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A conceptual geochemical model of the geothermal system at Surprise Valley, CA

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Highlights

- A conceptual geochemical model of the Surprise Valley geothermal system is presented
- Optimized multicomponent geothermometry suggests thermal springs equilibrated at progressively lower temperatures
- Thermal springs have D/H values lower than any modern cold recharge source

Abstract

Characterizing the geothermal system at Surprise Valley (SV), northeastern California, is important for determining the sustainability of the energy resource, and mitigating hazards associated with hydrothermal eruptions that last occurred in 1951. Previous geochemical studies of the area attempted to reconcile different hot spring compositions on the western and eastern sides of the valley using scenarios of dilution, equilibration at low temperatures, surfaceevaporation, and differences in rock type along flow paths. These models were primarily supported using classical geothermometry methods, and generally assumed that fluids in the Lake City mud volcano area on the western side of the valley best reflect the composition of a deep geothermal fluid. In this contribution, we address controls on hot spring compositions using a different suite of geochemical tools, including optimized multicomponent geochemistry(GeoT) models, hot spring fluid major and trace element measurements, mineralogical observations, and stable isotope measurements of hot spring fluids and precipitated carbonates. We synthesize the results into a conceptual geochemical model of the Surprise Valley geothermal system, and show that high-temperature (quartz, Na/K, Na/K/Ca) classical geothermometers fail to predict maximum subsurface temperatures because fluids re-

equilibrated at progressively lower temperatures during outflow, including in the Lake City area. We propose a model where hot spring fluids originate as a mixture between a deep thermal brine and modern meteoric fluids, with a seasonally variable mixing ratio. The deep brine has deuterium values at least 3 to 4‰ lighter than any known groundwater or high-elevation snow previously measured in and adjacent to SV, suggesting it was recharged during the Pleistocene when meteoric fluids had lower deuterium values. The deuterium values and compositional characteristics of the deep brine have only been identified in thermal springs and groundwater samples collected in proximity to structures that transmit thermal fluids, suggesting the brine may be thermal in nature. On the western side of the valley at the Lake City mud volcano, the deep brine-meteoric water mixture subsequently boils in the shallow subsurface, precipitates calcite, and re-equilibrates at about 130 °C. On the eastern side of the valley, meteoric fluid mixes to a greater extent with the deep brine, cools conductively without boiling, and the composition is modified as dissolved elements are sequestered by secondary minerals that form along the cooling and outflow path at temperatures <130 °C. Re-equilibration of geothermal fluids at lower temperatures during outflow explains why subsurface temperature estimates based on classical geothermometry methods are highly variable, and fail to agree with temperature estimates based on dissolved sulfate-oxygen isotopes and results of classical and multicomponent geothermometry applied to reconstructed deep well fluids. The proposed model is compatible with the idea suggested by others that thermal fluids on the western and eastern side of the valley have a common source, and supports the hypothesis that low temperature re-equilibration during west to east flow is the major control on hot spring fluid compositions, rather than dilution, evaporation, or differences in rock type.

Keywords

Surprise Valley
Geothermal
Geochemical modeling
Optimized multicomponent geothermometry
Rare earth elements
Trace elements

1. Introduction

Surprise Valley, northeastern California, is an active geothermal area located on the western edge of the Basin and Range extensional province and at the northern terminus

of the Walker Lane dextral-slip belt (Egger et al., 2010). Hot and warm springs occur throughout the valley; the main locations are near Eagleville, Lake City, and Fort Bidwell on the western side; and at the Surprise Valley Hot Springs Resort (SVHS), Leonards hot spring, and Seyferth hot spring on the eastern side of the valley (Fig. 1). Geochemical studies related to energy exploration of the geothermal areas in Surprise Valley have been conducted periodically since the 1950s. The purpose of this study is revisit the conceptual geochemical model of the Surprise Valley geothermal system, taking advantage of the large body of historical data, advances in geochemical modeling software, and accessibility to high-resolution trace element analytical data.

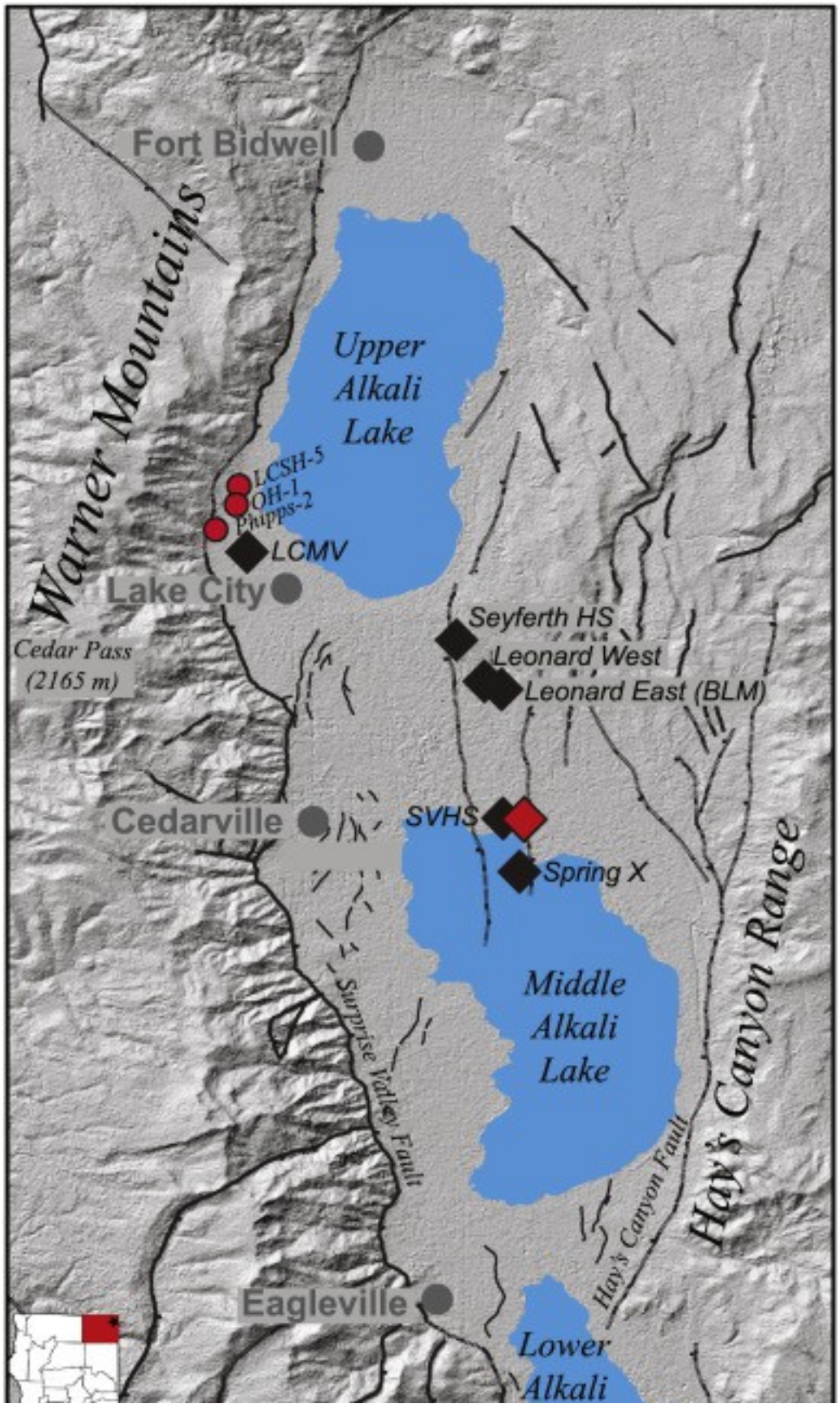
Fort Bidwell
Warner Mountains
Upper
Alkali
Lake
LCSH-5
OH-1
Phipps-2
LCMV
Lake City
Cedar Pass
(2165 m)
Seyferth HS
Leonard West
Leonard East (BLM)
Cedarville
SVHS
Spring X
Middle
Alkali
Lake
Surprise Valley Fault
Hay's Canyon Fault
Hay's Canyon Range
Eagleville
Lower
Alkali

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Fig. 1. Surprise Valley showing sampling locations. Spring E of SVHS (northern and southern) and Spring SW of SVHS (see Table 1) are located adjacent to SVHS.

1.1. Background

Direct use of the Surprise Valley geothermal resource began in the 1950s with construction of the SVHS, where boiling water from a 27 m deep well is still used to heat spas. Interest in the geothermal energy potential of Surprise Valley followed eruption of the Lake City mud volcano (LCMV) in March 1951 on the western side of the valley (White, 1955). Magma Energy, Inc. subsequently drilled three exploratory wells in the LCMV area between 1959 and 1962. Parman-1 reached 140 °C at 655 m, Parman-2 reached 125 °C at 600 m depth, and Parman-3 reached 92 m when a blowout destroyed the rig and expelled boiling water (Woods, 1974; Reed, 1975). Following designation of Lake City as a known geothermal resource area (KGRA) under the Geothermal Steam Act of 1970 (Godwin et al., 1971), six more deep test wellswere drilled by Magma Energy, Inc., Gulf Oil Corporation, and American Thermal Resources between 1970 and 1974. This included the 1508 m deep Phipps-2 exploration well just to the northwest of LCMV, which achieved the maximum measured subsurface temperature in the valley of between 160 °C and 170 °C (Duffield and Fournier, 1974; Rigby and Zebal, 1981).

A lack of local demand for hot water and electricity led to a hiatus in Surprise Valley geothermal exploration (Rigby and Zebal, 1981) until the 2000s, when interest in the Surprise Valley geothermal resource renewed. A series of temperature gradient and core holes were drilled in the LCMV (Benoit et al., 2004; Benoit et al., 2005a; Benoit et al., 2005b) and Fort Bidwell (Barker et al., 2005; LaFleur et al., 2010) areas. During these efforts, holes OH-1 and LCSH-5 were drilled to the north of Phipps-2 and near the Surprise Valley Fault (SVF). OH-1 and LCSH-5 were drilled to 1047 m and 1441 m, respectively, and the wells both achieved maximum temperatures of approximately 160 °C during testing, comparable to the bottom hole temperature measured in Phipps-2 (Benoit et al., 2005b). In 2016, the California Energy Commission (CEC) funded drilling of three closely spaced temperature gradient holes on the eastern side of the valley near SVHS, including one for which water samples were collected. The results of water sampling from the CEC project are discussed herein.

In addition to exploration drilling, several geophysical and geologic studies have been conducted to evaluate geologic and structural controls on subsurface geothermal fluid flow in Surprise Valley using high-quality gravity, magnetic, and audio magnetotelluric

measurements (Glen et al., 2008; Kell-Hills et al., 2009; Lerch et al., 2010; Glen et al., 2013; Hawkes et al., 2013; Egger et al., 2014; Athens et al., 2016; Tanner et al., 2016). These studies show a close association of hot springs with faults in Surprise Valley, and support the contention of Duffield and Fournier (1974) that thermal fluid flow is structurally controlled (Egger et al., 2014). A dominant structural control on thermal fluid flow appears to be the SVF, a major offset normal fault located along the eastern front of the Warner Mountains (Duffield and McKee, 1986; Egger et al., 2010). A number of authors (e.g. Glen et al., 2013) argued for the existence of a northwest striking "Lake City Fault" connecting the Lake City hydrothermal system with the system on the east side of the valley. Hawkes et al. (2013) argue against a major fault in this location based on audiomagnetic studies. Egger et al. (2014) also found little evidence for a distinct 'Lake City Fault', and instead proposed a model where small offset N–S trending and westward dipping normal faults intersect the SVF at depth and facilitate flow of thermal waters to the eastern side of the valley. Magnetotelluric surveys conducted by Tanner et al. (2016) recognized that hot spring locations fall off-axis of the westward dipping faults identified by Egger et al. (2014), and proposed that porous basalts within fault-tilted blocks provide a fluid pathway. Fowler et al. (2017) identified two distinct groundwater trends with a thermal signature using a statistical analysis of historical groundwater geochemical data. One subsurface trend is coincident with the SVF on the western side of the valley between Lake City and Fort Bidwell, and the other trend is located on the eastern side of the valley and is coincident with the trend of the small N–S trending westward dipping faults and porous basalts.

Renewed interest in the Surprise Valley geothermal resource provides a need to revisit geochemical models of the geothermal system. Conceptual geochemical models of the Surprise Valley geothermal system have been based on classical geothermometry calculations, which rely upon variations of dissolved concentrations as a function of temperature. We refer to classical geothermometers as the empirical and thermodynamic temperature-solubility relations for silica, feldspar and micas, termed the quartz, chalcedony, Na/K, and Na/K/Ca geothermometers (e.g. Fournier, 1977; Giggenbach, 1988). All geothermometer relations are dependent on the assumptions that: 1) dissolved concentrations reflect fluid-mineral equilibrium at the maximum subsurface temperature, 2) fluids did not re-equilibrate at lower temperatures along the outflow path, and 3) there was no mixing with fluids of a different composition (Fournier, 1977). Additional caveats apply to specific geothermometers; however, it is beyond the scope of this study to review and reiterate these details. Temperature agreement between several different geothermometer formulations is

generally thought to indicate that these assumptions are robust. When these geothermometers disagree, the primary assumptions must be revisited. Previous studies of the Surprise Valley geothermal system have utilized discrepancies between results for various classical geothermometers to propose conceptual geochemical models of dilution or low temperature re-equilibration.

Duffield and Fournier (1974) proposed that conservative element concentrations indicate LCMV fluids are undiluted outflow of deep geothermal fluids that equilibrated between 153 °C to 174 °C based on quartz and Na-K-Ca geothermometer temperature estimates, while fluids on the eastern side of the valley are diluted by low-concentration meteoric water. When corrected for dilution, the calculations suggested that the SVHS fluids equilibrated between 135 °C and 145 °C, and Leonard's hot spring fluids equilibrated between 170 °C and 185 °C.

Reed (1975) reported a range of inferred subsurface temperatures for hot springs throughout Surprise Valley using several classical geothermometry formulations without making any corrections for dilution, and estimated a maximum resource temperature of 200 °C to 205 °C based on dissolved sulfate oxygen isotope measurements of SVHS and Seyferth hot spring fluids. Mariner et al. (1993) showed that the dissolved sulfate oxygen isotope geothermometer indicates higher temperatures than cation geothermometers in a study of geothermal waters from the broader Modoc Plateau region, and included the Reed (1975) samples from SVHS and Seyferth hot spring in their study. Mariner et al. (1993) suggested that many dissolved constituents, particularly K, Mg, Li, SiO_2, and HCO_3, may have re-equilibrated at intermediate temperatures along the fluid outflow path, and suggested that cation geothermometers may not preserve evidence of maximum subsurface temperatures in many Modoc Plateau waters, including Surprise Valley.

Sladek et al. (2004) presented concentration and stable isotope data for hot spring fluids from several locations throughout Surprise Valley. They pointed out that conservative element variations in hot spring fluids are actually quite small, and suggested that differences in rock type along flow paths are responsible, rather than effects of dilution. Sladek et al. (2004) also suggested that springs on the eastern side of the valley had partially re-equilibrated at lower temperatures during outflow, and supported this hypothesis by calculating equilibration temperatures using an average of results for the quartz, chalcedony and Na-K-Ca geothermometers. They also argued that δD and $\delta^{18}O$ values of hot spring fluids lie on a line that reflects surface evaporation of springs, and speculated that δD and $\delta^{18}O$ values of spring waters are influenced by recharge from snow at high elevations, recharge from isotopically light Pleistocene

groundwater, interaction with different rock types along different flow paths, or dilution by groundwater.

Cantwell and Fowler (2014) and Fowler et al. (2015) used published major element data in combination with multicomponent geothermometry modeling techniques to evaluate various dilution and boiling scenarios proposed for Surprise Valley thermal waters. Their models of deep fluids sampled from the Phipps-2 well indicated equilibration temperatures of up to 228 °C, when steam loss and pH changes owing to boiling-induced CO_2 loss were accounted for. The models suggested that thermal springs on the eastern side of the valley could simply have re-equilibrated with a lower temperature mineral assemblage than fluids in the LCMV area, and were not necessarily diluted as suggested by Duffield and Fournier (1974). The models also indicated that only thermal waters from Fort Bidwell could be explained by dilution with low total dissolved solids meteoric water. Their work was unable to address the influence of rock type and evaporation on hot spring fluid compositions, owing to a lack of published fluid trace element and stable isotope data for springs on the eastern side of the valley.

In this contribution, we examine the relationship between thermal springs on the eastern and western side of Surprise Valley using a new and comprehensive geochemical dataset coupled with multicomponent geochemical modeling. We provide analytical and stable isotope data for fluids from the LCMV, Seyferth, Leonards, SVHS, and several small hot springs in the SVHS area. We also present fluid analytical results from a recent California Energy Commission (CEC) funded temperature gradient hole drilled on the eastern side of the valley (hereafter referred to as the CEC borehole). We utilize optimized multicomponent geothermometry (e.g. Peiffer et al., 2014; Spycher et al., 2014) and corrections for CO_2 loss to model fluid equilibration temperatures, and assess the feasibility of previously proposed models of dilution and low-temperature re-equilibration. We synthesize our results into a conceptual geochemical model of the Surprise Valley geothermal system. We show that dilution is unlikely because unrealistic concentration factors are required to reconstruct deep fluids to reflect equilibrium with a reasonable reservoir mineral assemblage. We suggest that hot spring fluids throughout the valley have re-equilibrated at lower temperatures after undergoing boiling on the west side of the valley at LCMV, and conductive cooling on the east side of the valley in SVHS area springs, Seyferth, and Leonards hot springs. We also identify the geothermal source fluid as a mixture between modern meteoric fluids and a brine with deuterium values lower than any known modern meteoric waters in the valley and bounding ranges. An important implication of this work is that classical geothermometers (i.e. quartz, chalcedony, Na/K, and Na/K/Ca) applied to surface hot

spring fluid samples do not reflect the maximum geothermal reservoir temperatures in Surprise Valley. Our results show how Surprise Valley thermal fluids can originate from a single source. While distinct compartmentalized geothermal fluid reservoirs cannot be ruled out, they are not required to describe observed compositional variability. Our revised conceptual model provides context to discuss potential triggering mechanisms of the LCMV mud volcano eruption, which presents an unquantifiable hazard without a better understanding of the Surprise Valley geothermal system plumbing.

2. Methods

2.1. Sampling and analysis

Hot spring samples were collected using all-plastic HDPE syringes (NormJect®), dedicated Tygon® tubing, HDPE luer stop-cock valves, and were stored in acid-cleaned HDPE bottles. Samples from the California Energy Commission (CEC) temperature gradient well (TG-2) were sampled from at a depth of 274 m in the auger barrel using the airlift method. Separate sample aliquots were used for field pH and conductivity measurements. Samples for cation and trace element analysis were filtered (0.45 μm) and acidified in the field using 1 mL HNO_3 (67–69% Optima™ grade, Fisher Scientific) per 120 mL. Samples for stable isotope, anion, pH and conductivity measurements were filtered in the field, but not acidified. Samples were stored on ice for transport and refrigerated pending analysis. Sampling locations and field measurements are provided on Table 1.

Table 1. Fluid sample locations and field parameters (see Fig. 1 for locations).

Sample ID	Sampling date	Site name	UTM grid	Easting	Northing	Elevation (m)	Temp. (°C)	Field pH	Field conductivity (mS/cm)	Notes
20150824-1	8/24/2015	SVHS Hot Well	10T	743766	4602055	1373	97	8.46	1.372	Boiling
20150824-2	8/24/2015	Spring E of SVHS (northern)	10T	744167	4602264	1377	91	8.29	1.432	
20150824-3	8/24/2015	Spring E of SVHS (southern)	10T	744200	4602174	1371	89	8.20	1.390	
20150824-4	8/24/2015	Spring SW of SVHS	10T	743386	4601797	1368	97	8.17	1.404	Boiling
20150824-5	8/24/2015	Cold water well at Desert Rose	10T	744634	4603365	1369	14	8.47	0.293	
20150824-	8/24/2015	Spring X	10T	744332	4599812	1354	55	9.33	1.520	57 °C in

Sample ID	Sampling date	Site name	UTM grid	Easting	Northing	Elevation (m)	Temp. (°C)	Field pH	Field conductivity (mS/cm)	Notes
6										mud
20150825-1	8/25/2015	Seyferth (chicken) Hot Spring	10T	741317	4611137	1395	83	7.81	1.690	
20150825-2	8/25/2015	Leonard's Hot Spring East	10T	742898	4609625	1381	62	7.85	1.647	
20150825-3	8/25/2015	Leonard's Hot Spring West (BLM)	10T	743354	4609507	1400	69	8.29	1.320	72 °C in mud
20150825-4	8/25/2015	LCMV	10T	732275	4616634	1362	99	7.47	1.721	Boiling
20160321-1	3/21/2016	SVHS Hot Well	10T	743765	4602052	1380	79	8.51	1.505	Could not reach direct discharge
20160321-2	3/21/2016	SVHS Reed Spring	10T	743896	4601867	1372	40	7.95	1.321	
20160321-3	3/21/2016	Spring SW of SVHS	10T	743381	4601796	1375	90	8.12	1.720	Cinnabar Present
20160321-4	3/21/2016	SVHS Flat Shack Spring	10T	742965	4601684	1372	83	8.17	1.573	
20160321-5	3/21/2016	Spring E of SVHS (small)	10T	744193	4602244	1374	76	8.15	1.637	Cinnabar Present
20160321-6	3/21/2016	Spring E of SVHS (northern)	10T	744168	4602263	1374	77	8.06	1.553	
20160321-7	3/21/2016	Spring E of SVHS (tiny)	10T	744170	4602199	1376	68	8.16	1.779	
20160321-8	3/21/2016	Spring E of SVHS (southern)	10T	744194	4602181	1377	82	8.03	1.751	Cinnabar Present
20160321-9	3/21/2016	SVHS Cold Well	10T	743765	4602052	1380	13	8.81	0.367	Sampled at Resort, not wellhead.
20160321-10	3/21/2016	SVHS Hot Wellhead Near Ponds	10T	743602	4602110	1383	81	8.05	1.714	
20161101-1	11/2016	CEC Exploratory Borehole	10T	744164	4602191	1372	~50	–	–	Airlift sample from

Sample ID	Sampling date	Site name	UTM grid	Easting	Northing	Elevation (m)	Temp. (°C)	Field pH	Field conductivity (mS/cm)	Notes
										274 m

SVHS = Surprise Valley Hot Springs.

BLM = Bureau of Land Management.

LCMV = Lake City Mud Volcano.

CEC Exploratory Borehole – Recent temperature gradient hole drilled adjacent to SVHS in October 2016. Coordinates and elevations were recorded by GPS (NAD83), and vary within the limitations of the device used.

Cation and trace element analyses were completed at the University of California (UC Davis) Interdisciplinary Center for Plasma Mass Spectrometry using inductively coupled plasma mass spectrometry (ICP-MS; Agilent 4500 quadrupole). Boron and anion (Cl, SO_4, NO_3, HCO_3, and CO_3) measurements; along with sodium, calcium, and magnesium for select samples; were completed by the UC Davis Analytical Laboratory (AnLab) using ICP atomic emission spectrometry (ICP-AES). Laboratory measurements of electrical conductivity and pH were also completed at AnLab. Fluid stable isotope (oxygen and hydrogen) analyses were completed at the UC Davis Stable Isotope Facility using laser spectroscopy (Los Gatos Instruments) (e.g. Kerstel et al., 1999). Fluid samples for rare earth element (REE) analysis were prepared using a modified (offline) version of the Zhu et al. (2010) pre-concentration method, which is described by Fowler and Zierenberg (2015). Analytical accuracy and detection limits for REE analyses were quantified through repeated analyses of the NASS-6 seawater standard. The detection limit is defined as 3 times the standard deviation of 6 replicate analysis of REE in the NASS-6 seawater standard.

Carbonate blocks ejected from the 1951 LCMV eruption were sampled for stable carbon isotope (δ^{13}C PDB) and oxygen isotope (δ^{18}O SMOW) analysis. Calcite samples were also collected from a fossil hot spring (FHS) travertinedeposit exposed in a nearby road cut. Calcite samples were observed to have different crystal habits or distinct generations of growth, as observed in hand sample, in thin section, and using cathodoluminescence (CL). Different calcite generations and morphologies were sampled using a microdrill. Powdered Carrera Marble standard, and powdered calcite samples were placed under vacuum and roasted at 375 °C to drive off atmospheric or organic material contamination, and a liquid nitrogen trap was used to capture and remove these contaminants. The powdered, roasted samples were then dissolved in

anhydrous phosphoric acid at 90 °C under vacuum. Non-condensable gasses and sulfur were removed by cryogenic vacuum distillation using liquid nitrogen and a pentane slurry at its freezing point in a two-step process. Sealed vacuum tube samples of purified CO_2 gas were then analyzed by mass spectrometerfor $\delta^{18}O$ and $\delta^{13}C$. Isotope values are reported with a 1σ precision of ±0.03 for $\delta^{13}C$ and ±0.06 for $\delta^{18}O$. Equilibrium calcite-water fractionation temperatures were calculated using the equation of Friedman and O'Neil (1977).

2.2. Geochemical modeling

Geochemical models were completed using GeoT version 2.1 (Spycher et al., 2014) and the associated tk-slt.h06_jun16.dat database (Reed and Palandri, 2006), coupled with the parameter optimization software iTOUGH2 (Finsterle and Zhang, 2011) using the PEST protocol (Doherty, 2008; Finsterle and Zhang, 2011). The software and methods are described in detail by Spycher et al. (2014). GeoT coupled with iTOUGH2 (Spycher et al., 2016) automates the identification of processes described by Reed and Spycher (1984) that influence the clustering of mineral saturation indices about a given equilibration temperature (e.g. dilution, degassing, mixing). This method (optimized multicomponent solute geothermometry) has previously been applied to studies of various geothermal waters (e.g. Battistel et al., 2014; Peiffer et al., 2014; King et al., 2016).

3. Results

Fluid major and trace element results are presented in Table 2 and Fig. 6A through D. REE results are presented in Table 3 and Fig. 7. Fluid δD and $\delta^{18}O$ values are presented in Table 4 and Fig. 10. $\delta^{13}C$ and $\delta^{18}O$ isotope measurements of calcite and equilibrium temperature calculations are presented in Table 5.

Table 2. Major and trace element analytical results for Surprise Valley hot spring fluids.

	Units	SVHS Well	Seyferth's HS	Leonard's HS (BLM)	LCMV	CEC Exploratory Drill Hole	Spring E of SVHS (northern)	Spring E of SVHS (southern)	Spring SV of SVHS
Sample ID		20150824-1	20150825-1	20150825-3	20150825-4	20161101-1	20150824-2	20150824-3	20150824-4
Temperature	°C	97	83	69	99	~50	91	89	97
Conductivity (field)	mS	1.372	1.690	1.320	1.721	–	1.432	1.390	1.404
Conductivity (Lab)	mS	–	–	–	–	–	1.390	1.380	1.380
pH (field)	pH	8.46	7.81	8.29	7.47	–	8.29	8.20	8.17

	Units	SVHS Well	Seyferth's HS	Leonard's HS (BLM)	LCMV	CEC Exploratory Drill Hole	Spring E of SVHS (northern)	Spring E of SVHS (southern)	Spring SV of SVHS
pH (lab)	pH	8.64	8.05	8.47	8.05	8.6	8.45	8.48	8.5
Major elements (ICP-MS)									
Si	mg/L	44.8	49.8	49.2	89.0	44.6	–	–	–
Na	mg/L	266	306	320	316	282	–	–	–
K	mg/L	5.2	8.9	8.3	16.2	5.4	–	–	–
Ca	mg/L	16.7	29.5	26.9	24.8	19.2	–	–	–
Mg	mg/L	0.03	0.20	0.54	0.36	0.12	–	–	–
Major elements (ICP-AES)									
Na (soluble)	mg/L	–	–	–	–	–	273.6	273.6	273.6
Ca (soluble)	mg/L	–	–	–	–	–	18.8	19.0	18.6
Mg (soluble)	mg/L	–	–	–	–	–	<	<	<
B (soluble)	mg/L	5.9	7.8	5.3	6.6	5.8	5.9	5.9	5.8
Anions (ICP-AES)									
Cl	mg/L	178	197	164	201	186	174	173	173
SO_4	mg/L	327	407	312	333	333	–	–	–
NO_3	mg/L	<	<	<	<	<	–	–	–
HCO_3	mg/L	36.6	67.1	42.7	164.7	48.8	–	–	–
CO_3	mg/L	9.0	<	3.0	<	9.0	–	–	–
Charge balance error	%	−0.8	−0.4	13.1	0.4	0.4	–	–	–
Trace elements (ICP-MS)									
Li	µg/L	85.1	140	127	251	90.8	–	–	–
Al	µg/L	51.7	3.9	<	12.4	163	–	–	–
P	µg/L	8.1	8.7	11.5	23.4	52.7	–	–	–
V	µg/L	0.39	0.49	0.22	0.26	0.89	–	–	–
Cr	µg/L	0.05	0.07	0.09	0.06	0.23	–	–	–
Mn	µg/L	0.6	7.9	94.9	69.1	110.4	–	–	–
Fe	µg/L	1.08	2.02	5.46	12.64	2682	–	–	–
Cu	µg/L	0.17	0.06	0.07	0.13	0.31	–	–	–
Zn	µg/L	1.10	0.16	14.44	0.24	82	–	–	–
As	µg/L	191	365	378	305	71	–	–	–

	Units	SVHS Well	Seyferth's HS	Leonard's HS (BLM)	LCMV	CEC Exploratory Drill Hole	Spring E of SVHS (northern)	Spring E of SVHS (southern)	Spring SV of SVHS
Se	µg/L	2.7	3.2	2.8	2.0	<	–	–	–
Rb	µg/L	18.8	35.4	26.9	78.7	21.0	–	–	–
Sr	µg/L	219	542	170	1162	155	–	–	–
Mo	µg/L	33.0	37.7	39.1	36.2	20.9	–	–	–
Cd	µg/L	0.05	0.05	0.05	0.03	0.02	–	–	–
Sb	µg/L	3.5	7.4	5.4	14.8	2.7	–	–	–
Cs	µg/L	9.4	20.2	14.6	61.4	11.8	–	–	–
Ba	µg/L	5.8	21.4	6.3	31.9	6.1	–	–	–
Pb	µg/L	<	<	0.102	<	2.3	–	–	–
U	µg/L	<	<	<	<	0.01	–	–	–

Na, Ca and Si exceeded the calibration range at 1× dilution, thus, values are reported for analyses made on samples that were diluted 40× and adjusted accordingly.

The limit of detection (LOD) is 3σB/a, where ‘σB’ is the standard deviation of the replicate analyses of the ratio of the analyte counts per second (CPS) to the internal standard (IS) CPS found in the calibration blank, and ‘a’ is the coefficient from the IS corrected calibration curve's regression equation: y = ax + blank.

% Recovery is the average ($n = 5$) percent recovery of a 100 ppb standard solution (1000 ppb for B, Na, Mn, Al, Si, P, K, and Ca).
–Not analyzed.

<Less than the specified LOD.

Table 3. Rare earth element results.

Units	SVHS Well	Seyferth HS	Seyferth HS	Seyferth HS	LCMV	LCMV	NASS-6 seawater	*LOD*
	20150824-1 (F)	**20150825-1 (F)**	**20150825-1 (F-DUP)**	**20150825-1 (U)**	**20150825-4 (F)**	**20150825-4 (F-DUP)**		
Y	<	<	<	<	7.9	7.8	18.3	2.4
La	2.1	2.5	2.3	2.0	7.3	7.0	10.4	1.4
Ce	3.5	3.9	3.8	3.4	13.6	13.2	4.0	0.6
Pr	0.27	0.30	0.29	0.28	1.26	1.22	1.3	0.2
Nd	<	<	<	<	3.9	4.0	5.7	0.8
Sm	0.36	<	<	<	0.84	0.84	1.0	0.2

Units	SVHS Well	Seyferth HS	Seyferth HS	Seyferth HS	LCMV	LCMV	NASS-6 seawater	*LOD*
	20150824-1 (F)	20150825-1 (F)	20150825-1 (F-DUP)	20150825-1 (U)	20150825-4 (F)	20150825-4 (F-DUP)		
Eu	<	<	<	<	<	<	0.21	0.04
Gd	<	<	<	<	1.2	1.1	1.3	0.3
Tb	<	<	<	<	0.16	0.16	0.2	0.02
Dy	<	<	<	<	0.9	0.9	1.4	0.2
Ho	<	<	<	<	0.2	0.2	0.4	0.1
Er	<	<	<	<	0.6	0.6	1.2	0.2
Tm	–	–	–	–	–	–	–	–
Yb	<	<	<	<	0.5	0.5	1.1	0.1
Lu	<	<	<	<	0.08	0.08	0.2	0.02
% Tm spike recovery	98	98	99	92	93	92	95–107	–

Values in parts per trillion (picogram/kg).

(F) Filtered.

(U) Unfiltered.

(DUP) Duplicate sample run independently through entire preconcentration method.

% Recovery based on a 5 ppb TM spike.

LOD limit of detection.

LOD = 3.143 (Student's *t*-test value)*SD of $n = 6$ independently processed NASS-6 aliquots.

Table 4. Stable isotope (δD and $\delta^{18}O$) results for Surprise Valley hot spring fluids. Stable isotope measurements of some of these features have been made by other workers previously (Reed, 1975; Ingraham and Taylor, 1986; Mariner et al., 1993; Sladek et al., 2004).

Sample ID	Site name	δD (VSMOW)	$\delta^{18}O$ (VSMOW)
Sample			
20150824-1	Surprise Valley Hot Springs Well (SVHS)	−119	−14.3
20150824-2	Spring S of SVHS (northern)	−118	−14.2
20150824-3	Spring S of SVHS (southern)	−117	−14.2
20150824-4	Spring NW of SVHS	−119	−14.4

Sample ID	Site name	δD (VSMOW)	$\delta^{18}O$ (VSMOW)
20150824-5	Cold water well at Dessert Rose	−115	−14.9
20150824-6	Spring X	−120	−14.6
20150825-1	Seyferth/Chicken Hot Spring	−120	−14.2
20150825-2	Leonards Hot Spring East	−119	−14.1
20150825-3	Leonards Hot Spring West (BLM)	−117	−14.2
20150825-4	Lake City Mud Volcano (LCMV)	−114	−13.5
20160321-1	SVHS Hot Well	−117	−14.2
20160321-2	SVHS Reed Spring	−116	−13.5
20160321-3	Spring SW of SVHS	−119	−14.3
20160321-4	SVHS Flat Shack Spring	−118	−14.2
20160321-5	Spring E of SVHS (Small)	−117	−14.0
20160321-6	Spring E of SVHS (Northern)	−118	−14.2
20160321-7	Spring E of SVHS (Tiny)	−118	−13.8
20160321-8	Spring E of SVHS (Southern)	−118	−14.2
20160321-9	SVHS Cold Well	−113	−14.7
20160321-10	SVHS Hot Wellhead Near Ponds	−118	−14.4
	Drill Hole	−116	−14.0
	Laboratory standard		
	Known value	−55.7	−8.04
	Mean (*n* = 11)	−55.3	−7.80
	1 SD	0.9	0.11

H_2O stable isotope analysis by laser spectroscopy (Los Gatos Research Instruments).

University of California-Davis Stable Isotope Facility.

Table 5. Stable isotope ($\delta^{13}C$ and $\delta^{18}O$) results for carbonate blocks ejected during the 1951 Lake City Mud Volcano Eruption, and carbonate from an adjacent fossil hot spring deposit.

Sample ID	$\delta^{18}O$ VSMOW	$\delta^{13}C$ PDB	[a]Temp. °C	
LCMV3-MC	0.99	−5.11	126	Multiple generations of bladed calcite
LCMV3-WR	1.33	−5.19	122	Carbonate mud on one side of bladed calcite sample
LCMV6-GB	3.04	−4.24	104	Bladed calcite away from Qz, Chl, Ad, and Py mineralization
LCMV6-BB	1.92	−4.38	115	Bladed calcite adjacent to minor Qz, Chl, Ad, and Py

Sample ID	$\delta^{18}O$ VSMOW	$\delta^{13}C$ PDB	[a]Temp. °C	
LCMV7	7.04	−3.40	71	Actively forming travertine from a small pool with abundant organic matter
LCMV8F-B	1.44	−4.97	121	Honeycomb network of rhombic and bladed calcite veins surrounding voids - fine vein
LCMV8F-V	0.82	−5.30	128	Honeycomb network of rhombic and bladed calcite veins surrounding voids - large vein
LCMV8F-H	0.83	−5.03	127	Honeycomb network of rhombic and bladed calcite veins surrounding voids - fine lamination
LCMV9-O	5.18	−4.74	85	Vein composed of interlocking dogtooth calcite
FHS-1	4.43	−3.27	91	Fossil hot spring deposit with multiple generations of dogtooth calcite
FHS-2F	1.33	−5.43	122	Fossil hot spring deposit with rhombic calcite, clays and biogenic material
FHS-3F-MC	5.25	−3.40	85	Rhombic calcite, siliceous microbialites on one side of sample
FHS-3F-B	12.78	−2.08	35	Rhombic calcite, siliceous microbialites on one side of sample
FHS-3F-B	12.88	−1.93	35	Rhombic calcite, siliceous microbialites on one side of sample

Qz = quartz; Chl = chlorite; Ad = adularia; Py = pyrite.

a Equilibrium temperature for calcite-water fractionation (O'Neil et al., 1969) using the $\delta^{18}O$ value measured for the LCMV hot spring water.

Fluid major element and stable isotope results are consistent with the results of previous studies (e.g. Duffield and Fournier, 1974; Reed, 1975; Clawson et al., 1986; Sladek et al., 2004). LCMV fluids have lower pH, but elevated bicarbonate, silica, and alkali and alkaline earth metals (Li, K, Rb, Cs, Sr, and Ba) and REE, in both absolute concentrations and when normalized to a conservative element (e.g. Cl) compared to thermal waters from the eastern side of Surprise Valley (Table 2, Table 3; Figs. 6A through D and 7). Of the REE, only the light rare earth elements La, Ce and Pr (and Sm in SVHS) were detected in fluid samples from the eastern side of the Valley (Seyferth and SVHS). In contrast, only Eu was below the detection limit in the LCMV fluid sample from the western side of the valley (Table 3). Duplicate reproducibility for the LCMV sample was better than 5.5% for all REE, and 10% for the lower concentration Seyferth sample, except for La (16%). REE in an unfiltered sample from Seyferth hot spring had marginally lower values than the filtered and primary and

duplicate samples. The lower REE values in the unfiltered Seyferth sample are considered insignificant, as the difference is comparable to that between the primary and duplicate filtered samples. Eu was not detected in any of the samples, therefore quantification of an Eu anomaly is not possible. Qualitatively, there must be a negative Eu anomaly based on the magnitude of the Eu detection limits compared to the concentration magnitude of REE adjacent to Eu in the periodic table (Sm in the SVHS and Sm and Gd in the LCMV sample).

Hot spring fluids are shifted to heavier $\delta^{18}O$ values than local meteoric water, and δD values span a range from local meteoric and groundwater (e.g. LCMV sample) up to 4.5‰ lighter (e.g. Seyferth HS) than the isotopically lightest groundwater (e.g. Desert Rose), and 3.1‰ lighter than the isotopically lightest snow measured by Ingraham and Taylor (1989) from Cedar Pass in the Warner Mountains (Fig. 10; Table 4). Oxygen isotope equilibrium temperatures calculated for calcite blocks ejected from the LCMV eruption with bladed crystal forms range from 104 °C to 128 °C (mean 120 °C), assuming equilibrium with modern LCMV spring fluids (Table 5). Calcite with the lowest calculated equilibrium temperature (71 °C) was observed to be actively forming from a small LCMV thermal pool, and did not have a bladed crystal form. Equilibrium temperatures calculated for the fossil hot spring adjacent to the LCMV were all lower than 100 °C, again, assuming equilibrium with modern LCMV spring fluid. With one exception, calcite from the fossil hot springs had a rhombic or dogtooth crystal form. Calcite/water oxygen isotope equilibrium temperatures are approximations, and assume calcite formed from fluids with similar oxygen isotope values as modern LCMV fluids. Only limited historical data is available to evaluate if the isotopic composition of LCMV spring fluids have shifted over time. Hot springs with periodic and mild mud eruptions were present at LCMV prior to the 1951 mud volcano eruption, however, the temperature, chemistry and flow is relatively unknown as the main pools were in an area overgrown by tule (White, 1955 and references therein). Following the 1951 LCMV eruption, geothermal features in the LCMV eruption crater include one boiling spring with weak geyser activity, at least two near-boiling springs, several small (<30 cm diameter) mudpots, and hot springs submerged by a small lake that fills part of the eruption crater (Sladek et al., 2004). Reed (1975) and Sladek et al. (2004) reported $\delta^{18}O$ values of −14.8 and −13.5‰ and δD values of −113 and −114‰, respectively, for boiling LCMV spring waters, in good agreement with values measured in this study.

4. Discussion

4.1. Classical geothermometry results

Classical geothermometers (Table 6) applied to sample results in Table 2 yield temperatures that span a wide range for each location, consistent with results from previous basin-wide studies (e.g. Duffield and Fournier, 1974; Reed, 1975; Sladek et al., 2004). Lack of agreement between classical geothermometry results listed on Table 6 preclude directly inferring maximum fluid equilibration temperatures, however, the relationships between results are useful for informing more detailed geochemical models. In the following discussion, we initially focus on geothermometry results for LCMV fluids. Previous studies suggested that high conservative element (Cl, B) concentrations in LCMV spring fluids reflect an undiluted primary deep geothermal fluid in equilibrium with quartz at depth, an assumption that has provided the basis for many conceptual models of the Surprise Valley geothermal system.

Table 6. Classical geothermometry calculations using results from Table 2 and equations from the cited studies.

	SVHS Well	Seyferth HS	Leonard HS (BLM)	LCMV	Drill hole	Phipps-2corrected for steam loss (Sladek et al., 2004)
Measured temperature	97	83	69	99	~50	170
Quartz conductive (Fournier and Potter, 1982)	135	141	140	177	135	208
Chalcedony conductive (Fournier, 1977)	108	115	114	155	108	190
Alpha Cristobalite (Fournier, 1977)	84	90	90	127	84	158
Amorphous Silica (Fournier, 1977)	15	20	20	53	15	82
Na/K (Fournier, 1977)	108	130	123	166	107	202
Na/K (Giggenbach, 1988)	129	150	143	184	128	218
Na-K-Ca (Fournier and Truesdell, 1973)	92	100	100	155	91	194
K/Mg (Giggenbach, 1988)	129	114	98	123	107	Mg below detection
Li/Mg (Kharaka and Mariner, 1989)	110	95	80	103	90	Mg below detection

Quartz geothermometry results (assuming conductive cooling) predict LCMV fluids equilibrated at 177 °C (Table 6), a similar value to those obtained in previous studies and similar to the maximum bottom hole temperature of 170 °C measured in the Phipps-

2 well (Rigby and Zebal, 1981), but much lower than the geothermometry results calculated for deep thermal fluids from the Phipps-2 geothermal well of 208 °C (Sladek et al., 2004; Table 6). The quartz geothermometer works best at temperatures above about 150 °C (Fournier, 1977). At lower temperatures, slow quartz precipitation kinetics leads to controls on dissolved silica concentrations by lower–order silica polymorphs (e.g. chalcedony, cristobalite, amorphous silica) or possibly by silicate mineralsother than quartz. For example, silica is an important component of reactions (2) and (3), shown below. Silica geothermometers underestimate equilibration temperatures upon mixing with dilute waters, because calculated temperatures directly depend on the absolute silica concentration.

Na/K geothermometer results for the LCMV sample are within 11 °C of the quartz geothermometer value for the LCMV sample (Table 6), and span the maximum measured temperature of 170 °C in Phipps-2. The Na/K geothermometers closely approximate, or are based on thermodynamic equilibrium between albite and potassium feldspar (Fournier, 1979; Giggenbach, 1988):

(1)albite+K+=K−feldspar+Na+

The kinetics of reaction (1) proceed slowly below about 180 °C. Thus, Na/K ratios are readily modified at lower temperatures during outflow by leaching of Na along flow paths and/or removal of K into secondary minerals, particularly if flow rates are low (Giggenbach, 1988). This results in elevated Na/K ratios and lower calculated Na/K temperatures, a process possibly responsible for lower LCMV Na/K geothermometry results compared to deep geothermal water from the Phipps-2 well (Table 6). Considering the maximum measured well and borehole temperatures of 160–170 °C, and very low flow rates for most LCMV hot springs as reported by Sladek et al. (2004), Na/K geothermometer results for Surprise Valley waters are not likely set by reaction (1), and close agreement with the classical quartz geothermometer is probably coincidental.

In contrast to the Na/K geothermometer, the kinetics of reactions that form the basis of the K/Mg geothermometer proceed rapidly, even below 100 °C (Giggenbach, 1988):

(2)0.8muscovite+0.2clinochlore+5.4silica+2Na+=2albite+0.8K−feldspar+1.6H2O+Mg2+

(3)0.8muscovite+0.2clinochlore+5.4silica+2K+=2.8K−feldspar+1.6H2O+Mg2+

Comparing temperatures obtained using the Giggenbach, 1988 Na/K and K/Mg geothermometers form the basis of the Na-K-Mg triangular ‘Giggenbach’ plot routinely used to evaluate the equilibrium state of geothermal waters. When temperatures calculated using Na/K and K/Mg geothermometers agree, waters are considered fully equilibrated (Giggenbach, 1988). The K/Mg geothermometer applied to the LCMV

sample yields a temperature of 123 °C, much lower than feldspar and quartz equilibrium would predict, suggesting possible fluid equilibration at lower temperatures. Mg is typically present at higher concentrations in dilute cold fluids than thermal fluids, so even small degrees of mixing can reduce calculated K/Mg temperatures. Likewise, dissolution of an Mg-rich evaporite mineral would lower K/Mg temperature estimates. On the other hand, if the K/Mg geothermometer accurately reflects the fluid equilibration temperature, then it is unlikely that silica concentrations are controlled by quartz solubility at these low temperatures. Controls on silica concentrations by minerals other than quartz at low temperatures are expressed in Eqs. (2), (3).

The empirical Na-K-Ca geothermometer was developed to accommodate shortcomings in the temperature limits of the Na/K geothermometer, and can provide a reliable indicator of last equilibration temperatures for fluids in the 4 to 340 °C temperature range (Fournier and Truesdell, 1973). The predicted Na-K-Ca equilibration temperature for LCMV (155 °C) is lower than that calculated for Phipps-2 (194 °C) (Table 6). Calcite precipitation and associated Ca-loss from fluids increases predicted Na-K-Ca temperatures, while mixing with dilute Ca-bearing waters tends to underestimate Na-K-Ca temperatures (c.f. Fournier and Truesdell, 1973). Calcite is known to precipitate in the subsurface of the LCMV area based on observations from drill cores (Benoit et al., 2005b), calcite blocks ejected from the 1951 LCMV eruption, and calcite observed to be actively forming (and sampled in this study) from one LCMV spring. Calcite precipitation would suggest that Na-K-Ca geothermometer results overestimate LCMV spring temperatures, however mixing with dilute Ca-bearing waters and modification of Na and K by equilibration at lower temperatures would counter this effect.

The Li-Mg geothermometer was developed to estimate subsurface temperatures in the 30 to 200 °C for sedimentary basin formation waters, where fluid salinities and hydraulic pressures are typically higher than for convective geothermal systems (Kharaka and Mariner, 1989). In this study, the calculated Li-Mg temperature is lower than, but comparable to, results for the low-temperature K/Mg geothermometer but inconsistent with Na/K, Na/K/Ca, or quartz geothermometry results. The empirical Li-Mg geothermometer was calibrated using sedimentary formation water samples, thus, results applied to Surprise Valley should be viewed with some skepticism. Li-based geothermometers are also sensitive to processes including steam loss and dilution, which can lead to erroneous results (Fouillac and Michard, 1981). An additional problem is that Li is typically present at much lower concentrations than ions used in other geothermometer formulations, thus, analytical results are susceptible to higher relative

analytical error and measurement accuracy can negatively influence geothermometry results.

In summary, disagreement between results for different classical geothermometer formulations are consistent with modification of Surprise Valley hot spring fluids relative to deep geothermal fluids. Possible mechanisms include mixing with dilute waters (dilution) or low temperature equilibration (re-equilibration); models proposed previously to describe the relationship of fluids on the east side of the valley to the LCMV area (i.e. Duffield and Fournier, 1974; Sladek et al., 2004). It is also possible that dissolution of Mg, K and Na-bearing evaporite minerals by hot spring fluids could influence cation geothermometer results, considering hot springs in Surprise Valley manifest in proximity to alkali lake waters that are predicted to form Mg, K and Na-bearing minerals upon evaporation (Fowler et al., 2017). Identifying the primary modification mechanism is essential for informing a conceptual model of the geothermal system, but is not possible using classical geothermometry techniques alone.

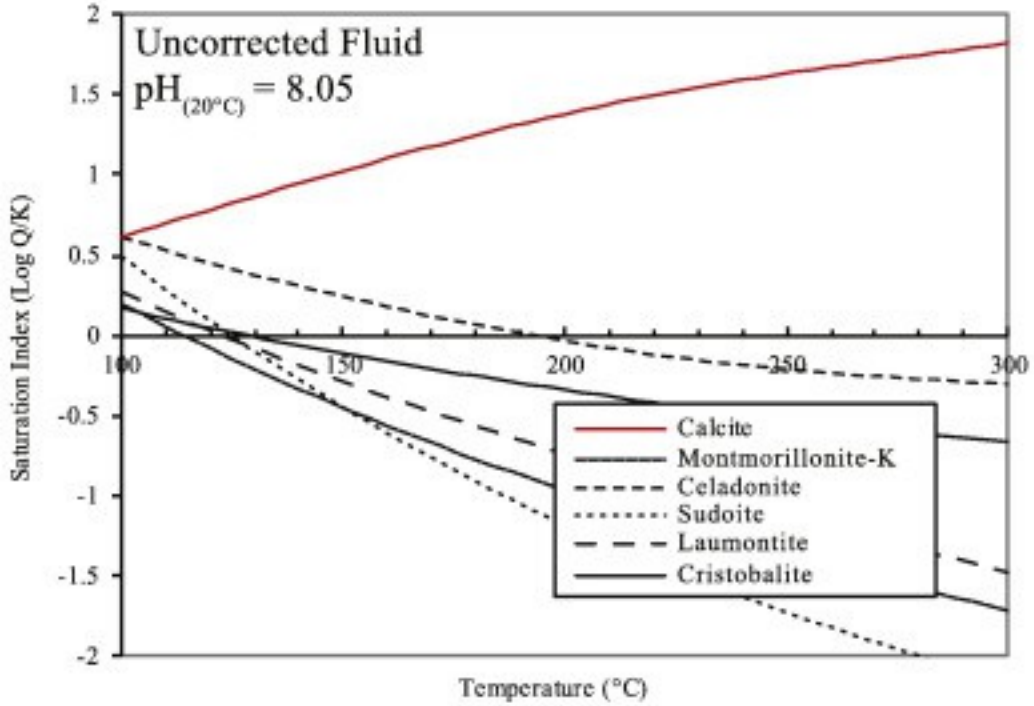
4.2. Multicomponent geothermometry modeling

We constructed multicomponent geothermometry models of measured spring fluid chemistries to test dilution and low temperature equilibration models. We completed models for samples analyzed from LCMV, SVHS, Seyferth, and Leonards hot springs. We did not model the sample from the CEC exploratory drillhole because the sample had no associated pH measurement and anomalously high Fe (as well as V, Cr, and Se), probably sourced from contamination by metal alloys in the drill bit, grease on the drilling equipment, or drilling fluids (Table 2). Based on this observation, we didn't have sufficient confidence in results for other dissolved components to complete rigorous geochemical modeling on the sample. We note that many dissolved components in the CEC drillhole fluid sample are nearly identical to those in the fluid sample from the adjacent SVHS well (Table 2), so fluids in these two locations likely have a similar history.

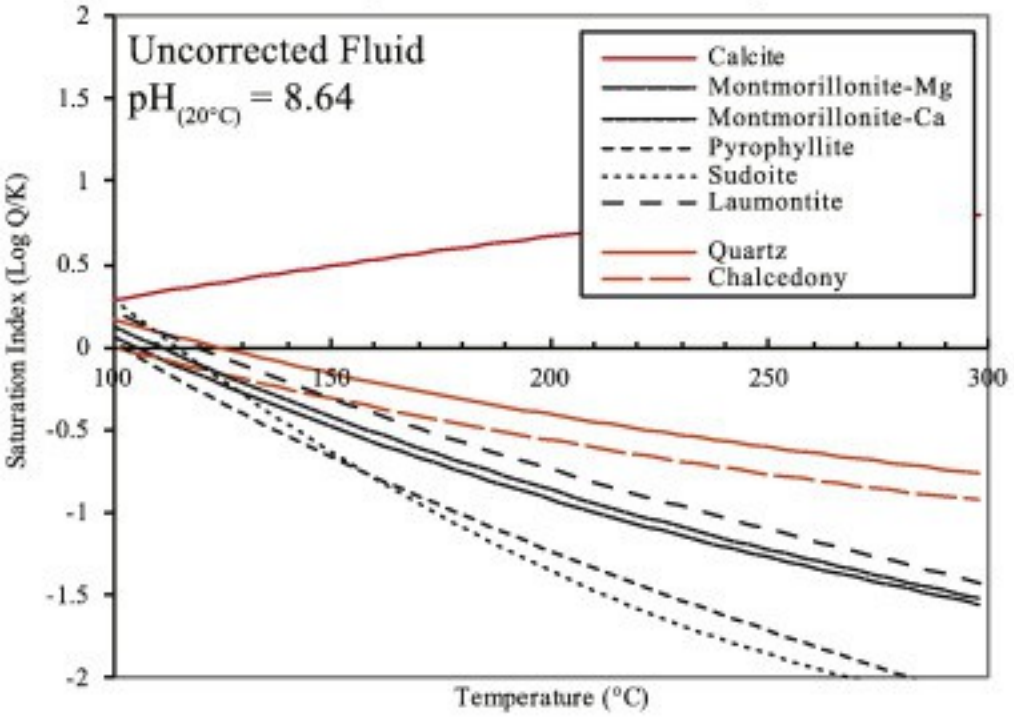
For our models, we utilized laboratory measurements of pH, Si, Na, K, Ca, Mg, Al, SO_4, Cl, and HCO_3. We modeled three scenarios for each sample. The first model was run in GeoT using only measured pH values and the chemical species listed above (uncorrected model; Fig. 2A through C). The second model explored mixing with infinitely dilute waters (dilution model; Fig. 3A through C), and the third model explored low temperature re-equilibration of spring fluids (re-equilibration model; Fig. 4A through D). In the dilution and reequilibration models, we accounted for the effect of CO_2-bearing vapor loss from boiling. This approach is supported by observations of bladed calcite in

LCMV calcite blocks and veins in OH-1 and LCSH-5 drill cores, a calcite morphology associated with CO_2 flux (Simmons and Christenson, 1994). Bladed calcite is usually associated with boiling, which would result in gas phase separation (Browne, 1978). Field observations of weak but active bubbling in several Surprise Valley hot springs was also observed during sampling. To account for CO_2 loss on boiling in the models, we assumed the vapor contained 99.9% H_2O and 0.1% CO_2, and used parameter estimation(PEST; Finsterle and Zhang, 2011) coupled with the steam water fraction (stwf) input option in GeoT to calculate the ideal fraction of this hypothetical vapor that would be compatible with assumed mineral assemblage. Al was below detection in the sample from Leonards spring, so we optimized both the stwf and Al concentration in this sample.

LCMV Multicomponent Geothermometry Calculations



SVHS Multicomponent Geothermometry Calculations



Seyferth Multicomponent Geothermometry Calculations

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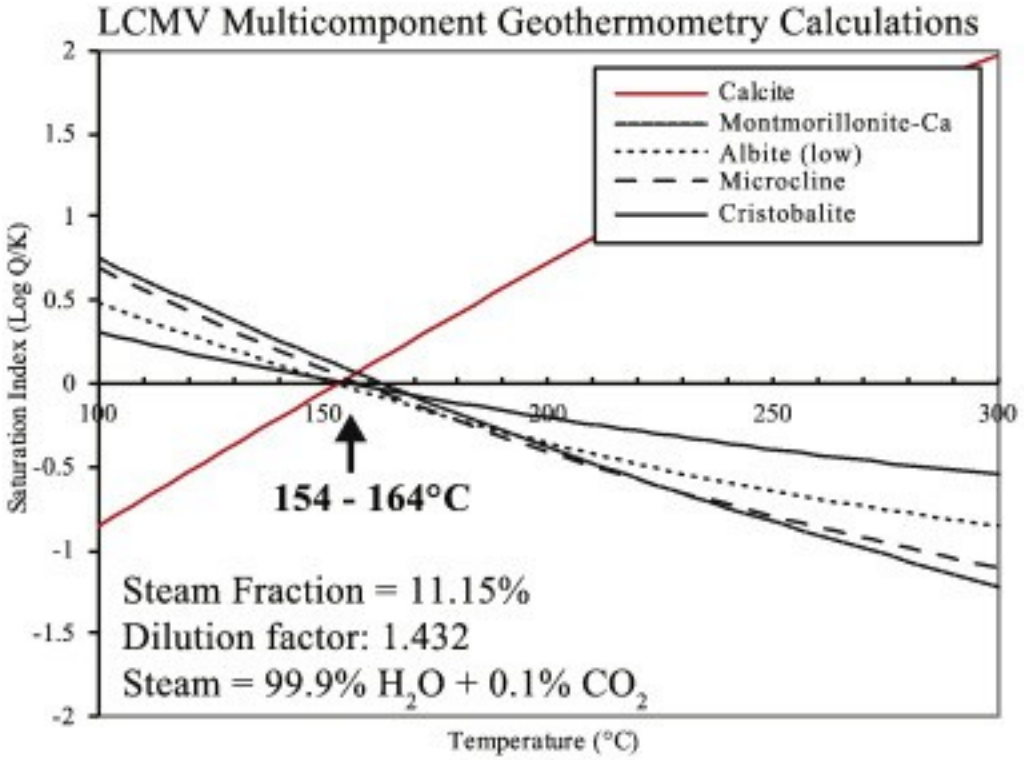
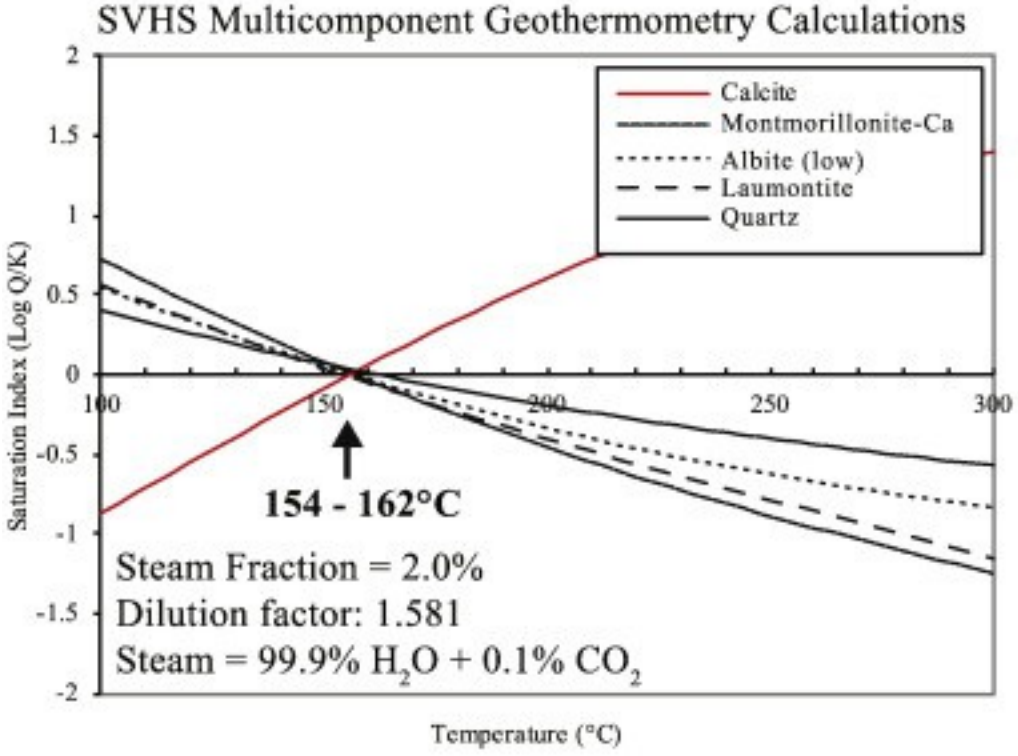
Fig. 2. A through C: Mineral saturation indices computed using GeoT with uncorrected (as-is) fluid analyses listed in Table 2.


LCMV Multicomponent Geothermometry Calculations
Calcite
Montmorillonite-Ca
Albite (low)
Microcline
Cristobalite
Saturation Index (Log Q/K)
Temperature (°C)
154 - 164°C
Steam Fraction = 11.15%
Dilution factor: 1.432
Steam = 99.9% H2O + 0.1% CO2


SVHS Multicomponent Geothermometry Calculations
Calcite
Montmorillonite-Ca
Albite (low)
Laumontite
Quartz
Saturation Index (Log Q/K)
Temperature (°C)
154 - 162°C
Steam Fraction = 2.0%
Dilution factor: 1.581
Steam = 99.9% H2O + 0.1% CO2

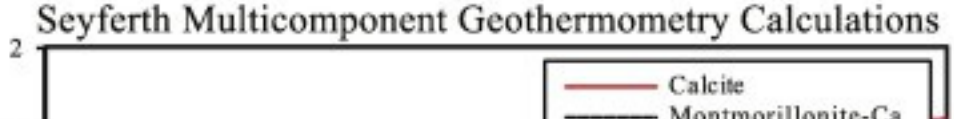

Seyferth Multicomponent Geothermometry Calculations
Calcite

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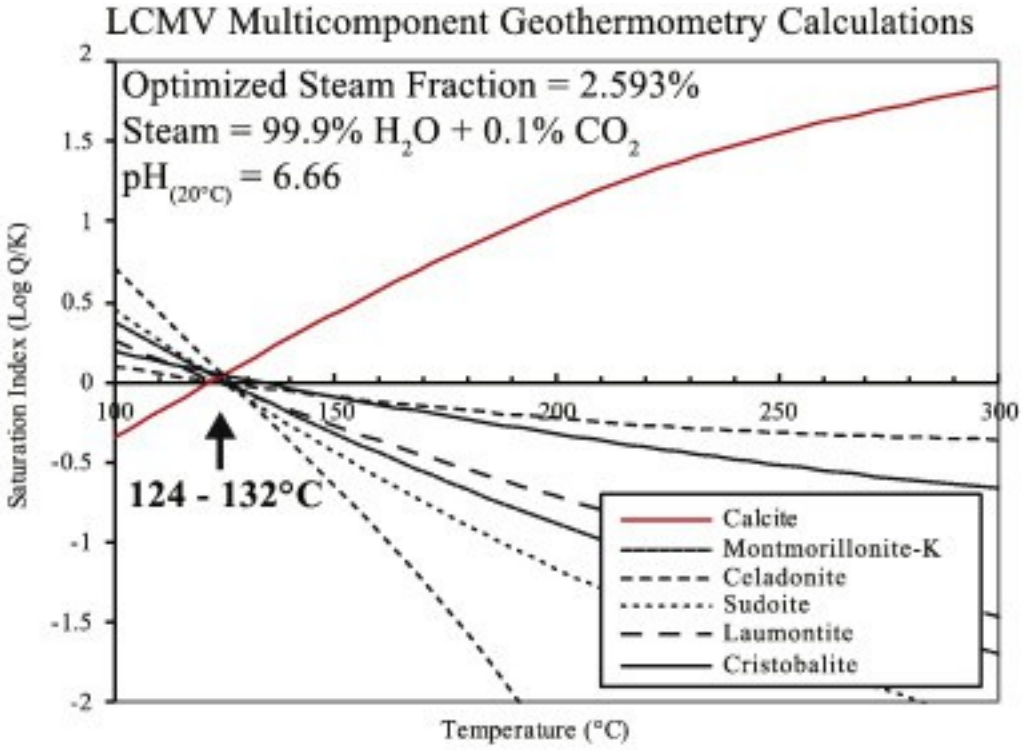
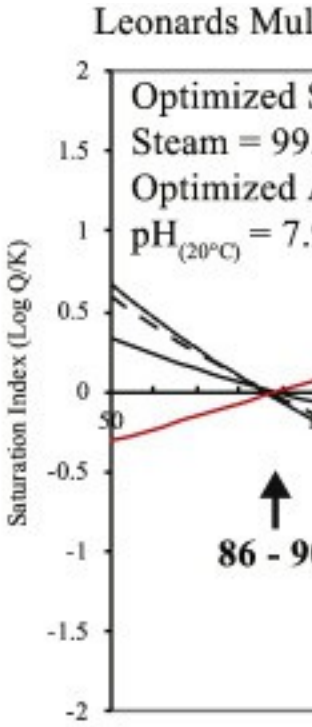
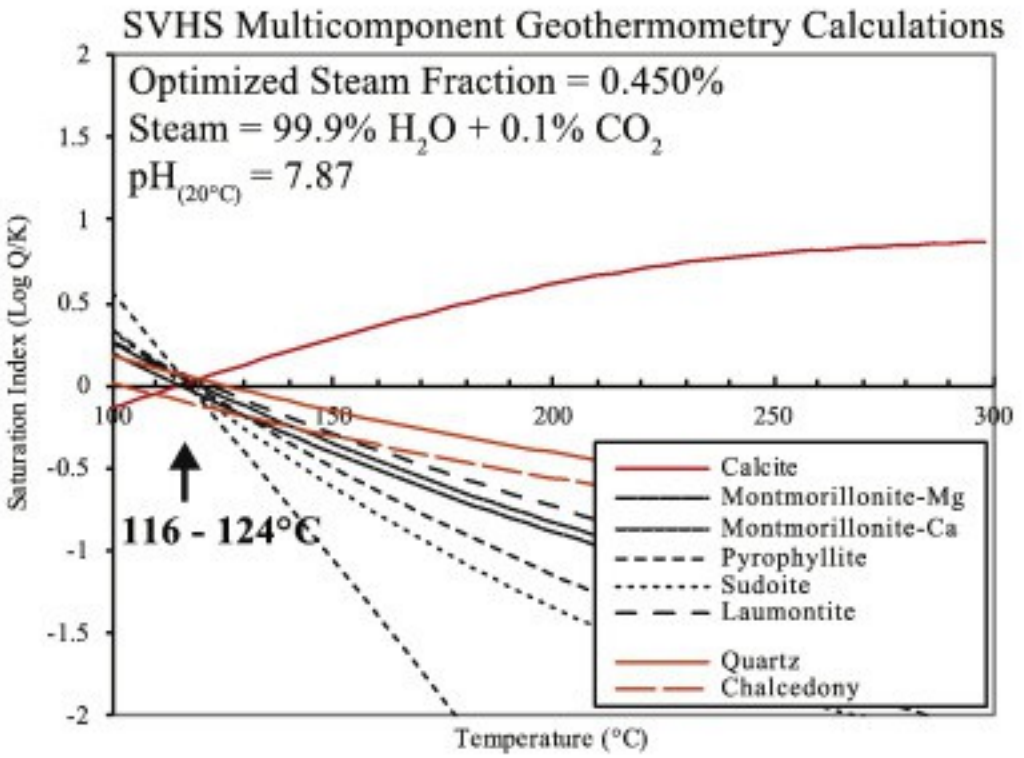
Fig. 3. A through C: Mineral saturation indices computed using GeoT with fluid analyses listed in Table 2 but corrected to account for dilution.







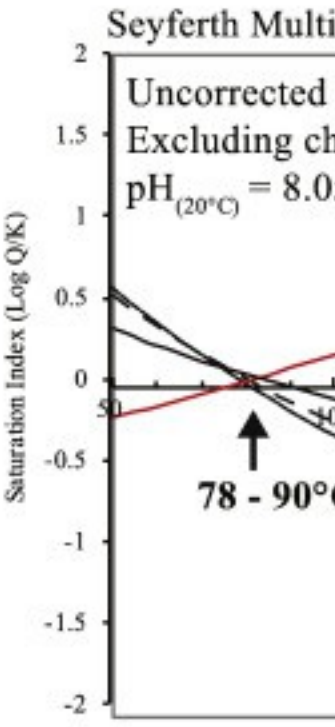


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Fig. 4. A through D: Mineral saturation indices computed using GeoT with fluid samples listed in Table 2 and low-temperature equilibration minerals. LCMV and SVHS mineral saturation indices corrected for CO_2 loss, Seyferth and Leonards spring results as-is.

We constrained mineralogy in the three model scenarios using secondary minerals identified in an extensive study of altered rocks drilled from holes OH-1 and LCSH-5 by Moore and Segall (2005). Holes OH-1 and LCSH-5 were drilled nearby to Phipps-2 in 2002, and both wells achieved maximum temperatures of approximately 160 °C during testing, comparable to the bottom hole temperature measured in Phipps-2 (Benoit et al., 2005b). Two main stages of secondary mineralization were identified in these rocks: 1) a clay (smectite and chlorite), quartz, zeolite, and calcite assemblage, and 2) a later stage of silica as quartz, chalcedony, or possibly amorphous silica deposition (Benoit et al., 2005b; Moore and Segall, 2005).

In the uncorrected models, calcite is supersaturated in surface spring waters, consistent with the observation of calcite actively precipitating from an LCMV spring (Table 5), but saturation indices do not cluster about a given temperature for other minerals in the models for LCMV and SVHS (Fig. 2A and B). The uncorrected model for Seyferth spring resulted in clustering of mineral saturation indices at the measured spring temperature, except for sudoite and celadonite.

Mineralogy in the dilution models were constrained using minerals identified near the base (934 to 4565 m) of holes OH-1 and LCSH-5, where calcite and quartz fluid inclusion temperatures range from 132 °C to 183 °C (Moore and Segall, 2005). Clay-sized minerals identified in this depth range include calcite, laumontite, silica (quartz, cristobalite and amorphous silica), trace smectite, and unidentified feldspar. The following minerals were selected from the GeoT database to represent the observed mineralogy in the dilution models: calcite, laumontite, cristobalite, quartz, beidellite-Na and montmorillonite-Ca (smectite group), albite and microcline (feldspar group). In addition, we found that anhydrite and pyrophyllite equilibration temperatures were compatible with the dilution models, however these secondary minerals have not been reported in Surprise Valley rocks to our knowledge, and are, thus, excluded from the models.

In the dilution models, CO_2-bearing steam loss of 0.3 to 12.4% coupled with concentration factors of ~1.5 are required for saturation indices of the selected mineral assemblage to cluster about a given temperature (Fig. 3A through C). The resulting equilibration temperatures range from 140 to 166 °C for LCMV, SVHS and Seyferth,

comparable to measured temperatures in geothermal wells and exploration boreholes. While the dilution model temperatures and dilution factors of about 1.5 are very similar for the LCMV and SVHS samples, the mineral assemblages and fractions of steam loss differ. Cristobalite is included in the LCMV sample while quartz is included in the SVHS assemblage, and the LCMV sample requires correction for a steam fraction of 11.2 %, while the SVHS sample requires only 2 %.

The re-equilibration models were constrained using the mineralogy of an active feed zone identified in well OH-1 at a depth of 288.6 m and a measured (sub-boiling) temperature of 133 °C. The temperature of this zone is close to the maximum calcite-fluid oxygen isotope fractionation temperature of 128 °C calculated for blocks ejected from the LCMV eruption (Table 4). The temperature similarity is perhaps coincidental, considering the calcite blocks may not have formed from modern subsurface temperature conditions and the only age constraint is pre-1951, the year the mud volcano erupted. Mineralization associated with the feed zone and core samples within 4 to 60 m of the feed zone include: Mg-rich chlorite, celadonite, and botryoidal silica initially deposited as a silica polymorph other than quartz, trace smectite, laumontite, and calcite (Moore and Segall, 2005). The following minerals were selected from the GeoT database for the re-equilibration model: calcite ($CaCO_3$), celadonite ($KMgAlSi_4O_{10}(OH)_2$), laumontite ($Ca(AlSi_2O_6)_2 \cdot 4H_2O$), cristobalite ($SiO_2$), montmorillonite-K (smectite group; $K_{0.33}AlMg_2Si_4O_{10}(OH)_2$), and sudoite (Mg-chlorite; $Mg_2Al_3(Si_3Al)O_{10}(OH)_8$). Thus, the re-equilibration model differed from the dilution model in that albite, microcline and quartz were excluded, minerals that are not stable at low temperatures. Several options for cristobalite are available in the GeoT database, including b-cristobalite and cristobalite. We chose not to use b-cristobalite, as data for this phase was originally sourced from experiments performed on a natural sinter from Yellowstone National Park that was not true cristobalite but more likely opal-cristobalite.

The GeoT-iTOUGH2 simulation for CO_2-bearing vapor loss results in clustering of the mineral saturation indices around 124–132 °C for the LCMV sample, if 2.6% loss of the modeled vapor is accounted for (Fig. 4A). We attempted this model using different values for the CO_2 ratio in steam, and this resulted in slight variations in the calculated steam fraction, but little difference in the calculated equilibrium temperature. Thus, pH changes associated with CO_2correction rather than the H_2O fraction (i.e. dilution) is the variable influencing mineral solubility and clustering of saturation indices. For SVHS, a minor steam fraction correction (0.1%) resulted in convergence of the mineral assemblage between 116 and 124 °C (Fig. 4B). Both quartz and chalcedony saturation indicies are in close agreement with, but span, the estimated equilibration temperature.

Quartz and chalcedony were not included in the optimization calculation because these silica polymorphs are usually kinetically controlled at low temperatures and therefore may not control silica concentrations at the model temperature. For Seyferth spring, the lack of sudoite and celadonite equilibrium at the measured spring temperature can be reconciled if the lower limit of formation for these minerals is assumed to be over 100 °C. If sudoite and celadonite are excluded from the model for this reason, the saturation indices for the remaining minerals cluster around 78–90 °C compared to the measured temperature of 83 °C (Fig. 4C). No CO_2 loss correction is required, suggesting spring waters are in equilibrium with the measured spring temperature. A similar result was obtained for Leonards spring (Fig. 4D).

In summary, the multicomponent geothermometry models yield plausible results for both dilution and low-temperature equilibration models. The multicomponent geothermometry models have the benefit over classical geothermometry methods in that they readily provide numerical values for a variety of conditions (e.g. steam loss, dilution factors, CO_2 loss) required to achieve equilibrium with a selected mineral assemblage. These results provide a basis to further evaluate the plausibility of each fluid evolution scenario. It is emphasized that the models are subject to the underlying assumption of equilibrium and limitations of the thermodynamic data used (see Spycher et al., 2014 for discussion).

4.3. Reconciling dilution and re-equilibration models: dissolved major and trace element data

Mineral saturation indices in the dilution models cluster about higher temperatures (122 to 166 °C; Fig. 3A–C) than in the re-equilibration models (78 to 132 °C; Fig. 4A–D). For mineral saturation indices to cluster about a given temperature, the dilution models require a greater steam loss fraction than in the re-equilibration models (up to 11.15% for LCMV), in addition to high concentration factors (around 1.5) to correct for dilution. Fig. 5A and Bgraphically show the results of correcting hot spring major and trace elementconcentrations for the steam loss and dilution factors in the computed GeoT re-equilibration and dilution models. The steam loss correction is very small in the GeoT re-equilibration models, thus, the results shown in Fig. 5A are almost indistinguishable from the measured concentrations shown in Fig. 6A. Absolute and relative concentrations of Na, B, Cl, and SO_4 are very similar in all hot springs and compared to the steam-loss corrected deep geothermal fluid from Phipps-2 in the re-equilibration models (Fig. 5A). For the dilution models, Na, B, Cl, and SO_4 concentrations in the LCMV, SVHS, and Seyferth samples are higher than in the

steam-loss corrected Phipps-2 sample after correction for dilution using the respective computed concentration factors of around 1.5 (Fig. 5B).

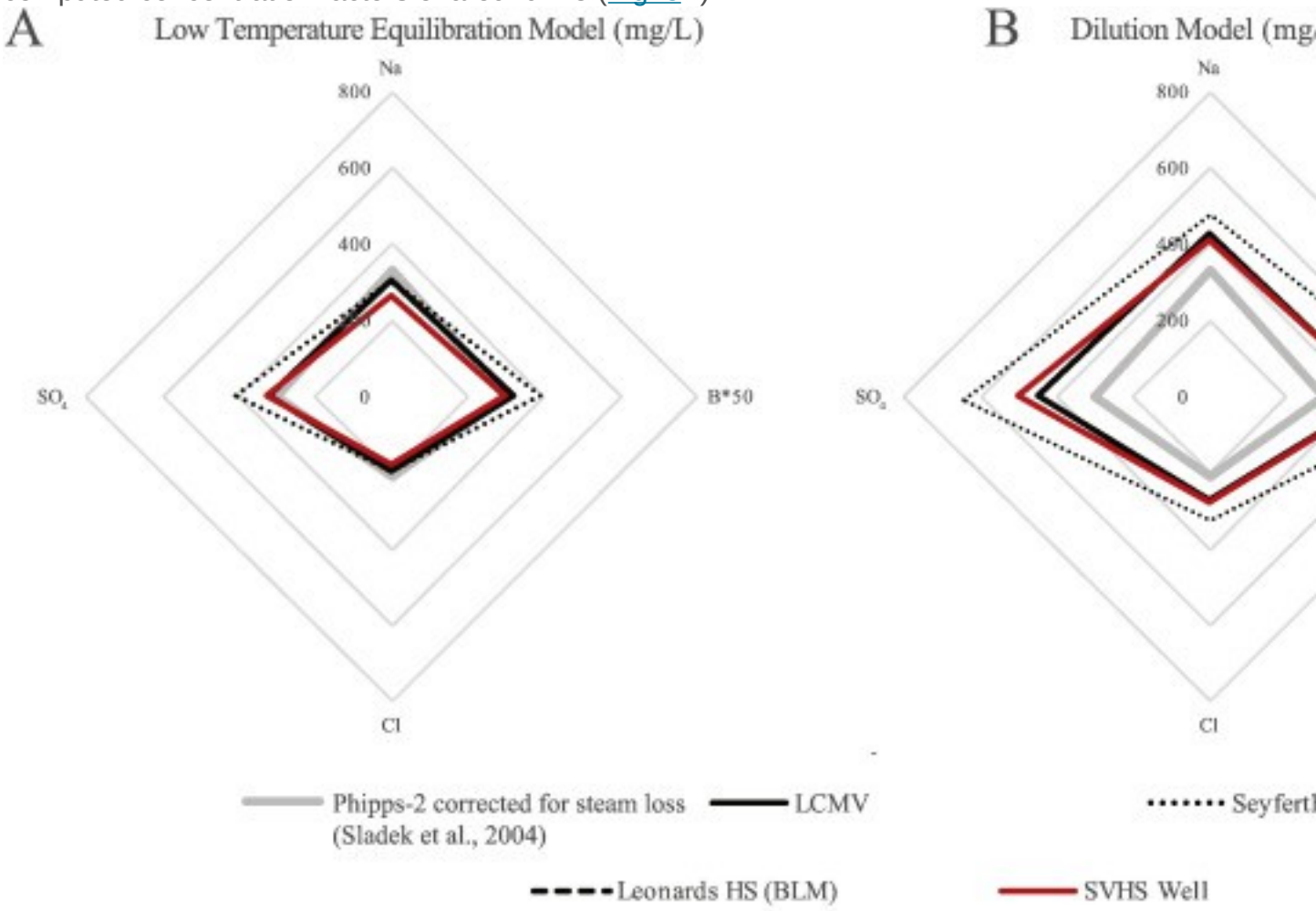

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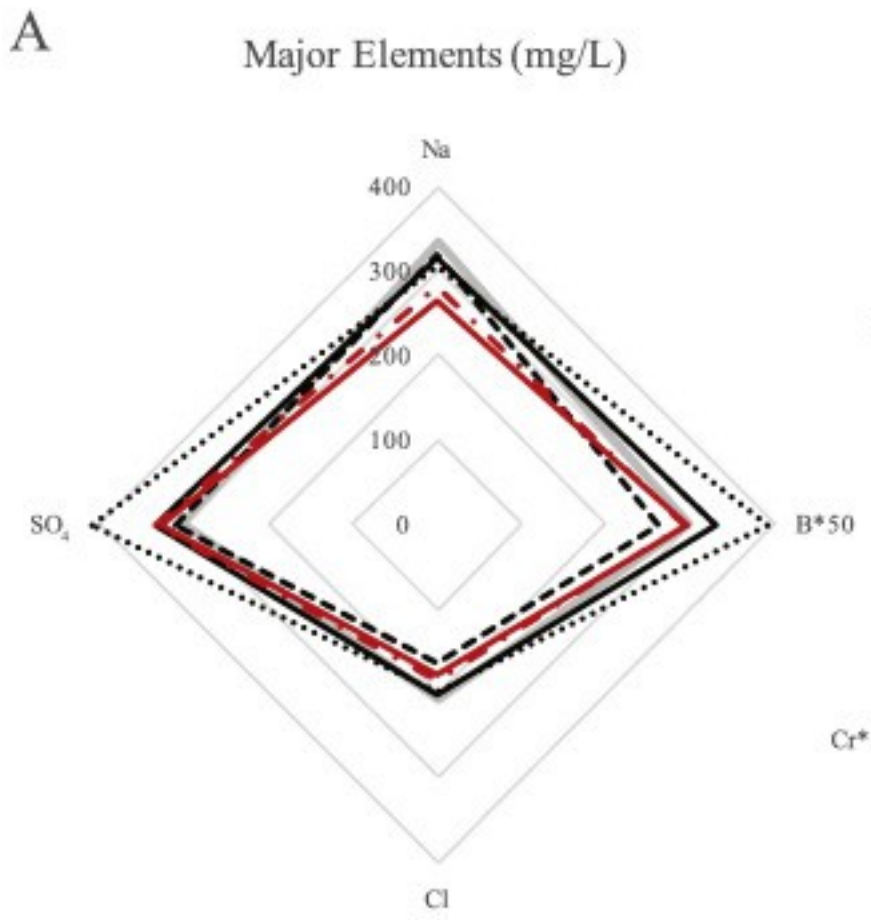
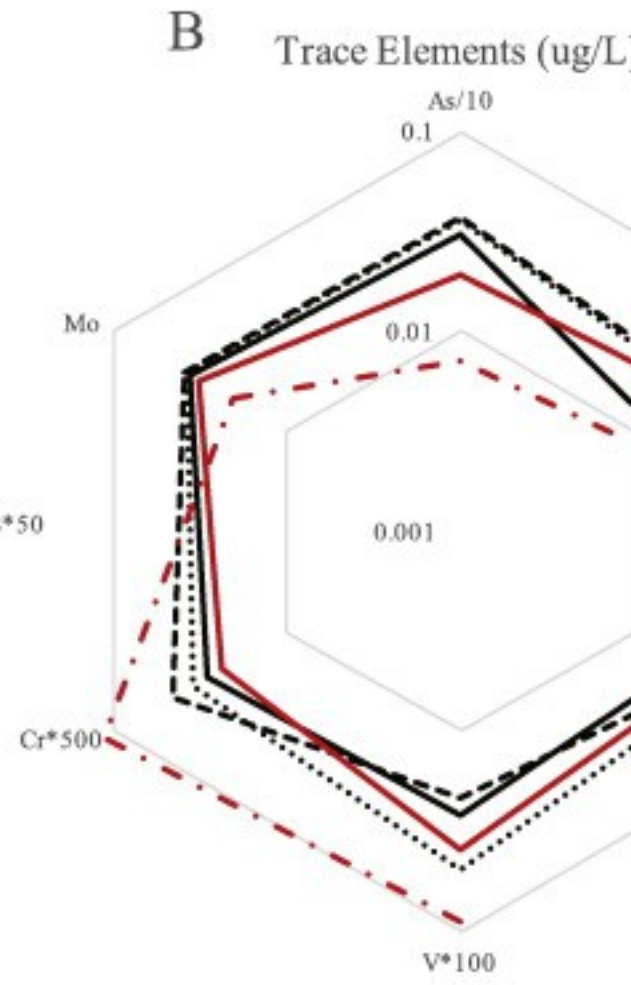
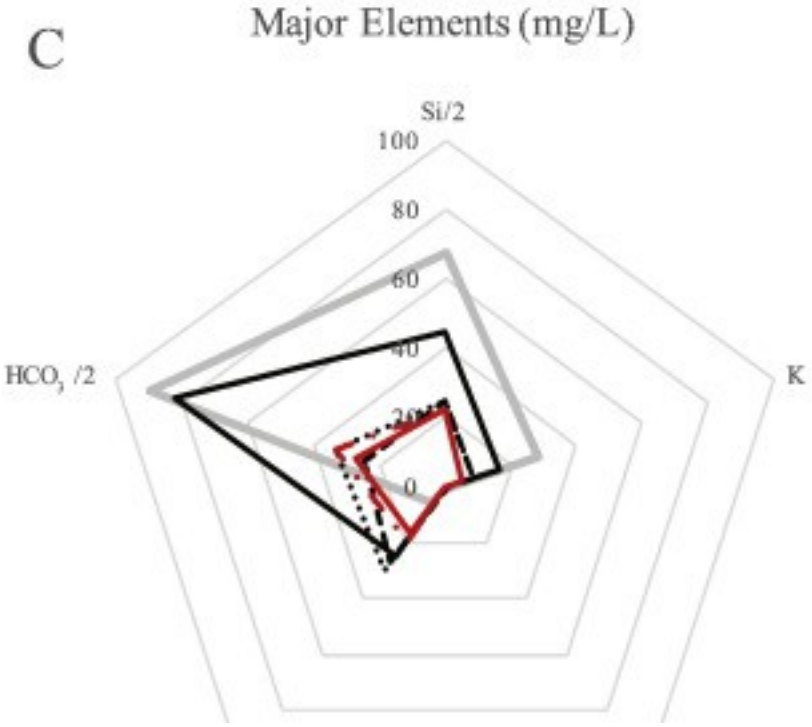
Fig. 5. Graphical relationships of conservative element concentrations in the steam loss-corrected sample from Phipps-2 (Sladek et al., 2004) compared to computed concentrations in Surprise Valley hot spring waters, assuming: A) re-equilibration and B) dilution.


A
Major Elements (mg/L)
Na
400
300
200
100
0
SO4
B*50
Cl


B
Trace Elements (ug/L)
As/10
0.1
0.01
0.001
Mo
Cr*500
V*100


C
Major Elements (mg/L)
Si/2
100
80
60
40
20
0
HCO3 /2
K

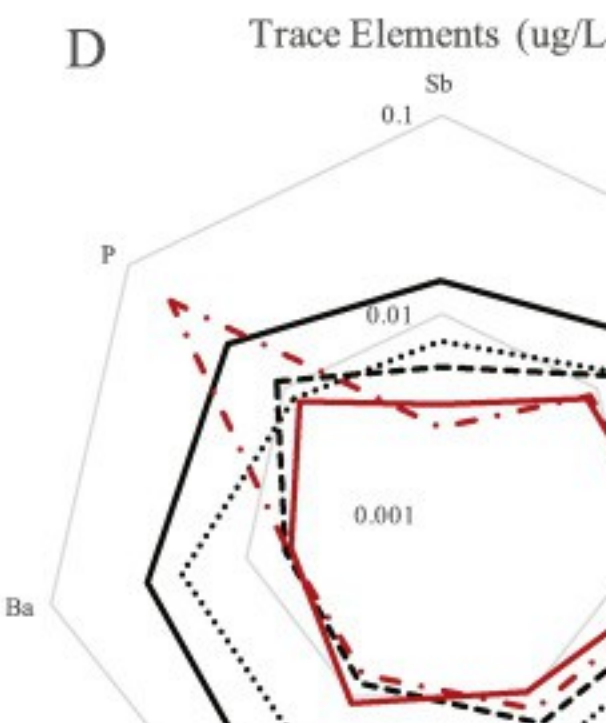

D
Trace Elements (ug/L)
Sb
0.1
0.01
0.001
P
Ba

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Fig. 6. A through D: Graphical relationships of major element concentrations in Surprise Valley hot spring waters compared to the steam loss-corrected sample from Phipps-2 (Sladek et al., 2004). Note that panels B and D are displayed on a logarithmic scale, and trace element data shown in panels B and D are unavailable for the Phipps-2 sample.

Fowler et al. (2015) modeled the Sladek et al. (2004) Phipps-2 well sample (reconstructed for steam loss) using GeoT, and showed that dilution was not required for the fluid to be in equilibrium with a reasonable mineral assemblage at 228 °C, when the reported steam loss fraction and CO_2 degassing were accounted for. Results of various classical geothermometers applied to the steam loss-corrected Phipps-2 sample suggest equilibration temperatures of 194 to 218 °C (Table 6), in accordance with dissolved sulfate oxygen isotope temperature estimates for hot springs on the eastern side of the valley, which range from 200 °C to 208 °C (Reed, 1975; Nehring et al., 1979). The higher temperatures predicted by these various methods suggest the Phipps-2 sample is the best available example of an undiluted endmember geothermal fluid in Surprise Valley. As such, corrections for processes including steam loss and dilution should yield element concentrations that approach those in the reconstructed Phipps-2 sample. The Na, B, Cl, and SO_4 concentrations in the LCMV, SVHS and Seyferth samples, after correction for computed concentration factors in the GeoT dilution models, significantly exceed steam-loss corrected values of the same components in the geothermal fluid from the Phipps-2 well (Fig. 5B). This result suggests that the high computed concentration factors required for hot spring samples to be in equilibrium with a mineral assemblage at elevated temperatures are unrealistic.

If dilution is discounted and the measured fluid compositions (uncorrected for dilution) are instead examined, the major dissolved components and trace element concentrations broadly fall into two groups. One group has absolute and relative concentrations comparable in all hot spring samples (Fig. 6A and B), while the other group has systematic variations in absolute concentration between different hot springs (Fig. 6C and D). The major dissolved components Na, B, Cl, and SO_4 have similar concentrations in all hot springs, aside from slightly elevated B and SO_4 in the Seyferth sample (Fig. 6A). The same is largely true of As, Cd, Se, V, Cr and Mo (Fig. 6B). The second group of dissolved components, which include Si, HCO_3^-, and K, consistently have the highest concentrations in Phipps-2, intermediate concentrations in the LCMV sample, and lower concentrations in samples from Seyferth, Leonards, SVHS and the

CEC borehole from the eastern side of the valley (Fig. 6C). Ca concentrations follow the inverse of this pattern. Trace element data are not available for the Phipps-2 sample, but alkali and alkaline earth elements (Li, Rb, Cs, Sr, and Ba), along with P, Sb, and Fe, also generally follow the same pattern of highest concentrations the LCMV spring to lowest in springs on the eastern side of the valley (Fig. 6D and Table 2). The CEC drillhole water sample proves an exception to this general grouping of elements, and has elevated Cr, V, Fe, P and lower Mo, As, Cd and Se relative to surface hot springs (Fig. 6B, D and Table 2). The elements with elevated concentrations in the CEC sample are potentially sourced from Fe-alloys in drilling equipment, drilling mud/grease, or host rocks/sediments that were disturbed during drilling.

Rare earth elements also fall into the second group of elements; LCMV fluids have higher absolute concentrations but similar chondrite normalized patterns to SVHS and Seyferth spring on the east side of the valley (Fig. 7; Table 3). Dilution factors ranging from 2.3 to 5 would be required to produce the measured REE in the SVHS and Seyferth samples from the LCMV sample. The magnitude of the REE-based dilution factors and required dilution relationship between different springs is inconsistent with the concentration factors computed in the GeoT dilution models (i.e. Fig. 3A through C). Rather than dilution, mineral precipitation and sorption of REE onto mineral surfacesmay control dissolved REE concentrations. REE are strongly partitioned into carbonate compared to geothermal fluids (see review by Debruyne et al., 2016), therefore carbonate precipitation provides one mechanism to remove REE from fluid. Fluid REE concentrations are also controlled by sorption onto clay mineral surfaces, Fe-oxides and carbonates (Coppin et al., 2002; Quinn et al., 2006), and this effect is increased as temperature decreases (Bau, 1991). Thus, partitioning of REE into secondary minerals formed during low temperature re-equilibration, or sorption onto mineral surfaces present along an eastward flow path, could explain lower REE concentrations in Seyferth and SVHS fluids on the eastern side of the valley compared to LCMV.

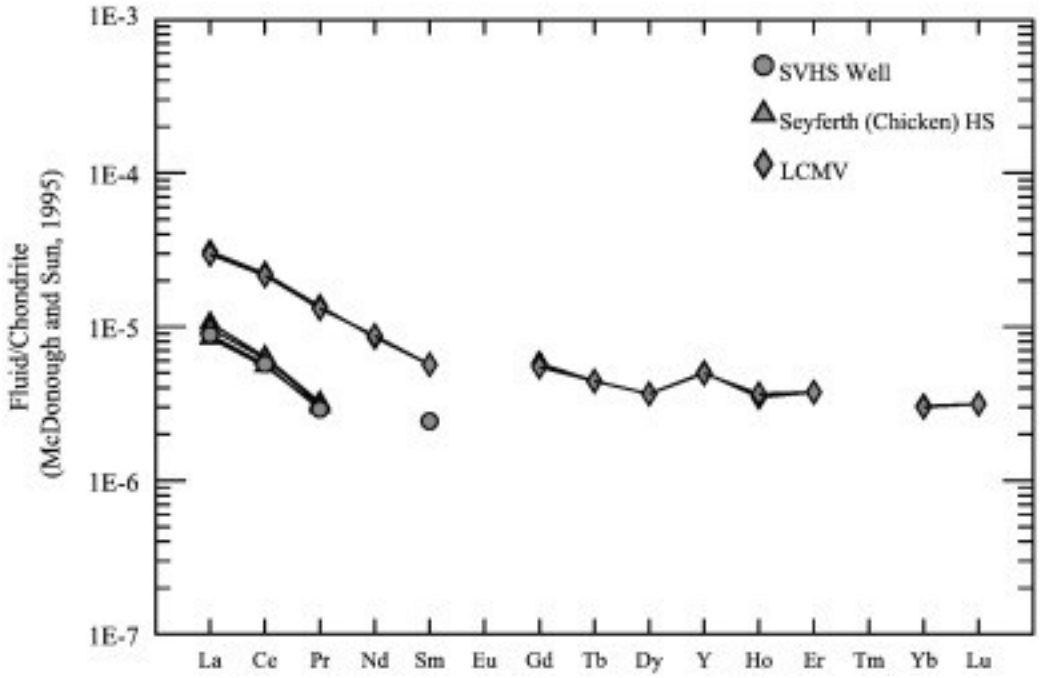

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Fig. 7. Chondrite normalized rare earth element concentrations of Surprise Valley hot spring fluids.

Modification of spring concentrations through dilution by relatively pure water is also inconsistent with the fluid major and trace element characteristics. The group of elements with generally similar concentrations includes elements that behave conservatively through mixing and dilution (e.g. Cl, B). Dilution at different concentration factors should result in different conservative element concentrations between hot springs. On the other hand, equilibration of fluids at progressively lower temperatures would maintain consistent conservative element ratios, but deplete fluids in more reactive elements. If hot spring fluids originated with a composition similar to the reconstructed Phipps-2 well sample, elements undersaturated with respect to minerals that would remove them from solution during re-equilibration at progressively lower temperatures would behave conservatively. Elements incorporated into secondary minerals that supersaturated at progressively lower temperatures would be removed from solution. As such, the observed groupings of major and trace elements support a model where hot spring fluids have re-equilibrated at progressively lower temperatures in Surprise Valley along an easterly-trending flow path.

Closer examination of concentration differences of specific elements in hot spring fluids compared to the reconstructed Phipps-2 sample also support progressive re-

equilibration of Surprise Valley thermal fluids along an eastward flow path. Si solubility in geothermal fluids is temperature dependent with higher Si concentrations at elevated temperatures, and the formation of silicateminerals leads to lower Si concentrations in fluids during cooling and outflow (White et al., 1956). With increasing pH and progressively lower temperatures in Na-Cl geothermal waters (conditions that characterize hot springs in Surprise Valley), Ba and Sr partition into carbonate, Ca-bearing zeolites or major Ca-bearing alteration mineral phases, and Li, Rb and Cs are incorporated into clay minerals and zeolites (Giggenbach and Goguel, 1989; Kaasalainen and Stefánsson, 2012; Kaasalainen et al., 2015). The sample from Seyferth spring generally follows this pattern, but is anomalous from other eastern hot springs in that Sr and Ba concentrations approach those from the LCMV hot spring (Fig. 6D).

Carbonate supersaturation and precipitation in the subsurface (i.e. re-equilibration of fluids by secondary mineral formation) is also supported by the observation of large calcite blocks that were ejected from the LCMV during the 1951 mud volcano eruption. Calcite has a bladed crystal form in many of the blocks (Table 4), which is a typical product when near-neutral to alkaline geothermal fluids boil and CO_2 gas exsolves (Browne, 1978; Simmons and Christenson, 1994). Assuming the LCMV calcite blocks formed from fluids with a similar $\delta^{18}O$ value to modern LCMV hot spring fluids, the maximum calculated boiling temperature in the subsurface when the calcite formed was 128 °C (Table 5). It cannot be confirmed, however, if the calcite formed at an earlier time from fluids with a different $\delta^{18}O$ value as the only age constraint is pre-1951. The calculated temperatures are, however, remarkably consistent with shallow subsurface temperatures measured in wells Parman 1 (140 °C) and Parman 2 (125 °C) that were drilled in the LCMV, and with the equilibration temperature of 132 °C computed in the GeoT re-equilibration model for LCMV (Fig. 4A). Evidence for persistent subsurface boiling and steam loss, as opposed to surface evaporation, comes from superheated conditions measured in one LCMV pond of 96.7 °C (Sladek et al., 2004) and 99 °C in August 2015 (this study), compared to the boiling point for pure water of 95.5 °C at the LCMV sample elevation of 1368 m. The superheated fluid temperature could result from the influx of steam that initially separated at a higher boiling temperature and pressure in the subsurface. The idea of subsurface boiling is further supported by the drilling history, where well Parman 3 was destroyed when drilling intercepted boiling fluids at a depth of 92 m.

4.4. Fluid stable isotope (δD and $\delta^{18}O$) and conservative element characteristics

Relationships between conservative elements in fluids that don't readily participate in temperature-dependent equilibrium reactions (e.g. Cl, B, F) provide a useful tool to identify geochemical processes that may influence hot spring compositions, and to further examine the dilution and re-equilibration models. Duffield and Fournier (1974) suggested that variable B and Cl concentrations in Surprise Valley hot spring fluids reflect variable dilution of geothermal fluids from a common source by low concentration meteoric waters. Rather than dilution, Sladek et al. (2004) suggested that Surprise Valley springs undergo evaporative concentration at the ground surface owing to low flow rates and the arid climate, particularly at LCMV, which has the lowest flowrates of springs in the area (e.g. Reed, 1975). This idea was supported using binary plots of B vs. Cl and F vs. Cl, and showing that δD and $\delta^{18}O$ values for hot springs throughout Surprise Valley fall on an evaporation line. Evaporative modification has also been invoked to explain hot spring fluid stable isotope systematics in the similarly arid and nearby Klamath Basin (Palmer et al., 2007).

Fluid δD and $\delta^{18}O$ measurements form an evaporation line for SVHS area samples and Leonards Spring West samples. The evaporation line is defined at the isotopically heaviest (most evaporated) end by the sample from the LCMV spring and isotopically lightest end (least evaporated) by several samples from the SVHS area, and samples from Leonards Spring West (BLM) (Fig. 8). However, δD and $\delta^{18}O$ values of the sample from Seyferth spring are inconsistent with evaporation of a parent geothermal fluid. The Seyferth spring δD value (δD = −120‰) is the same as the corrected deep Phipps-2 fluid (δD = −120‰), when δD and $\delta^{18}O$ values in the Sladek et al. (2004) Phipps-2 sample are corrected for continuous steam loss from 180 °C (deep temperature) to 100 °C (sampling temperature) using the equations of Truesdell et al. (1977). Similar δD values of Phipps-2 and Seyferth fluids suggest they have a similar source fluid. The Seyferth spring $\delta^{18}O$ value ($\delta^{18}O$ = −14.3‰) is somewhat heavier than the corrected deep Phipps-2 fluid ($\delta^{18}O$ = −14.8‰), suggesting more extensive water-rock reaction for the Seyferth sample possibly owing to a longer outflow path (Fig. 8). Mixing of the Seyferth fluid with modern meteoric water could produce the measured isotopic compositions of other springs on the eastern side of the valley. This mixing relationship is reinforced by locations from which multiple samples were taken at different time periods (SVHS, Leonards Spring West (BLM), and several of the SVHS area springs), which trace the proposed mixing line in terms of δD and $\delta^{18}O$. This relationship supports the idea that the mixing ratio between a deep fluid and meteoric water varies seasonally, possibly in relation to increased groundwater recharge during spring snowmelt runoff.

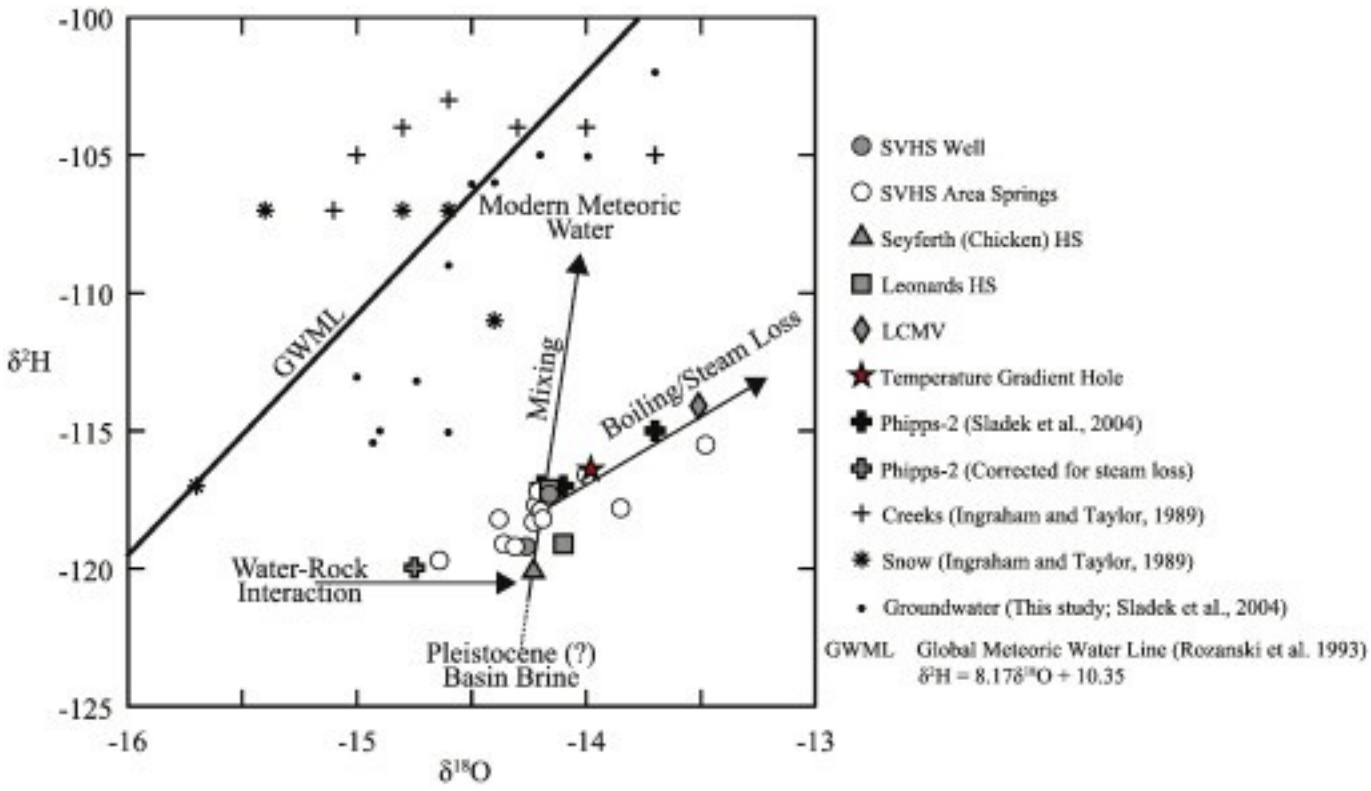

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Fig. 8. Stable isotope results for hot springs, thermal fluids and groundwater from Table 4of this study and Surprise Valley groundwater, creek, and snow samples from Sladek et al. (2004) and Ingraham and Taylor (1989). Many thermal fluids from the east side of the valley have lighter deuterium values than any meteoric source identified in Surprise Valley. Springs from the eastern side of the valley (SVHS, Leonards, and Seyferth) trace a mixing line between fluids with the lightest deuterium values and modern meteoric water. Phipps-2 waters sampled by Sladek et al. (2004) fall on an evaporation/boiling trend owing to boiling in different parts of the sampling apparatus during sampling of ~180 °C fluid. LCMV, CEC borehole, and a couple of springs in the SVHS area fall on an evaporation line. When oxygen and hydrogen isotope values for the Phipps-2 sample are corrected for continuous steam loss between 180 °C and 100 °C using the equations of (Truesdell et al., 1977), the resulting values are similar to those in the isotopically lightest samples collected in this study.
GWML from Rozanski et al. (1993).

This interpretation of isotopic data is also supported by B and Cl concentrations. A binary plot of B and Cl concentrations measured in this and previous studies shows two distinctive trends. B and Cl concentrations in Seyferth and Leonards Spring East are distinctively high, while SVHS, Leonards Spring West (BLM), and LCMV spring fluids fall

on a line with a 1:1 slope (Fig. 9). This linear trend formed by SVHS, Leonards Spring West, and LCMV suggests a relationship of evaporative concentration between these three fluids. By contrast, B and Cl concentrations in Seyferth and Leonards Spring East do not plot on this line, and instead form a cluster of higher B/Cl ratios. When considered along with the isotopic data, Seyferth fluids appear to have interacted with relatively less meteoric fluid. The interpretation that other fluids in the valley may be influenced by a mixture of Seyferth fluids and meteoric fluids is supported by the intersection of the B/Cl evaporation line with this Seyferth-meteoric fluid mixing line. The intersection of this evaporation line at an intermediary point on the primary mixing line suggests that fluids emerging in the west (Leonards, LCMV, and SVHS) may be influenced by a higher meteoric component than Seyferth and Leonards.

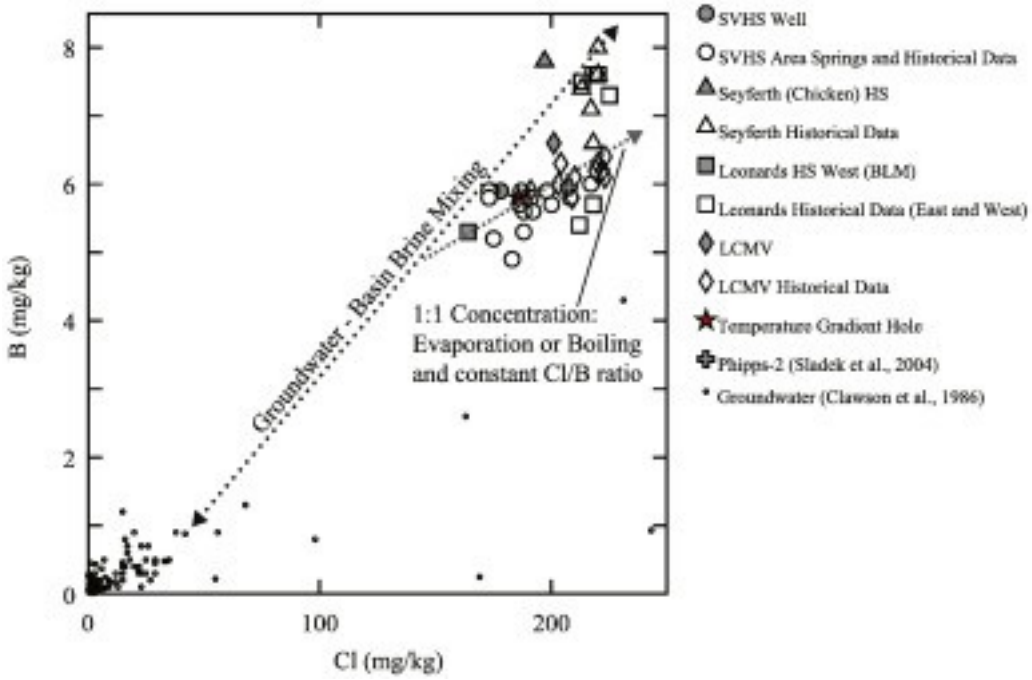

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Fig. 9. Data from this study (grey symbols) coupled with a compilation of historic hot spring fluid data (open symbols), including a deep subsurface sample (corrected for steam loss) from the Phipps-2 well.
Historical data from: (Duffield and Fournier, 1974; Reed, 1975; Bliss, 1983; Clawson et al., 1986; Sladek et al., 2004).

A model of deep brine dilution by meteoric water is not necessarily inconsistent with the low temperature re-equilibration model, or counter to the assertion that high dilution factors required for equilibrium with a high temperature mineral assemblage are unrealistic. A plot of δD and Cl (Fig. 10) traces a mixing line between modern meteoric

water and a brine with similar δD and Cl values to Seyferth spring, Spring X, and the reconstructed deep fluid from Phipps-2, which are proposed to approximate the δD and Cl of the parent geothermal fluid. The LCMV fluid cannot be related back to the parent geothermal fluid by direct dilution or evaporation, but could result from boiling of a mixture between the deep brine and modern meteoric water (Fig. 10). This relationship requires that mixing occurred prior to boiling rather than in the shallow subsurface at the end of the flow path and emergence of the hot spring. Therefore, mixing between a brine and modern meteoric water was not necessarily the final modification to hot spring fluids, but conceivably occurred in the deep subsurface prior to temperature-dependent equilibration with rocks and the formation of secondary minerals that initially set element concentrations.

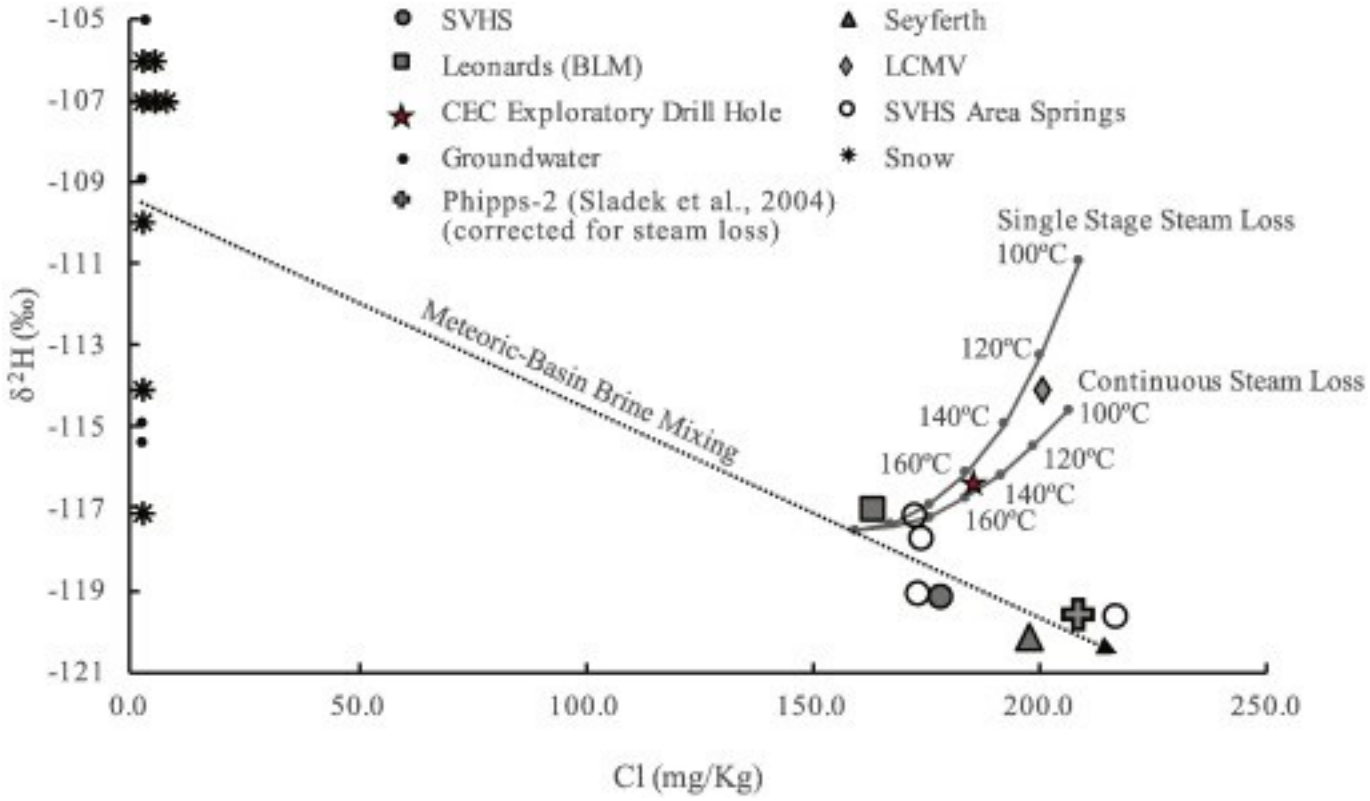

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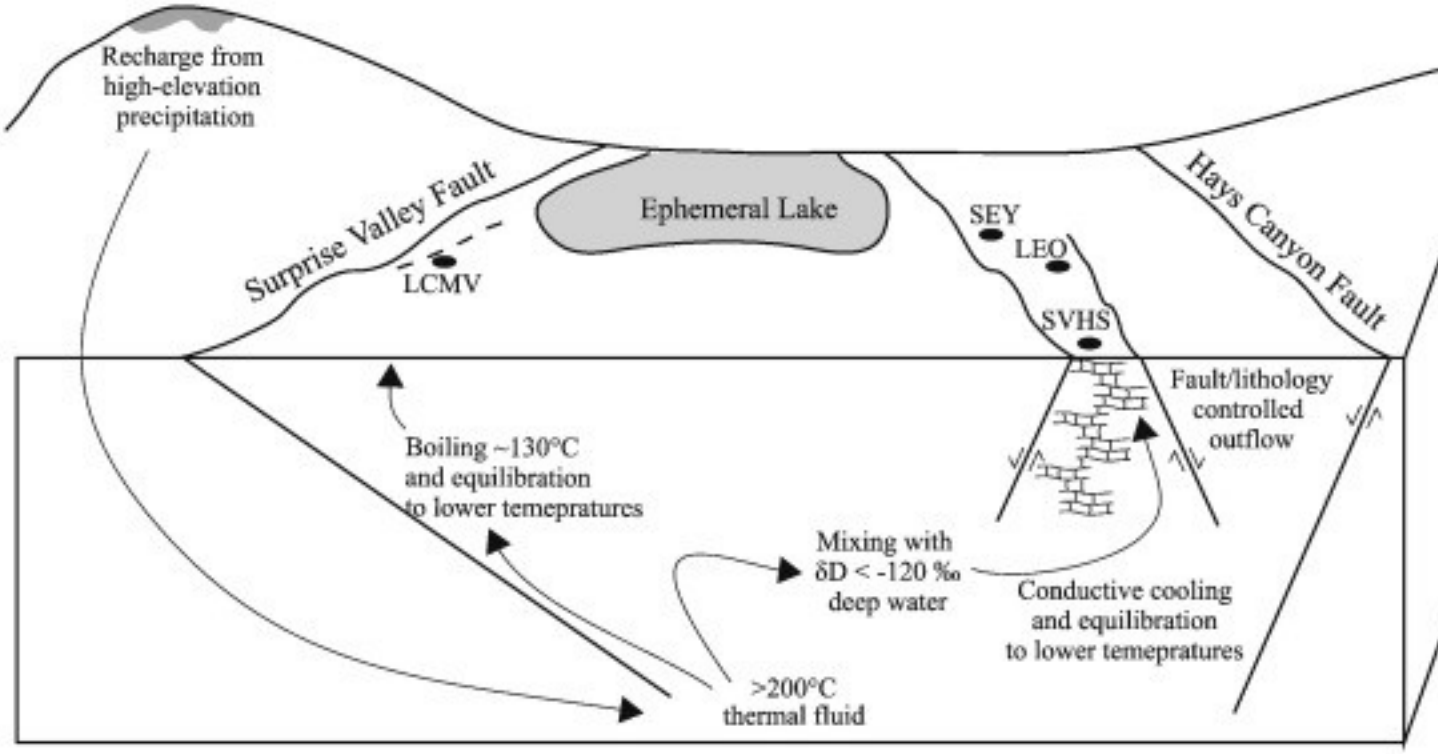
Fig. 10. The deuterium-chloride relationship for Surprise Valley thermal fluids and meteoric waters support a model where the thermal fluid source has deuterium values lighter than any meteoric or snow source identified in the valley. A mixture of this isotopically light fluid and modern meteoric water boils to produce fluids in the CECexploratory borehole and LCMV fluids. Curves are shown for evolution of a hypothetical fluid arbitrarily assigned values of δD = −117.5 and Cl = 160 ppm through

single stage steam loss and continuous steam loss from 220 °C to 100 °C, based on the equations of Truesdell et al. (1977). The deuterium value for the Phipps-2 sample is corrected for continuous steam loss from 180 °C to 100 °C using the equation of Truesdell et al. (1977), and Cl is corrected for 11% steam loss. The result shows the Phipps-2 sample falls near the isotopically lightest thermal fluids sampled in the valley. As noted earlier, some of the Surprise Valley thermal waters have δD values that are lower than any of the local non-thermal groundwater or recent precipitation sources. Similar discrepancies have been noted between geothermal fluids and non-thermal waters in other basins within the Basin and Range Province. This shift has been interpreted to indicate that the geothermal fluids represent recharge from Pleistocene waters. Such waters would be depleted in deuterium relative to modern-day precipitation due to cooler climatic conditions (e.g. Mariner et al., 1983; Flynn and Buchanan, 1990; Smith, 2002). In Surprise Valley, this deep water is ubiquitously associated with thermal features, and geologic structures that transmit thermal fluids to the ground surface. Indeed, this Pleistocene brine is probably synonymous with the thermal fluid signature in groundwater samples identified by (Fowler et al., 2017) using statistical methods.

4.5. Conceptual model of the Surprise Valley geothermal system

As noted earlier, deep thermal temperature estimates based on dissolved sulfate–water oxygen isotope exchange temperatures for Surprise Valley hot spring waters and multicomponent geothermometry applied to the Phipps-2 sample predict maximum reservoir temperatures in the 200 to 228 °C range (Reed, 1975; Nehring et al., 1979; Fowler et al., 2015). This is somewhat higher than the maximum temperature of 170 °C measured at the base of the Phipps-2 well (Fig. 11). It is not possible to extrapolate temperature gradient hole and Phipps-2 temperature profiles and estimate the depth to the hotter estimated temperatures, as the temperatures profiles have a near-vertical convective character at the base (Fig. 11). If a hotter reservoir is present vertically below the Phipps-2 and temperature gradient wells, it is possible that it is partially isolated from shallower convective fluids in the Phipps-2 by a low permeability unit. Alternatively, Phipps-2 and other temperature gradient holes may be laterally offset from a higher temperature zone with focused upflow closer to, or directly below, the LCMV. In this scenario, Phipps-2 and temperature gradient holes may sample the slightly cooled outflow from the main reservoir that has flowed laterally along the Surprise Valley Fault. The location and depth of the hottest fluids in Surprise Valley remain speculative.


Recharge from
high-elevation
precipitation
Surprise Valley Fault
LCMV
Ephemeral Lake
SEY
LEO
SVHS
Hays Canyon Fault
Fault/lithology
controlled
outflow
Boiling ~130°C
and equilibration
to lower temepratures
Mixing with
δD < -120 ‰
deep water
Conductive cooling
and equilibration
to lower temepratures
>200°C
thermal fluid

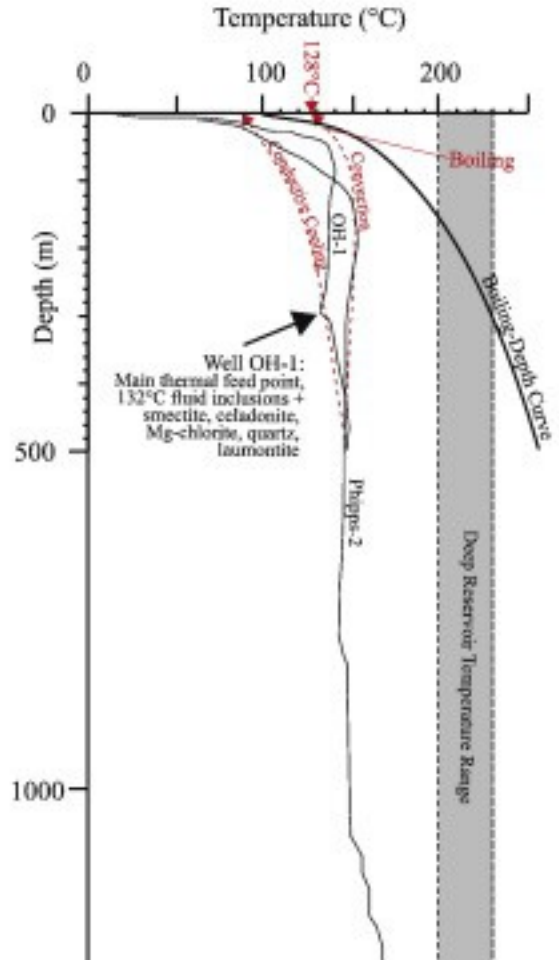

Temperature (°C)
0
100
200
128°C
0
500
1000
Depth (m)
Boiling
Conductive Cooling
Convective
OH-1
Boiling-Depth Curve
Well OH-1:
Main thermal feed point,
132°C fluid inclusions +
smectite, celadonite,
Mg-chlorite, quartz,
laumontite
Phggs-2
Deep Reservoir Temperature Range

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Fig. 11. Conceptual model for the Surprise Valley geothermal system. Angles, depths, and distances are for illustrative purposes only. Potential temperature profiles of fluids emerging at LCMV (Lake City Mud Volcano) on the western side of the valley and SVHS, SEY and LEO (Surprise Valley Hot Spring, Seyferth hot spring and Leonards hot spring) on the eastern side of the valley that are compatible with fluid geochemical and stable isotope measurements are shown in the lower diagram. Faults are simplified from (Egger et al., 2014). Fluid inclusion and mineral data from Moore and Segall (2005); Phipps-2 well and OH-1 temperature gradient hole static temperature curve from Benoit et al. (2005b).

Processes influencing fluid compositions on leaving the deeper reservoir are better constrained. The overall picture for Surprise Valley geothermal fluids based on spring water compositional and stable isotope data coupled with optimized multicomponent geochemical modeling is: 1) Variable (seasonal) mixing between modern meteoric water and an older, deep thermal brine sourced during a time meteoric fluids had lower deuterium values followed by equilibration with rocks at elevated temperatures; 2) at LCMV, boiling of the mixed fluid around 130 °C, precipitation of calcite, and exsolution of CO_2; and 3) along an eastward flow path, equilibration of the mixed fluids without boiling at progressively lower temperatures through conductive cooling, little or no exsolution of CO_2, loss of several elements probably to silicate, carbonate and clay mineral formation, and emergence as hot springs on the eastern side of Surprise Valley. This model is summarized in Fig. 11, which shows different boiling with depth relationships. This model implies that assumptions of equilibrium with quartz or feldspar may not apply to surface hot spring samples from Surprise Valley. The implication is that classical geothermometry estimates of the maximum temperature of the Surprise Valley geothermal resource applied to hot spring fluid samples are unreliable.

The idea of subsurface boiling at LCMV has implications for the driving force behind the 1951 LCMV eruption, and earlier eruptions that were hypothesized by White (1955). Over-pressurization of a subsurface boiling system likely triggered the LCMV eruption, a mechanism commonly responsible for hydrothermal eruptions elsewhere (e.g. Browne and Lawless, 2001). The cause for over-pressurization is speculative and requires focused study, but here we provide some intriguing possibilities. The receding Pleistocene Lake Surprise (Ibarra et al., 2014) may have reduced confining pressure and led to periodic eruptions. Increased demands on groundwater supplies for irrigation that reduced pressure from an overlying aquifer is another a potential cause of

the eruption. Explosive hydrothermal features can present hazards to human life (e.g. Escobar Bruno et al., 1992). Determining the triggering mechanism for the 1951 LCMV eruption is beyond the scope of this study, but a developing a conceptual model of the geothermal system provides a foundation for future investigations focused on possible climatic and anthropogenic influences on hydrothermal hazards.

5. Conclusions

A conceptual geochemical model of the Surprise Valley geothermal system is presented. The model is supported by multicomponent geothermometrymodels, as well as compositional and stable isotope measurements of hot spring fluids. Multicomponent geothermometry models are compatible with fluid re-equilibration after emergence from a hotter source by the formation of silicate minerals (clays, zeolites and cristobalite) and calcium carbonate during outflow at temperatures lower than about 132 °C. Model equilibration temperatures are supported by oxygen isotope exchange temperatures calculated from samples of LCMV spring waters and calcite blocks ejected from 1951 LCMV eruption. Fluid stable isotope (δD and $\delta^{18}O$) results suggest LCMV area fluids boiled and lost steam in the subsurface, while fluids on the eastern side of the valley did not boil, cooled conductively, and equilibrated at lower temperatures along an eastward flow path. These results are consistent with models of structural control on fluid flow proposed by Egger et al. (2014)and Fowler et al. (2017), whereby the principal geothermal upflow zone is related to the SVF on the western side of the valley near the LCMV, and outflow to the eastern side of the valley is controlled by a distinct fault that intersects the SVF at depth. δD values for hot spring fluids are at least 3 to 4‰ lighter than any modern meteoric water source in Surprise Valley, and require a Pleistocene groundwater component. This deep component is best represented by the sample from Seyferth hot spring, which would suggest the Pleistocene groundwater has elevated total dissolved solids, likely from prolonged water/rock interaction. The implication of the proposed conceptual model is that the maximum temperature of the Surprise Valley geothermal resource is poorly constrained by classical geothermometers applied to hot spring compositions. We suggest that results for the dissolved sulfate oxygen isotope geothermometer (Reed, 1975) and multicomponent geothermometry results applied to deep fluids corrected for steam loss (Fowler et al., 2015), which suggest maximum subsurface temperatures in the 200 °C to 228 °C range, provide more robust estimates for deep reservoir temperatures at Surprise Valley than classical geothermometry methods.

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