locations (Figure 7). We term these linear arrays the Eagleville-Seyferth trend and the Lake City-Fort Bidwell trend. The Eagleville-Seyferth trend is coincident with a normal fault that is predicted to intersect the southern length of the Surprise Valley fault at the Warner Mountain range front at depth. The Lake City-Fort Bidwell trend is coincident with the northern portion of the Surprise Valley fault. The break in the newly identified thermal water trends is consistent with the structural mapping of Egger et al. (2014), who predict a complex discontinuity in the Surprise Valley fault precisely at the location where the identified thermal trends diverge. The two distinct linear trends are also consistent with geochemical and isotopic differences in Surprise Valley geothermal fluids identified by Cantwell and Fowler (2014) and Fowler et al. (2015). These authors identified fluids lying on the Eagleville-Seyferth trend as having distinct hydrogen isotope ratios from fluids lying on the Lake City-Fort Bidwell trend. These authors also identified that Fort Bidwell thermal waters are geochemically similar to Lake City waters, and can be formed by direct dilution by cold groundwater.

Figure 6: The Na/Ca ratio provides a useful measure of groundwater affected by evaporation or mixing with evaporated waters, while the SO₄/HCO₃ ratio provides a useful measure for groundwater that has mixed with thermal waters. Plots of these two ratios scaled for different levels of detail provide a means to identify groundwater samples influenced by each of these processes. Unevolved waters are considered to have Na/Ca ratios < 8 and SO₄/HCO₃ ratios < 0.1, values determined visually as distinct breaks in clustering of groundwater sample values.

Figure 7: Groundwater with an evaporative signature is largely confined to the edges of the alkali lakes, suggesting that these samples are a mixture of groundwater and alkali lake waters rather than being influenced by soil vadose evaporation under elevated P_{CO_2} conditions. Groundwater with a thermal signature is defined by two major linear trends; an Eagleville - Seyferth trend that is coincident with faults mapped by Egger et al. (2014), and a Lake City – Fort Bidwell trend that is coincident with the northern portion of the Surprise Valley fault located the Warner Mountains range front.

6. Conclusions

We provide a method to identify thermal signatures in groundwater affected by evaporated alkaline brines, using compositional statistical analysis of a large groundwater quality dataset. Geochemical modeling is used to identify dissolved constituents most useful for distinguishing evaporated and thermally evolved waters. We identify two major thermal fluid trends that are likely controlled by distinct fault systems; a more southerly Eagleville-Seyferth trend and more northerly Lake City-Fort Bidwell trend. Groundwater samples that are influenced by evaporation processes are located adjacent to alkali lakes, suggesting mixing of evaporated lake waters with cold groundwater in the subsurface. This study shows that compositional PCA combined with geochemical modeling can be a powerful method to identify thermal signature in areas with large groundwater quality datasets where thermal fluids are suspected. Similar methods could be applied to agricultural areas in the Basin and Range, the Snake River Plain in Idaho and the Imperial Valley in southern California. This study benefits from the availability of end-member evaporated and thermal water samples to constrain our interpretations. In locations where samples of end-member fluids representing evaporative or thermal water-rock interaction are not available, estimates of fluid composition can be made with carefully considered geochemical models.

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References

- Aitchison, J., 1982. The statistical analysis of compositional data. *Journal of the Royal Statistical Society*, 44(2): 139-177.
- Aitchison, J., 1986. The statistical analysis of compositional data. Chapman & Hall, London.
- Benoit, D., Blackwell, D.D., Capuano, L., Goranson, C., Moore, J.N. and Carey, D., 2005a. Phase 2 and 3 slim hole drilling and testing at the Lake City, California geothermal field, AMP Resources (Surprise Valley), LLC.
- Benoit, D., Goranson, C., Wesnousky, S. and Blackwell, D.D., 2004. Overview of the Lake City, California Geothermal System. *Geothermal Resources Council Transactions*, 28: 311-315.
- Benoit, D., Moore, J.N., Goranson, C. and Blackwell, D.D., 2005b. Core hole drilling and testing at the Lake City, California geothermal field. *Geothermal Resources Council Transactions*, 29: 203-208.
- Bethke, C.M., 2008. *Geochemical and biogeochemical reaction modeling*. Cambridge University Press. 547.
- Bliss, J.D., 1983. Basic data for thermal springs and wells as recorded in GEOTHERM, Part A. USGS Open File report 83-428A, July 1983.
- CADWR, 2014. August, 13. California Department of Water Resources, Water Data Library. Retrieved from <http://www.water.ca.gov/waterdatalibrary/>.
- Cantwell, C.A. and Fowler, A.P.G., 2014. Fluid geochemistry of the Surprise Valley geothermal system. *Proceedings, Thirty-Ninth Workshop on Geothermal Reservoir Engineering*. Stanford University, California, February 24-26, 2014.
- Carmichael, I.S.E., Lange, R.A., Hall, C.M. and Renne, P.R., 2006. Faulted and tilted Pliocene olivine-tholeiite lavas near Alturas, NE California, and their bearing on the uplift of the Warner Range. *Geological Society of America Bulletin*, 118(9-10): 1196-1211.
- Clawson, R.F., Gibson, L.R. and Beach, S.L., 1986. Surprise Valley Ground Water Basin Water Quality Study. California Department of Water Resources, Northern District.
- Duffield, W.A. and Fournier, R.O., 1974. Reconnaissance Study of the Geothermal Resources of Modoc County, California. USGS Open File Report 74-1024.
- Duffield, W.A. and McKee, E.H., 1986. Geochronology, structure, and basin-range tectonism of the Warner Range, northeastern California. *Geological Society of America Bulletin*, 97(2): 142-146.
- Duffield, W.A. and Weldon, R.D., 1976. Mineral resources of the South Warner Wilderness, Modoc County, California, with a section on aeromagnetic data by W.E. Davis: U.S. Geological Survey Bulletin 1385D, 31 p.
- Egger, A.E., Glen, J.M.G. and Ponce, D.A., 2010. The northwestern margin of the Basin and Range province. *Tectonophysics*, 488(1-4): 150-161.

- Egger, A. and Miller, E.A., 2011. Evolution of the northwestern margin of the Basin and Range: The geology and extensional history of the Warner Range and environs, northeastern California. *Geosphere*, 7(3): 756.
- Egger, A.E., Glen, J.M.G. and McPhee, D.K., 2014. Structural controls on geothermal circulation in Surprise Valley, California: A re-evaluation of the Lake City fault zone. *Geological Society of America Bulletin*, 126(3-4): 523-531.
- Egger, A.E., Glen, J.M.G. and Ponce, D.A., 2010. The northwestern margin of the Basin and Range province. *Tectonophysics*, 488(1-4): 150-161.
- Eugster, H.P. and Hardie, L.A., 1978. *Saline Lakes*. Springer, New York, pp. 237-293.
- Filzmoser, P., Hron, K. and Reimann, C. (2009) Principal component analysis for compositional data with outliers. *Environmetrics* 20: 621-632.
- Fowler, A.P.G., Cantwell, C.A., Spycher, N., Siler, D., Dobson, P.F., Kennedy, M. and Zierenberg, R., 2015. Integrated geochemical investigations of Surprise Valley thermal springs and cold waters. *Proceedings, Fourtieth Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, California, January 26-28, 2015.
- Garrels, R.M. and Mackenzie, F.T., 1967. Origin of the Chemical Compositions of Some Springs and Lakes. *Equilibrium Concepts in Natural Water Systems*, 67: 222-242.
- Giggenbach, W.F. and Goguel, R.L., 1989. *Collection and analysis of geothermal and volcanic water and gas discharges*. DSIR report CD 2401, 4th edition., Petone, New Zealand.
- Glen, J.M.G., Egger, A.E., Ippolito, C. and Athens, N., 2013. Correlation of geothermal springs with sub-surface fault terminations revealed by high-resolution, UAV-acquired magnetic data. *Proceedings, Thirty-Eighth Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, California, February 11-13, 2013.
- Glen, J.M.G., Egger, A.E. and Ponce, D.A., 2008. Structures controlling geothermal circulation identified through gravity and magnetic transects, Surprise Valley, California, Northwestern Great Basin. *Geothermal Resources Council Transactions*, 32: 279-283.
- Hedel, C.W., 1981. Map showing geothermal resources of the Lake City-Surprise Valley geothermal resource area, Modoc County, California: U.S. Geological Survey Miscellaneous Field Studies Map MF-1299, scale 1:62,500.
- Ibarra, D.E., Egger, A.E., Weaver, K.L., Harris, C.R. and Maher, K., 2014. Rise and fall of late Pleistocene pluvial lakes in response to reduced evaporation and precipitation: Evidence from Lake Surprise, California. *Geological Society of America Bulletin*, 126(11-12): 1387-1415.
- Ingraham, N.L. and Taylor, B.E., 1986. Hydrogen isotope study of large-scale meteoric water transport in northern California and Nevada. *Journal of Hydrology*, 85: 183-197.

- Ingraham, N.L. and Taylor, B.E., 1989. The effect of snowmelt on the hydrogen isotope ratios of creek discharge in Surprise Valley, California. *Journal of Hydrology*, 106: 233-244.
- Kell-Hills, A., Thompson, M., Dhar, M., Louie, J. and Pullammanappallil, S., 2009. A study of the Surprise Valley Fault using a high-resolution shallow seismic reflection profile. *Geothermal Resources Council Transactions*, 33: 477-480.
- LaFleur, J., Carter, A., Moore, K., Barker, B., Atkinson, P., Jones, C., Moore, J.N. and Paollard, B., 2010. Update on geothermal exploration at Fort Bidwell, Surprise Valley California. *Geothermal Resources Council Transactions*, 34: 581-583.
- Lerch, D.W., Klemperer, S.L., Egger, A.E., Colgan, J.P. and Miller, E.L., 2010. The northwestern margin of the Basin-and-Range Province, part 1: Reflection profiling of the moderate-angle (~30°) Surprise Valley Fault. *Tectonophysics*, 488(1-4): 143-149.
- Livingstone, D.A., 1963. Chemical composition of rivers and lakes Ed. Fleischer, M., in *Data of Geochemistry*, USGS professional paper 440-G, United States Government Printing Office, Washington DC.
- Moore, J.N. and Segall, M., 2005. Hydrothermal alteration of the Surprise Valley reservoir rocks. Energy and Geoscience Institute at the the University of Utah, Salt Lake City, Technical Report 54900900-7-30-05, 40 p.
- O'Connell, J.F., 1975. The prehistory of Surprise Valley. *Ballena Press Anthropological Papers*, 4: 57.
- Otero, N., Tolosana-Delgado, R., Soler, A., Pawlowsky-Glahn, V. and Canals, A., 2005. Relative vs. absolute statistical analysis of compositions: a comparative study of surface waters of a Mediterranean river. *Water Res*, 39(7): 1404-1414.
- Pearson, K., 1896. Matematical contributions to the theory of evolution. On a form of spurious correlation which may arise when indicies are used in the measurement of organs. *Proceedings of the Royal Society of London*, 60: 489-498.
- Reed, M.J., 1975. Chemistry of thermal water in selected geothermal areas of California. California Division of Oil and Gas, Publication No. TR15: 35.
- Rigby, F.A. and Zebal, G.P., 1981. Case history on geothermal-well-log interpretation: Surprise Valley, California. Los Alamos Scientific Lab., NM (USA), Report No. LA-8598-MS, 58 p.
- Singh, K.P., Malik, A., Mohan, D. and Sinha, S., 2004. Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomti River (India)--a case study. *Water Res*, 38(18): 3980-3992.
- Sladek, C., Arehart, G.B. and Benoit, W.R., 2004. Geochemistry of the Lake City Geothermal System, California, USA. *Geothermal Resources Council Transactions*, 28: 363-368.
- van den Boogaart, K.G. and Tolosana-Delgado, R., 2008. "compositions": A unified R package to analyze compositional data. *Computers & Geosciences*, 34(4): 320-338.

van den Boogaart, K.G. and Tolosana-Delgado, R., 2013. Analyzing compositional data with R. Berlin: Springer, 2013.

Ver Planck, W.E. and Heizer, R.F., 1958. Salt in California. California Department of Water Resources.

White, D.E., 1955. Violent mud-volcano eruption of Lake City hot springs, northeastern California. Bulletin of the Geological Society of America, 66: 1109-1130.