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Evolution of carbon and water through the subsurface of a semi-arid basin: A geochemical and geophysical approach

By

Jennifer L. Souza

A thesis

submitted in partial fulfillment

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To the Graduate Faculty:

The members of the committee appointed to examine the thesis of Jennifer L. Souza find it satisfactory and recommend that it be accepted.

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Dedication and Acknowledgements

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List of Abbreviations

‰	Per mille
¹⁴ C	Radiocarbon
$^{234}U/^{238}U$	Isotopic ratio of uranium isotopes
³ H	Tritium
⁸⁷ Sr/ ⁸⁶ Sr	Isotopic ratio of strontium isotopes
ARS	Agricultural Research Service
BDL	Below detection limit
BP	Years before present
Ca ²⁺	Calcium
CAMAS	Center for Archaeological, Materials, and Applied Spectroscopy
CBE	Charge balance error
CFCs	Chlorofluorocarbons
Cl	Chloride
CO_2	Carbon dioxide
CO ₃ -	Carbonate
CZO	Critical Zone Observatory
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
F	Fluoride
GMWL	Global meteoric water line
HCO ₃ -	Bicarbonate
HDPE	High-density polyethylene

ICP MS	Inductively Coupled Plasma Mass Spectrometer
ISU	Idaho State University
JD	Johnston Draw
K^+	Potassium
LMWL	Local meteoric water line
LSB	Lohse Soil and Biogeochemistry Laboratory
Mg^{2+}	Magnesium
Na ⁺	Sodium
NO ₃ -	Nitrate
PCA	Principal component analysis
pCO ₂	Partial pressure of carbon dioxide
pmc	Percent modern carbon
RCEW	Reynolds Creek Experimental Watershed
REE	Rare earth elements
RME	Reynolds Mountain East
SI	Saturation indices
SIF	Stable Isotope Facility
SO ₄ ²⁻	Sulfate
TU	Tritium units
V-PDB	Vienna PeeDee Belemnite
VSMOW	Vienna Mean Standard Ocean Water
δ ¹³ C	Isotopic ratio of stable carbon isotopes
$\delta^{18}O$	Isotopic ratio of stable oxygen isotopes

 $\delta^2 H$ Isotopic ratio of stable hydrogen isotopes

List of Equations

Eq 2.1
$$\delta^{18}O_{sample} = \left(\frac{({}^{18}O/{}^{16}O)_{sample}}{({}^{18}O/{}^{16}O)_{reference}} - 1\right) \times 1000 \% VSMOW$$

Eq 2.2
$$\delta^{18}O_{\text{groundwater}} - \delta^{18}O_{\text{precipitation}} = \varepsilon^{18}O_{\text{total}} * \ln f$$

Eq 2.3
$$CO_{2(g)} + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^{-}$$

Eq 2.4
$$CO_2 + H_2O \rightarrow O_2 + CH_2O$$

Eq 2.5
$$CO_{2(g)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$

Eq 2.6 Pore Volume
$$(m^3) = \pi * (Radius(m))^2 * (Height of Water (m))$$

Eq 2.8
$$CBE = (cations - anions) / (cations + anions) * 100$$

Eq 3.1
$$\delta^{13}C_{sample} = \left(\frac{({}^{13}C/{}^{12}C)_{sample}}{({}^{13}C/{}^{12}C)_{reference}} - 1\right) \times 1000 \% V-PDB$$

Eq 3.2 Pore Volume
$$(m^3) = \pi * (Radius(m))^2 * (Height of Water (m))$$

Eq 3.3
$$t = 17.77*\ln({^{3}H}/{^{3}H_{0}})$$

Eq 3.4
$$t = -8267 * ln \frac{{}^{14}C_{DIC}}{{}^{14}C_0}$$

Evolution of carbon and water through the subsurface of a semi-arid basin: A geochemical and geophysical approach

Thesis Abstract – Idaho State University (2022)

Groundwater is a significant reservoir for freshwater and carbon, especially in semi-arid regions. With the changing climate, interpreting recharge characteristics, geochemical evolution, architecture of subsurface flow, and residence times is essential to assess the vulnerability of aquifers. In this study, we collected groundwater samples along a longitudinal and elevational transect as well as potential source signatures from springs, an irrigation pond, and precipitation. All samples were analyzed for a range of geochemical and age tracers. We found that springs emerged from shallow, undersaturated aquifers undergoing calcite dissolution in open-system conditions. Shallow aquifers, including springs, were recharged by modern waters indicating vulnerability to anthropogenic influence and the changing climate. Deeper aquifers developed in basaltic environments, reaching calcite saturation under closed-system conditions, and were recharged by paleowaters. Due to longer residence times, deeper aquifers become carbon sinks and therefore, unsustainable for use. In summation, the movement of water and carbon through the subsurface is spatially and temporally variable as geochemical evolution and residence time increase with aquifer depth.

Chapter 1: Introduction

Globally, the subsurface is an extensive and essential reservoir for freshwater and carbon. An estimated 22.6 million km³ of freshwater is stored in groundwater aquifers; only about 6% of which was recharged in the last hundred years (Gleeson et al., 2015). Groundwater aquifers are also active sinks for carbon, storing an estimated 1404 Pg C as dissolved inorganic carbon (DIC) and calcite precipitates (Monger et al., 2015). In semi-arid regions, where precipitation and surface water are limited, groundwater is critical for ecosystem sustainability and agriculture. For example, 89% of the public-supply water in Idaho is obtained from groundwater (Dieter et al., 2015). Unfortunately, not all groundwater is renewable because residence times— the length of time water is in the subsurface— can vary from a few to thousands of years (Monger et al., 2015).

Understanding the composition, sources, and residence times of groundwater should precede groundwater use, especially in dryland regions, to ensure the renewability and quality of the aquifer (de Vries and Simmers, 2002; Viviroli et al., 2011). While young aquifers seem like an ideal, renewable source of freshwater, shallow aquifers, most associated with younger waters, are susceptible to anthropogenic influence such as pollution and climate change (Salahat et al., 2014). As temperatures rise, snow-dominated regions are predicted to transition to become raindominated (Elsner et al., 2010; Klos et al., 2014). This change could affect the timing and chemistry of groundwater recharge (Taylor et al., 2013; Lindquist et al., 2019).

Geochemical evolution of groundwater is dependent on the redox conditions as well as the soils and bedrock which are the main sources of the geochemical constituents in groundwater (Glynn and Plummer, 2005). Because dissolution is positively correlated with temperature, temperature increases in recharge waters will increase weathering rates exponentially, affecting

the quality of and reactions within groundwater (White and Blum, 1995). For example, in basaltic catchments, a temperature increase of 5°C would increase the dissolved SiO₂ in runoff by about 100 μ mol/L (Ibarra et al., 2016). Limited access and visibility prove difficult when studying groundwater. Geochemical analyses provide insight into the sources, geochemical evolution, and residence times of the subsurface groundwater environment (Glynn and Plummer, 2005).

Reynolds Creek Experimental Watershed (RCEW) and Critical Zone Observatory (CZO) is a mountainous, semi-arid watershed located in southwest Idaho where researchers have monitored and evaluated the cycle of water and carbon through the critical zone— from the atmosphere to the subsurface (Seyfried et al., 2018). Established in 1960, researchers have monitored long-term climate data such as precipitation and temperature to establish long-term datasets across elevation, vegetation, and climate gradients (e.g., Seyfried et al., 2001; Seyfried et al., 2018; Pierson et al, 2001; Marks et al., 2007; Kormos et al., 2018; Godsey et al., 2018). Unfortunately, studies into groundwater geochemistry at RCEW, are limited, leaving a gap in our knowledge of subsurface reservoirs.

Historically, groundwater research at RCEW focused on physical measurements to interpret recharge characteristics and study surface-groundwater interactions (Stephenson, 1965, Stephenson, 1973, Stephenson and Zuzel, 1981). Researchers have advanced geochemical analyses substantially in the last 50 years (Glynn and Plummer, 2005), but groundwater geochemistry in RCEW remains relatively unconstrained (Seyfried et al., 2018). Analyzing samples for dissolved organic carbon (DOC), Radke et al. (2019) began developing a baseline for geochemical analysis to evaluate and monitor the movement of carbon through the subsurface, but they focused on groundwater-surface water interactions within a small, shallow

sub-basin. Age dating springs with chlorofluorocarbons revealed emerging groundwater evolved in shallow aquifers, recharged by modern waters (Warix and Godsey, 2019; Warix et al., 2021), but the residence times and geochemical evolution of deeper groundwater remain unconstrained.

In this study, we sought to fill the gap in our knowledge of the RCEW critical zone groundwater geochemistry, carbon evolution, and residence times through the subsurface, specifically deep groundwater systems. We aimed to gain a better understanding of the subsurface groundwater environment by discerning sources, evaluating water-rock interactions, and estimating residence times. We sampled groundwater wells along an elevational and longitudinal transect, potential source signatures (high elevation groundwater, surface waters, precipitation), and a nested well in a separate, heavily instrumented catchment to monitor spatial and seasonal changes in the groundwater geochemistry. To support interpretations of geochemical data and aquifer properties, we used geophysical borehole logs to visualize the architecture of the subsurface. We hypothesized that groundwater was recharged by modern waters (<100 years) in higher elevation, snow-dominated regions. Shallow aquifers, including springs, were expected to be younger and vulnerable to anthropogenic influences, evolving under open-system conditions. Alternatively, we hypothesized deeper aquifers would be older and evolve over the course of a few hundred years under closed-system conditions.

In chapter 2, we sought to define groundwater characteristics and evaluate the geochemical evolution of groundwater and carbon. We examined the sources and aquifer properties and modelled the geochemical evolution of carbon and water through the subsurface groundwater environment of RCEW. Field parameters, confirmed by principal component analysis (PCA), distinguished aquifers by depth across the basin— springs and wells— and within the Summit area— shallow, intermediate, and deep. Analysis of δ^2 H and δ^{18} O values

indicated recharge in the snow-dominated, high elevation regions. While shallow wells and springs represented modern waters, intermediate and deep wells accessed paleowaters that deviated from the local meteoric water line. Examination of carbon concentrations and isotopes established springs as evolving under open-system conditions whereas well samples reached calcite saturation under closed-system conditions. Ionic concentrations provided a geochemical baseline that allowed for geochemical modelling of water-rock interactions and reactions. Modelling results suggested dissolution of basaltic minerals— plagioclase and pyroxene— and precipitation of calcite, various clays, and some iron oxide. We concluded that the shallow aquifers, including springs, were vulnerable to anthropogenic influence and a changing climate while the deep aquifers acted as a carbon sink.

In chapter 3, we discuss the spatial and temporal flow of groundwater and carbon through the subsurface. Combining field measurements and isotopic ratios confirmed groupings established in chapter 2. ⁸⁷Sr/⁸⁶Sr values suggested a dominantly basaltic aquifer with some granitic end-member mixing, especially in the springs. ²³⁴U/²³⁸U values correlated with well depth suggesting an unknown source in the deeper flowpaths. Comparison of geochemical analyses with geophysical borehole logs depicted three distinct flowpaths within the Summit area— one shallow, two deep. The shallow wells solely accessed the shallow flowpath, while the deep wells accessed both of the deep flowpaths. Because of the lower ²³⁴U/²³⁸U values, we concluded that the intermediate wells accessed the shallow and one of the deep flowpaths resulting in mixing within the wells. Residence time calculations supported these findings. Shallow wells contained detectable tritium (³H) with ages ranging from 8.97-49.15 years before sampling. Intermediate wells had detectable ³H (35.55-68.53 years before sampling) and viable radiocarbon (¹⁴C) ages (1866-2520 years before present). Deep wells were ³H-dead (0.08 TU),

but only two of the deep wells had viable ¹⁴C ages (2146-9440 years before present). We identified a ³H-rich, shallow flowpath that was accessed by the shallow and intermediate wells while a deep (1) flowpath, ³H-dead with viable ¹⁴C ages, was accessed by the intermediate and deep wells. A deeper flowpath containing high ²³⁴U/²³⁸U was solely accessed by the deep wells. In conclusion, the shallow flowpaths were recharged by modern waters, while the deeper flowpaths had longer residence times, originally recharged by paleowaters.

Collectively, this research revealed that groundwater in RCEW evolved from high elevation, snow-dominated regions through basaltic aquifers toward calcite saturation. While shallow aquifers, including springs, were older than expected, these flowpaths were connected to the atmosphere and vulnerable to anthropogenic influence and climatic changes. Intermediate and deep wells accessed paleowaters, disconnected from the climate, and continued to evolve under closed-system conditions after reaching calcite saturation. Geophysical borehole logs combined with geochemical tracers distinguished three distinct flowpaths with a previously unidentified geothermal signature. These findings inform our understanding of the movement of carbon through the critical zone as shallow aquifers with shorter residence times undergo calcite dissolution and allow for increased transmissivity while deeper aquifers act as carbon sinks with longer residence times.

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Chapter 2: Interpreting recharge characteristics and geochemical evolution of groundwater in a semi-arid basin

2.1 ABSTRACT

Identifying sources of recharge and interpreting aquifer properties are essential to understanding and predicting the effects of a changing climate on the evolution and quality of groundwater, an important resource in semi-arid regions. In this study, we collected samples from groundwater wells along a longitudinal transect and potential recharge sources (high elevation springs, surface waters, and precipitation) in a mountainous, semi-arid watershed. Samples were analyzed for geochemical tracers including ion concentrations (DIC, DOC, NO₃⁻, Cl⁻, SO₄²⁻, F⁻, Na⁺, Ca²⁺, Mg²⁺, K⁺) and isotopic ratios (δ^2 H, δ^{18} O, δ^{13} C). We found that the low elevation aquifers were recharged in higher elevation, snow-dominated regions. Springs emerged from shallow, local flowpaths that were undersaturated in calcite and evolved in alkali-rich environments. In contrast, wells accessed aquifers that were calcite saturated and continue to evolve along the flowpaths by weathering olivine— and pyroxene-rich basalts. Results of geochemical modeling showed precipitation of calcite, various clays, and some iron oxide, and dissolution of plagioclase (albite and anorthite) and pyroxene. In this semi-arid basin, deeper aquifers were recharged by paleowaters and further geochemically evolved.

2.2 INTRODUCTION

Globally, groundwater is a major reservoir for freshwater with a volume of about 22.6 million km³ (Gleeson et al., 2016). The sustainability of groundwater is dependent on sources of recharge, aquifer properties, and geochemical evolution (Green et al., 2011; Zhu and Schwartz, 2011). As global temperatures rise, the timing and intensity of precipitation will be affected (Oki and Kanae, 2006). In particular, semi-arid basins, like Reynolds Creek Experimental Watershed

(RCEW) in southwestern Idaho, are predicted to transition from being snow-dominated to become rain-dominated in the next fifty years (Elsner et al., 2010; Klos et al., 2014). Changes in the type of recharge affect infiltration to groundwater and runoff to surface water (Taylor et al., 2013; Lindquist et al., 2019). Models show warmer waters have higher weathering rates of soils and bedrock which affects the chemistry of and reactions within the groundwater (White and Blum, 1995). Additionally, carbon species, dominant constituents in geochemical reactions, are important indicators of climatic changes, surficial influence, and aquifer properties (Clark and Fritz, 1997).

To predict the effect of the changing climate on groundwater, it is critical to identify sources and study the geochemical evolution of water through the subsurface. In semi-arid regions, a major source of groundwater is thought to be mountain block recharge— infiltration of precipitation at high elevations in the mountains (Wilson and Guan, 2004; Ajami et al., 2011; Kormos et al., 2015). Depth of flow and other aquifer properties influence groundwater geochemistry, specifically the evolution of carbon through the subsurface.

Springs, emerging groundwater, often evolve through shallow, unconfined aquifers under open-system conditions— interacting with the vadose zone (Cartwright et al., 2013). Deeper, confined aquifers tend to persist under closed-system conditions, where the groundwater cannot interact nor exchange with the vadose zone (Clark and Fritz, 1997; Cartwright et al., 2013). Aquifers grouped by relative depths and characteristics— shallow and deep— will be henceforth referred to as reservoirs.

Previous studies have used geochemical tracers to interpret aquifer properties and system conditions, evaluate geochemical evolution and bedrock weathering, detect anthropogenic influence on groundwater reservoirs, and pinpoint the sources of groundwater recharge (Glynn

and Plummer, 2005). It is particularly difficult to estimate recharge in mountainous arid to semiarid regions (de Vries and Simmons, 2002), because aquifers are often recharged in the higher elevations by winter precipitation, but the geochemical signature is influenced by bedrock weathering, redox reactions, and mixing (Meredith et al., 2017; Eastoe and Wright, 2019). Through the analysis of carbon concentrations, isotopes, and a suite of ions, the evolution of dissolved inorganic carbon (DIC) in groundwater is indicative of system conditions and aquifer properties (Meredith et al., 2017). Sources of carbon in groundwater include bedrock weathering, dissolution from soils, and redox reactions (Pearson and Friedman, 1970). Additionally, concentration-discharge relationships illustrate the evolution and estimate sources of DIC and dissolved organic carbon (DOC) (Olshansky et al., 2018).

Geochemical evolution within groundwater systems is defined by the chemical constituents in the bedrock and soils (Hem, 1985; Glynn and Plummer, 2005). To assess aquifer properties and environmental conditions, studies use ion plots according to the graphical method developed by Piper (1944). Ionic trends, conditions of geochemical evolution, and anthropogenic influence, often in shallow aquifers, are identified by plotting ion concentrations (Vikas et al., 2015). Incorporating rare earth elements (REE) expands these techniques by revealing correlations with other constituents such as DOC (Vázquez-Ortega et al., 2015). To further interpret geochemical evolution, studies utilize geochemical modelling programs such as NETPATH v. 2.0 (Reston, VA) (Plummer et al., 1994), NetpathXL (Reston, VA) (Parkhurst and Charlton, 2008), and PHREEQC (Lakewood, CO) (Parkhurst, 1995). NETPATH is used to model the evolution of groundwater with consideration of water-rock interactions, mixing of aquifers, surficial influence, and more (Plummer et al., 2004). PHREEQC is used to test potential sources of solutes such as bedrock weathering, redox reactions, and anthropogenic influence

(Rattray, 2015). By calculating saturation indices (SI) with PHREEQC, and modeling geochemical evolution with NETPATH, studies have distinguished aquifers, evaluated bedrock weathering, and estimated redox reactions driving geochemical evolution (Gastmans et al., 2016). Additional programs have been used to calculate initial partial pressure of carbon dioxide (pCO₂) and mineral SI (Pawar, 1993; Olshansky et al., 2018).

Groundwater geochemistry can also be affected by changing water inputs such as precipitation and surface waters as well as anthropogenic influences such as agriculture. Previous studies traced agricultural contaminants, such as nitrate, and estimated residence times to measure and monitor the impact of anthropogenic activities on groundwater flow and suitability (Böhlke, 2002; Brown et al., 2011; Carlson et al., 2011). Studies found that shallow aquifers are often influenced by agricultural practices and pollution by discovering the addition of modern waters and high levels of contaminants in the groundwater (Currell et al., 2012; Salahat et al., 2014; Marghade et al., 2021). While there are extensive geochemical studies on groundwater in semi-arid to arid regions, as mentioned above, RCEW— a heavily monitored semi-arid basin located in Owyhee County in southwest Idaho, USA (Figure 2.1)— has substantial research on the hydrologic and carbon cycles but limited research into the groundwater. One of the few studies that examined groundwater showed that shallow, emerging groundwater was temporally and spatially variable in RCEW (Radke et al., 2019; Warix et al., 2021). Further research into groundwater sources and geochemistry is required to fully understand these temporal changes and to predict the effects of the changing climate on the groundwaters.

In this study, we sought to assess the subsurface groundwater environment within RCEW by distinguishing aquifers, estimating recharge conditions, and evaluating water-rock interactions. Specifically, we ascertained the evolution of carbon and water through the

subsurface by identifying sources, interpreting aquifer properties, and modeling geochemical reactions. We first developed a map of the piezometric surface of a sub-basin to establish groundwater flow direction and calculated a local meteoric water line (LMWL) for the entire basin to evaluate sources of water. We then analyzed groundwater samples from monitoring wells and springs to interpret the evolution of carbon and water using multiple environmental tracers and geochemical modeling. We hypothesized that groundwater within the northeastern portion of RCEW, the Summit area, flowed west from higher elevation, snow-dominated mountain block toward the lower elevation outlet. Shallow aquifers, specifically those emerging as springs, were expected to be vulnerable to anthropogenic influence and climatic changes having evolved under open-system conditions. Because the Summit area is comprised of volcanic rocks, dominantly basalt, we hypothesized that the deep groundwater evolved in basaltic aquifers under closed-system conditions by weathering mafic minerals such as pyroxene. The results of this study are expected to have implications for future subsurface and hydrologic studies by providing baseline geochemical signatures of shallow and deep groundwater aquifers in RCEW as well as modeling the geochemical evolution of carbon and water through the subsurface of a semi-arid basin.



Figure 2.1 Map of Reynolds Creek basin with bedrock geology (Bonnichsen and Godchaux, 2006) and well locations.

2.2.1 Background

Recharge characteristics, such as precipitation type, are inferred from analysis of stable isotopes of water. Stable isotopes of water are analyzed as isotopic ratios, ${}^{2}H/{}^{1}H$ and ${}^{18}O/{}^{16}O$, reported in the δ notation (Eq 2.1) as per mille (‰) relative to Vienna Mean Standard Ocean Water (VSMOW), and compared to the meteoric water line (Clark and Fritz, 1997).

Eq 2.1
$$\delta^{18}O_{sample} = \left(\frac{({}^{18}O/{}^{16}O)_{sample}}{({}^{18}O/{}^{16}O)_{reference}} - 1\right) \times 1000 \% VSMOW$$

The global meteoric water line (GMWL) is based on isotopic ratios of freshwater sources around the world, primarily precipitation (Craig, 1961; Clark and Fritz, 1997). Because the relationship between δ^{18} O and δ^{2} H can vary by area and climate, a LMWL is necessary for interpretation of δ^{2} H and δ^{18} O in a specific location. The placement of values along the LMWL can indicate the type of precipitation because snow tends to be more depleted compared to rain (Clark and Fritz, 1997). In some areas, the type of source precipitation can suggest a relative elevation of recharge depending on the climate gradient (Meredith et al., 2017; Eastoe and Wright, 2019). Because lighter isotopes are more likely to be evaporated, exposed waters will vary from the LMWL depending on the percent evaporated (Eq 2.2), where *f* is the residual vapor fraction and 1-*f* is the degree of evaporation (Clark and Fritz, 1997).

Eq 2.2
$$\delta^{18}O_{\text{groundwater}} - \delta^{18}O_{\text{precipitation}} = \epsilon^{18}O_{\text{total}} * \ln f$$

For groundwater, evaporative signatures can indicate extended time in the vadose zone, longer residence times, seasonal variation, or mixing (Clark and Fritz, 1997). Because the climate is changing overtime, paleowaters are likely to have a different signature and not follow the LMWL (McIntosh and Walter, 2006; Schlegel et al., 2009; Eastoe and Wright, 2019).

Studying the evolution of carbon through the subsurface allows for a better understanding of the carbon cycle in a semi-arid environment as well as interpretation of subsurface

geochemical reactions and aquifer properties. Carbon in groundwater comes in the form of DIC and DOC (Keller, 2019). As water interacts with the bedrock within the aquifer, chemical weathering reactions result in the dissolution of carbonates to form DIC (Eq 2.3) (Clark and Fritz, 1997).

Eq 2.3
$$\operatorname{CO}_{2(g)} + \operatorname{H}_2O + \operatorname{CaCO}_3 \rightarrow \operatorname{Ca}^{2+} + 2\operatorname{H}^+ + 2\operatorname{CO}_3^{2-} \rightarrow \operatorname{Ca}^{2+} + 2\operatorname{HCO}_3^{-1}$$

Because this conversion increases the pH of the water, comparison of pH levels to DIC concentrations indicates the level of calcite saturation (Clark and Fritz, 1997).

Additionally, plants fix carbon dioxide (CO_2) from the atmosphere into organic forms through the process of photosynthesis (Eq 2.4) (Clark and Fritz, 1997). This organic carbon can be incorporated into soil through root exudates and litterfalls.

Eq 2.4
$$CO_2 + H_2O \rightarrow O_2 + CH_2O$$

Microbes can break down this organic matter through mineralization and release it back as an inorganic form of CO₂ into the soil (Keller, 2019).

As water percolates through the soils, it dissolves the soil CO_2 to form DIC (Eq 2.5) and leaches organic carbon from the decomposing litter to form DOC (Clark and Fritz, 1997).

Eq. 2.5
$$CO_{2(g)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$

In addition, isotopic ratios of carbon are indicative of sources, aquifer system conditions, and the level of calcite saturation (Han et al., 2012). Carbon can be found in three isotopes— 12 C, 13 C, and 14 C. 12 C and 13 C are stable isotopes while 14 C is radiogenic, meaning it decays over time (Clark and Fritz, 1997). Measuring δ^{13} C allows for interpretation of aquifer properties and the path of carbon from sources to sampling. Plants and microbes can preferentially process certain
isotopes of carbon depending on the type and process (Keller, 2019). For example, C₃ plants tend to be more depleted in ¹³C (-27‰) compared to C₄ plants (between -16 and -10‰) (Clark and Fritz, 1997; Pearson and Hanshaw, 1970; Cartwright et al., 2020). Additional fractionation occurs between different DIC species— bicarbonate (HCO₃⁻) and carbonate (CO₃²)⁻which is dependent on the pH of the system (Clark and Fritz, 1997). For example, systems with a pH between 6.4 and 10.3 will be dominated by HCO₃⁻ leading to δ^{13} C values around -15.1‰, varying with pH, temperature, and saturation levels (Clark and Fritz, 1997).

Further aquifer properties, specifically the level of water-rock interactions, are surmised from the geochemistry of the groundwater (Piper, 1944). Ion concentrations describe the bedrock environment and the evolution of the water. Anions often include sulfate (SO_4^{2-}), chloride (CI^-), and nitrate (NO_3^-). Some analyses also include carbon as HCO_3^- or CO_3^{2-} and fluoride (F^-). Cations include sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+). These ions characterize and classify the geochemical environment by their placement on a trilinear plot known as a piper diagram (Piper, 1944). Additional cations and REE trace the geochemical evolution and indicate saturation levels, occurrence of redox reactions, and bedrock type. Geochemical models use ion concentrations and isotopic ratios to estimate system conditions, calculate SI, and infer geochemical processes such as dissolution or precipitation of minerals and redox reactions.

2.2.2 Site description

Initially established in 1960, RCEW was established as a Critical Zone Observatory (CZO) in 2014 in collaboration with the Agricultural Research Service (ARS) (Seyfried et al., 2018). As a 238 km² basin with an elevation gradient of 2244 m to 1100 m, RCEW has a range of weather conditions including a wide rain-snow transition zone. Mean annual precipitation

varies from 200mm in the rain-dominated, lower elevation catchments and 1140mm in the snowdominated, high elevation catchments (Kormos et al., 2018). While mean annual temperature is 7.8°C, temperatures range depending on the season with mean temperatures of -2.3°C in December and 20.5°C in July (Kormos et al., 2018). RCEW receives the highest amount of precipitation during the coldest months from November through April (Kormos et al., 2018). The vegetation varies along the climate gradient from sagebrush in the lower elevations to aspens in the higher elevations. The vegetation is dominated by C_3 plants with some C_4 and CAM plants spread throughout the basin (Seyfried et al., 2018).

The geology of RCEW is dominantly volcanic rocks, including granite of the Silver City batholith, andesite of the upper Salmon Creek, and basalt of the Owyhee Mountains (Bonnichsen and Godchaux, 2006). The granitic basement rock was deposited during the Cretaceous then unconformably overlain by olivine-rich basalt flows in the Miocene (McIntyre, 1972). These basalt flows are dominantly composed of clinopyroxene (augite) and plagioclase (anorthite with some albite), with additional minerals including olivine and magnetite (McIntyre, 1972). Additionally, vesicles in the basalt are often lined or filled with calcite. During the Quaternary, surficial landforms such as landslides and floodplain alluviums formed within this area (McIntyre, 1972).

2.3 METHODS

2.3.1 Sampling design overview

In the 1960s, the ARS drilled and logged 41 groundwater wells in the lower basin and Summit sub-basin (Figure 2.1) to study the lithology and groundwater flow direction within the northeastern portion of the basin— Summit area (Stephenson, 1965, 1973). Water table elevation was estimated from depth to water measurements taken in the summer of 2019 and original water levels obtained from drill logs. A piezometric surface utilizing these data was re-created from the elevation of the water table using ordinary kriging in ArcGIS Pro v 2.8 (ESRI, California, USA) with a spherical model (Figure 2.2).



Figure 2.2 Piezometric surface mapped using ordinary kriging method in ArcGIS Pro v. 2.8 (ESRI, California, USA) with static water level measurements from sampled Summit wells in 2019 overlain on bedrock geology (Bonnichsen and Godchaux, 2006). Additional static water levels were obtained from original drill logs for private, Idaho Department of Water Resources (IDWR), and additional Summit wells (Stephenson, 1965, 1973).

Because the piezometric surface indicated a dominantly western flow direction (Figure 2.2), we chose eight research wells and two domestic wells based on proximity to an ideal eastwest transect, variation in total depth, and water level (Figure 2.3, Table 2.1). To identify endmember signatures, we located springs at higher elevations throughout the basin using satellite imagery. Because of the timing of sampling, only six springs were flowing (Figure 2.3). Additionally, an irrigation pond towards the western end of the transect was sampled twice as a potential influence on the domestic wells. Finally, in the fall of 2019, a new well was drilled using an air rotary drill in the middle portion of the basin in the Johnston Draw (JD) catchment. Nested monitoring wells were installed in the summer of 2020 to depths of 25 m and 39 m.



Figure 2.3 Map of sampling sites with bedrock geology (Bonnichsen and Godchaux, 2006).

	Sample Name	Sample Date	Easting	Northing	Elevation (m)	Well Depth (m)	Depth to Water (m)	Casing Depth (m)	Pump
	GW 2	7/25/19	523614	4788933	1266	27.02	8.16	9.4	1
	GW 6	7/24/19	523221	4788699	1238	7.86	3.15	7.86	1
Shallow	GW 14	7/23/19	522772	4788238	1219	9.98	5.62	9.98	1
	GW 16	7/22/19	521692	4788269	1167	13.5	4.76	5.5	1
	GW J	9/6/19	520324	4788320	1130	30.5	11.84	30.5	-
Intermediate	GW 35	9/5/19	520851	4788402	1140	63.50	9.44	1.4	2
Intermediate	GW OD	7/24/19	520568	4788394	1131	123	3.90	123	-
Deep	GW 23	10/3/19	523800	4788268	1286	171.06	4.17	5	2
	GW 22	7/22/19	521393	4788114	1157	236.43	0	236.43	-
	GW 25	10/17/19	520902	4788394	1140	192.68	20.46	85	2
	SW 1	8/5/19	512226	4788145	1734	-	-	-	-
	SW 2	8/5/19	515853	4782301	1516	-	-	-	-
C	SW 3	8/6/19	519811	4768306	2056	-	-	-	-
spring	SW 4	8/6/19	521321	4772133	1851	-	-	-	-
	SW 5	8/6/19	521451	4771901	1882	-	-	-	-
	SW 6	8/6/19	524206	4775866	1780	-	-	-	-
JD	JD 25	10/8/20	518217	4774475	1498	25	2.78	25	3
Dond	P1-inlet	7/16/20	520616	4787744	1145	-	-	-	-
rond	P2-mid	7/16/20	520662	4787954	1142	-	-	-	-
Precipitation	RME	-	519976	4768314	2043	-	-	-	-
	Breaks	-	518409	4772705	1585	-	-	-	-
	Quonset	-	520343	4783695	1203	-	-	-	-

Table 2.1 Sample locations and well descriptions.

¹Geotech (Denver, CO, USA) 1.66 Reclaimer (positive air displacement pump)

²Hallmark Industries (Streamwood, IL, USA) 3.3" Deep Well Submersible Pump

³Proactive Environmental Products (Hamilton, NJ, USA) Stainless Steel Monsoon XL Pump

2.3.2 Developing a local meteoric water line

To estimate precipitation type and evaporative signature, δ^2 H and δ^{18} O isotopic ratios were compared to the GMWL (Craig, 1961) and Boise's LMWL (Tappa et al., 2016). Boise's LMWL was a compilation of 393 precipitation samples, unweighted, collected throughout the year in the greater Boise area (Tappa et al., 2016). Because we observed deviations from these meteoric water lines, we developed a LMWL for Reynolds Creek. Three precipitation water samplers (Palmex (Zagreb, Croatia) RS-2i) were installed at three different elevations (1203 m, 1585 m, 2043 m) (Table 2.1). The samplers were designed to prevent evaporation of samples through pressure and thermal equilibration (Gröning et al., 2012). Precipitation samples, including both snow and rain, were collected at least once a month for over a year, hand filtered through 0.45 µm Whatman Puradisc nylon syringe filters, and analyzed for δ^2 H and δ^{18} O using an Off-Axis Integrated Cavity Output Spectroscopy at the Stable Isotope Facility (SIF) at the University of California, Davis. δ^2 H and δ^{18} O were reported in per mille (‰) relative to VSMOW. SIF reported <2.0‰ error for δ^2 H and <0.3‰ error for δ^{18} O. Because RCEW receives the highest precipitation from November through April (Kormos et al., 2018), we used linear regression to calculate the LMWL from winter and spring precipitation samples (November through April).

2.3.3 Groundwater sampling

In the summer and fall of 2019, we collected sixteen groundwater samples and two surface water samples (Table 2.1). Assuming everyday use, domestic wells were purged only one pore volume while the research wells were purged three pore volumes (Eq 2.6).

Eq 2.6 Pore Volume
$$(m^3) = \pi * (Radius(m))^2 * (Height of Water (m))$$

No purging was necessary for the artesian well, irrigation pond, and springs. Drilled in the fall of 2019 and installed in the summer of 2020, JD 25 was purged once a week for a month before sampling.

We measured field parameters, including pH, temperature, and electrical conductivity, during purging. To measure pH and temperature, we used an Oakton (Vernon Hills, Illinois, US) Handheld pH and Temperature Meter with a 3-point calibration (4.01, 7.00, 10.00) for a +/- 0.01 pH accuracy. To measure electrical conductivity, we used a YSI (Yellow Springs, Ohio, US) Model 30 Handheld Conductivity and Temperature Meter calibrated with a 500 μ S/cm solution for +/- 0.5% accuracy. All calibrations were completed before purging.

We began sampling when field parameters stabilized. For geochemical analyses, we collected three and a half liters of sample in amber high-density polyethylene (HDPE) bottles to be filtered. All sampling bottles were new or pre-conditioned HDPE bottles. The pre-

conditioning process included leaching the bottles with MilliQ deionized water for at least 24 hours and rinsing with sample three times before collection. Sample bottles were filled with no headspace, refrigerated immediately, and filtered within 24 hours, if necessary. Filter types for each analysis are described further below. Precipitation samples were collected every other week or after large precipitation events and filtered within 24 hours.

Within 24 hours of collection, we measured samples for alkalinity using a Hanna Instruments (Woonsocket, Rhode Island, US) Total Alkalinity Mini Titrator calibrated with Total Alkalinity Calibration standard (HI 84531-55) to ensure accuracy of +/- 1 mg/L. The titrator calculates the alkalinity by acidifying the sample with Total Alkalinity Titrant (HI 85531-50) and measuring the change in pH after each addition.

2.3.4 Environmental tracers

Groundwater samples were analyzed for anions, cations, REE, DIC, DOC, and isotopes $(\delta^2 H, \delta^{18}O, \text{ and } \delta^{13}C)$. Pond samples were analyzed for anions, cations, REE, DIC, DOC, $\delta^2 H$, and $\delta^{18}O$. Precipitation samples were analyzed for $\delta^2 H$ and $\delta^{18}O$. All analyses, except for carbon isotopes, required samples to be hand filtered through 0.45µm Whatman Puradisc nylon syringe filters. Alongside precipitation samples, $\delta^2 H$ and $\delta^{18}O$ of groundwater samples were measured by Off-Axis Integrated Cavity Output Spectroscopy at SIF at the University of California, Davis and reported as % relative to VSMOW.

For carbon concentrations and isotopes, we analyzed samples for DIC, DOC, δ^{13} C-DIC, δ^{13} C-DIC, and radiocarbon (¹⁴C-DIC). DIC and DOC concentrations were analyzed at the Lohse Soil and Biogeochemistry Laboratory (LSB) at Idaho State University (ISU) using a Shimadzu Corporation (Kyoto, Japan) TOC-V CSH with a less than 2% error. DOC concentrations were measured as NPOC by acidifying with 4 drops of concentrated HCl and

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removing DIC. Additional samples were analyzed at Arizona Laboratory for Emerging Contaminants at the University of Arizona for DIC using a Shimadzu Corporation (Kyoto, Japan) TOC-L and at the Environmental Analytical Agency at Brigham Young University for DOC. Concentrations of carbon were reported as mg/L with standard deviation. Samples analyzed for carbon isotopes were hand filtered with 0.2μ m Whatman Puradisc nylon syringe filters. δ^{13} C in DIC and DOC were analyzed at SIF and reported in ‰ relative to Vienna PeeDee Belemnite (V-PDB). δ^{13} C-DIC was analyzed using a Thermo Scientific (Bremen, Germany) GasBench system interfaced to a Delta V Plus IRMS with a long-term standard deviation of 0.1. δ^{13} C-DOC was analyzed with a Xylem Analytics (College Station, Texas, US) O.I. Analytical Model 1030 TOC Analyzer with an accuracy of +/- 0.4‰. ¹⁴C was analyzed by the University of Arizona AMS Laboratory and reported in percent modern carbon (pmc).

Anions— NO₃⁻, Cl⁻, SO4²⁻, F⁻— were measured using a Dionex (Sunnyvale, California, US) ICS-5000 with 2% error at the LSB lab. Samples were initially diluted 1:5 and diluted further (1:10, 1:30, and 1:50) if values reported were higher than 10 mg/L. 15 mL samples for cation and REE analysis were preserved with 2 drops of concentrated nitric acid. A full suite of cations was measured at the Center for Archaeology, Materials, and Applied Spectroscopy (CAMAS) facility at ISU using a Thermo Scientific (USA) Thermo X-II series Inductively Coupled Plasma Mass Spectrometer (ICP MS) with a 1:10 dilution. Cations were also analyzed at the Environmental Analytical Lab at Brigham Young University for quality assurance. REE were measured using ICP MS at CAMAS with a 2:10 dilution. To ensure all major ions were examined and accurate, we calculated charge balance (Eq 2.7) and charge balance error (CBE) (Eq 2.8)

Eq 2.7 Charge balance = Sum of cations – Sum of anions

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Eq 2.8 CBE = (cations - anions) / (cations + anions) * 100

where cations and anions are reported in mol/L and multiplied by the charge of the ion.

2.3.5 Statistical analyses

To distinguish spring and Summit reservoirs, two-sample t-tests, assuming unequal variance, were run using Microsoft Office (Redmond, WA) Excel and JMP (Cary, NC) Pro 15 based on field parameters. Principal component analysis (PCA) was run using JMP Pro 15 based on correlations because variables included were measured on different scales— field parameters, carbon concentrations, isotopic ratios (δ^2 H, δ^{18} O, δ^{13} C), and ions. PCA on correlations standardized the values in a correlation matrix before analysis.

2.3.6 Geochemical modeling

We input the results of the environmental tracer analyses into Aqion v. 7.4.2 (https://www.aqion.de/) and NetpathXL (Parkhurst and Charlton, 2008) to run geochemical models in order to interpret aquifer characteristics and water-rock interactions. Aqion is a hydrochemistry software that uses PhreeqC to calculate charge balance and mineral SI. Mineral SI is calculated based on the concentration of constituents and their solubility potential to determine if the solution is undersaturated— undergoing dissolution— or saturated undergoing precipitation. NetpathXL uses geochemical mass-balance reactions to model waterrock interactions, redox reactions, and flowpath mixing (Plummer et al., 1994). Based on the composition of the basalt in RCEW (McIntyre, 1972), we ran models based on six constraints (C, Ca, Mg, Na, Fe, Al) and ten phases allowing for dissolution of minerals— albite (Naplagioclase), anorthite (Ca-plagioclase), augite (pyroxene), magnetite, kaolinite (Al₂Si₂O₅(OH)₄), and goethite (FeO(OH))— and precipitation or dissolution of calcite and various clays— Ca, Mg, and Na montmorillonite.

2.4 RESULTS

2.4.1 Reynolds LMWL

Precipitation samples, snow and rain, plotted alongside the GMWL and Boise LMWL showed a slight deviation from the known meteoric water lines (Figure 2.4). While the GMWL and Boise LMWL had slopes of 8 and 7.1 respectively, Reynolds winter-spring precipitation samples plotted with a slope of 8.28 (Reynolds LMWL). Colder months tended to show less variation compared to samples from the warmer months which plotted closer to the Boise LMWL (Appendix A).



Figure 2.4 Plot of δ^{18} O and δ^{2} H values for precipitation samples from November through April used to estimate a Reynolds Creek local meteoric water line (LMWL) plotted alongside the global meteoric water line (GMWL) (Craig, 1961) and Boise LMWL (Tappa et al., 2016).

2.4.2 Groundwater and surface water field measurements

Field parameters varied across the reservoirs— shallow aquifers accessed by emerging springs and deep aquifers accessed by the Summit wells (Table 2.2). Springs had lower mean pH (6.4 + - 0.648), temperature (11.92 + - 3.772°C), electrical conductivity (112.6 + - 84.43 μ S/cm), and alkalinity (85.0 +/- 53.29 mg/L) compared to the Summit wells. Summit wells had less variation across samples with pH values from 7.03-9.27 (mean of 8.0 +/- 0.682), temperatures from 13.2-18.1°C (mean of 16.2 +/- 1.572°C), electrical conductivity from 377.8-1576 μ S/cm $(845.1 + - 381.36 \mu S/cm)$, and alkalinity from 151.9-291.9 mg/L (mean of 221.4 + - 46.838) mg/L). Additionally, field parameters separated Summit wells by depth (Table 2.2)— shallow wells were colder (mean temperature of 15.2 +/- 1.49°C) and more acidic (mean pH of 7.53 +/-(0.32) while intermediate wells had the highest electrical conductivity (mean of 1265 ± -441 μ S/cm). Deep wells had the highest pH values (8.45-9.27) and the lowest alkalinity (151.9-197) mg/L). Similar to the Summit wells, JD 25 had a pH of 8.2, temperature of 18.9°C, electrical conductivity of 1224 µS/cm, and alkalinity of 204.8 mg/L. Pond samples had a mean pH of 8.68 +/- 0.304, temperature of 21.85 +/- 0.354°C, electrical conductivity of 563.5 +/- $4.950 \,\mu$ S/cm, and alkalinity of $166.6 \pm 2.687 \text{ mg/L}$.

Table 2.2 Environmental parameters measured in the field after reaching stable conditions during purging and before sampling of wells— pH, temperature (°C), electrical conductivity (μ S/cm)— and within 24 hours of sampling— alkalinity (mg/L).

	Sample Name	pН	Temperature (°C)	Electrical Conductivity (µS/cm)	Alkalinity (mg/L)
	GW 2	7.6	16.1	675	222.6
Shallow	GW 6	7.46	15.4	697	273.6
	GW 14	7.9	14.3	614	198
	GW 16	7.64	17	1295	261.1
	GW J	7.03	13.2	1124	291.9
Tutomodiate	GW 35	7.9	18.1	953	216.1
Intermediate	GW OD	7.88	15.6	1576	243.5
Deep	GW 23	9.27	16.5	377.8	158.3
	GW 22	8.45	17.6	634	151.9
	GW 25	8.9	17.73	505	197
	SW 1	6.31	11	34.8	<30.0
	SW 2	7.09	12.4	258.8	152.5
Saning	SW 3	5.35	6	21.1	<30.0
spring	SW 4	6.99	10.3	148.7	142.5
	SW 5	6.64	15.3	115.1	86.5
	SW 6	6.07	16.5	97.1	68.2
Л	JD 25	8.2	18.9	1224	204.8
Dand	P1-inlet	8.46	21.6	567	164.7
Pond	P2-mid	8.89	22.1	560	168.5



Figure 2.5 Plot of δ^{18} O and δ^{2} H values of springs (green circles) and wells (blue symbols) alongside the global meteoric water line (GMWL) (Craig, 1961), Boise local meteoric water line (LMWL) (Tappa et al., 2016), and Reynolds Creek LMWL. The blue dotted line displays the shallow well (blue squares) trendline extended to the LMWL.

 δ^{18} O and δ^{2} H values distinguished reservoirs across the basin and aquifers within the Summit area (Figure 2.5, Table 2.3). Spring values fell along the Reynolds LWML with a mean

 δ^{18} O value of -15.74 +/- 0.59‰ (ranging from -16.63 to -15.03‰) and mean δ^{2} H value of -119.23 +/- 3.68‰ (ranging from -125.4 to -114.2‰) (Table 2.3). Based on the degree of depletion and depth, we separated Summit wells into shallow (depths from 7.86-27.02 m), intermediate (depths from 63.50-123 m), and deep (171.06-236.43 m) categories (Figure 2.5). Shallow wells had a mean δ^{18} O value of -12.16 +/- 0.604‰ (ranging from -12.92 to -11.56‰) and mean δ^{2} H value of -111.1 +/- 1.653‰ (ranging from -112.8 to -109.4‰). Using Eq. 2.8, we determined that the shallow well samples were about 24.5% evaporated. Intermediate wells had a mean δ^{18} O value of -14.86 +/- 1.146‰ and a mean δ^{2} H value of -124.5 +/- 8.061‰. Deep wells had δ^{18} O values ranging from -16.39 to -13.67‰ (mean of -14.61 +/- 1.54‰) and δ^{2} H values from -133.8 to -117.6‰ (mean of -123.36 +/- 9.01‰). Additionally, we separated GW J from the other shallow wells due to its similarity to the pond samples. GW J had a δ^{18} O value of -12.54‰ and a δ^{2} H value of -104.5‰ while the mean pond values were -12.3 +/- 0.141‰ and -102.8 +/- 0.283‰ respectively. Finally, JD 25 was slightly depleted with a δ^{18} O value of -15.4‰ and a δ^{2} H value of -121.7‰.

	Sample Name	$\delta^{18}O$	$\delta^2 \mathbf{H}$	DIC	$\delta^{13}C\text{-}DIC$	DOC	$\delta^{13}C\text{-}DOC$
	GW 2	-11.81	-110	37.524	-14.18	12.31	-23.35
Shallow	GW 6	-12.35	-112.2	56.774	-14.23	14.79	-23.7
	GW 14	-11.56	-109.4	67.245	-13.12	10.93	-23.66
	GW 16	-12.92	-112.8	55.304	-12.03	13.22	-23.53
	GW J	-12.54	-104.5	68.316	-15.54	2.64	-24.78
Intermediate	GW 35	-15.67	-130.2	49.303	-12.1	0.97	-23.825
Intermediate	GW OD	-14.05	-118.8	65.754	-13.89	14.34	-24.37
	GW 23	-13.67	-117.63	36.141	-13.06	0.4	-24.306
Deep	GW 22	-13.77	-118.7	60.964	-12.86	6.46	-24.29
	GW 25	-16.39	-133.75	46.049	-10.94	0.5	-22.78
	SW 1	-16.63	-125.4	6.66	-20.12	3.97	-25.8
	SW 2	-15.37	-119.2	38.53	-15.34	8.71	-24.39
Saming	SW 3	-16.12	-118.6	4.16	-21	1.45	-23.8
spring	SW 4	-15.38	-117.6	28	-12.03	5.82	-24.28
	SW 5	-15.03	-114.2	22.41	-13.7	5.83	-25.05
	SW 6	-15.9	-120.4	18.6	-16.86	5.22	-25.32
JD	JD 25	-15.4	-121.7	38.18	-13.41	71.06	-28.165
Pond	P1-inlet	-12.2	-102.6	36.59	-10.9	8.05	-25.865
	P2-mid	-12.4	-103	35.38	-10.24	8.375	-26.085

Table 2.3 Isotopic ratios (reported in ‰) and dissolved carbon concentrations (reported in mg/L).

2.4.3 Carbon concentration and isotopes

Compared to the wells, springs had lower DIC concentrations, more negative isotopic ratios (δ^{13} C-DIC), and lower pH values (Table 2.3, Figure 2.6). DIC concentrations for the springs ranged from 4.16-38.53 mg/L, with a mean of 19.73 +/- 12.99 mg/L. Shallow well samples had a mean concentration of 54.21 +/- 12.33 mg/L (ranged from 37.52-68.32 mg/L). Intermediate wells had a mean concentration of 57.53 +/- 11.63 mg/L while deep wells had a mean of 47.72 +/- 12.50 mg/L. GW J had the highest DIC concentration of 68.32 mg/L. JD 25 had a concentration of 38.18 mg/L.

 δ^{13} C-DIC values show more negative values for springs with a mean of -16.51 +/- 3.54‰ (ranging from -21.0 to -12.03 ‰). Shallow wells had δ^{13} C-DIC values ranging from -14.23 to - 12.03‰ with a mean of -13.39 +/- 1.04‰. Intermediate and deep wells were less negative with mean values of -13.00 +/- 1.27‰ and -12.29 +/- 1.17‰ respectively. GW J had the most

negative signature of the Summit wells with -15.54‰. With a δ^{13} C value of -13.41‰, the signature of JD 25 was similar to that of the shallow or intermediate wells.



Figure 2.6 Plot of pH levels versus dissolved inorganic carbon (DIC) concentrations with δ^{13} C-DIC values labelled. Circled values are theoretical initial δ^{13} C-DIC values, and lines represent theoretical paths of carbon evolution (Clark and Fritz, 1997).

All reservoirs showed substantial variation in DOC concentrations (Table 2.3). Springs ranged from 1.45-8.71 mg/L, Summit wells ranged from 0.4-14.79 mg/L, and JD 25 was 71.06 mg/L. Within the Summit area, the shallow wells had a mean of 12.81 +/- 1.62 mg/L while the deep wells had a mean of 2.45 +/- 3.47 mg/L (ranging from 0.4-6.46 mg/L). The intermediate wells ranged from 0.97 (GW 35) to 14.34 (GW OD). GW J had a concentration of 2.64 mg/L.

 δ^{13} C-DOC values were more consistent across reservoirs. Springs had a mean of -24.77 +/- 0.74‰ (ranged from -25.8 to -23.9‰). Shallow wells had a mean of -23.56 +/- 0.16‰,

intermediate wells had a mean of -24.10 +/- 0.29‰, deep wells had a mean of -23.79 +/- 0.88‰, and GW J had a value of -24.78‰. JD 25 had the most negative δ^{13} C-DOC value of -28.17‰.

2.4.5 Cations and anions



Figure 2.7 Piper (1944) diagram displaying aquifer characteristics based on relative ion levels.

Anion concentrations were lower in springs than Summit wells (Figure 2.7, Table 2.4). Springs had a mean NO_3^- concentration of 0.35 +/- 0.226 mg-N/L (ranging from 0.14-0.77 mg-N/L), mean Cl⁻ concentration of 1.52 +/- 0.733 mg/L (ranging from 0.78-2.72 mg/L), mean SO₄²⁻ concentration of 2.18 +/- 1.10 mg/L (ranging from 0.87-3.97 mg/L), and a mean F⁻ concentration of 0.10 +/- 0.066 mg/L (ranging from 0.018-0.2 mg/L). The signature of the shallow wells varied along the flowpath with NO_3^- levels ranging from 0.43-13.12 mg-N/L (mean of 3.66 +/- 0.43-13.12 mg-N/L (mean of 3.66 +/- 5.33 mg-N/L), Cl⁻ levels ranging from 20.40-54.35 mg/L (mean of 36.85 +/- 14.16 mg/L), SO₄²⁻ levels ranging from 29.87-223.17 mg/L (mean of 100.62 +/- 78.32 mg/L), and F⁻ levels ranging from below detection limit (BDL) to 1.04 mg/L (mean of 0.44 +/- 0.25 mg/L). SO_4^{2-} concentrations increased with depth of the well. Intermediate wells had higher mean anion concentrations of 0.425 +/- 0.60 mg-N/L for NO₃⁻, 107.47 +/- 25.59 mg/L for Cl⁻. 280.38 +/- 158.35 mg/L for SO₄⁻, and 0.67 +/- 0.52 mg/L for F⁻. The remaining deep wells had a mean NO₃⁻ concentration of 0.38 +/- 0.57 mg-N/L, Cl⁻ concentration of 31.98 +/- 16.62 mg/L, SO₄²⁻ concentration of 49.50 +/- 24.25 mg/L, and F⁻ concentration of 0.28 +/- 0.25 mg/L. Table 2.4 Concentrations of cations and anions.

	Sample	Nitrate	Chloride	Sulfate	Fluoride	Na	Mg	Ca	К
	Name	(mg-N/L)	(mg/L)	(mg/L)	(mg/L)	(ppm)	(ppm)	(ppm)	(ppm)
Shallow	GW 2	13.12	46.763	74.90	0.52	43.51	49.6*	67.77	2.658
	GW 6	1.50	25.594	45.67	0.49	28.77	40.5*	71.08	0.4153
	GW 14	2.22	20.403	29.87	-	42.85	23.6	57.1	0.9998
	GW 16	0.43	54.349	129.50	0.60	182*	30.88	60.05	1.077
	GW J	1.03	37.155	223.17	0.61	143*	27.6*	74.5*	1.552
Tertoneralista	GW 35	0.85	125.57	168.41	1.04	220.5	9.364	24.14	1.395
Intermediate	GW OD	-	89.377	392.35	0.30	249.5	17.04	74.07	1.86
	GW 23	1.04	12.795	22.73	0.46	86.63	0.7925	3.834	1.246
Deep	GW 22	0.075	42.154	69.99	0.38	106.3	1.812	14.83	0.9166
	GW 25	0.022	40.984	55.79	-	137.2	0.5755	7.109	0.8739
	SW 1	0.26	0.9725	1.72	0.15	5.075	0.9296	3.011	3.709
	SW 2	0.21	2.7178	3.97	0.062	14.17	7.179	39.66	2.814
Spring	SW 3	0.77	0.7789	0.87	0.018	3.755	0.3159	1.351	1.409
spring	SW 4	0.29	1.0398	1.98	0.11	10.31	13.81	19.25	1.742
	SW 5	0.14	1.7727	1.59	0.20	10.42	8.371	13.9	1.277
	SW 6	0.41	1.8521	2.93	0.073	9.518	5.68	12.58	1.313
Л	JD 25	0.024	112.32	1075.98	-	546.91	8.9311	65.907	8.0548
Dond	P1-inlet	0.0076	22.552	78.64	-	60.014	17.12	25.619	4.0296
rona	P2-mid	0.42	19.12	72.85	0.59	58.465	16.962	26.534	3.9126
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The signature of JD 25 varied by ion but most closely reflected the intermediate Summit well signature (Figure 2.7, Table 2.4). JD 25 had a low NO_3^- concentration of 0.024 mg-N/L, similar to the deep wells, but had a high Cl⁻ concentration of 112.32 mg/L, similar to the intermediate wells. Additionally, JD 25 had the highest concentration of SO_4^{2-} of 1075.98 mg/L. F⁻ concentration for JD 25 was BDL. The pond samples varied in NO_3^- with a mean of 0.21 +/-

0.29 mg-N/L and in F⁻ with a mean of 0.30 +/- 0.42 mg/L. Concentrations of Cl⁻ and SO₄²⁻ were more consistent with means of 20.84 +/- 2.43 mg/L and 75.75 +/- 4.09 mg/L, respectively.

Cations varied by ion and reservoir (Figure 2.7, Table 2.4). Springs had lower but highly variable levels of Na⁺ (mean of 8.87 +/- 3.84 ppm), Mg²⁺ (mean of 6.05 +/- 5.02 ppm), Ca²⁺ (mean of 14.96 +/- 13.88 ppm), and K⁺ (mean of 2.04 +/- 1.00 ppm). Shallow wells had a mean Na⁺ concentration of 88.03 +/- 69.62 ppm (ranging from 28.77-182 ppm), Mg²⁺ concentration of 34.44 +/- 10.53 ppm (ranging from 23.6-49.6 ppm), Ca²⁺ concentration of 66.1 +/- 7.34 ppm (ranging from 57.1-74.5 ppm), and K⁺ concentration of 1.34 +/- 0.84 ppm (ranging from 0.42-2.66 ppm). Intermediate wells had the highest Na⁺ levels of the Summit wells with a mean concentration of 13.20 +/- 5.43 ppm, mean Ca²⁺ concentration of 49.11 +/- 35.31 ppm, and mean K⁺ concentration of 1.63 +/- 0.33 ppm. The deep wells had a mean Na⁺ concentration of 110.04 +/- 25.49 ppm, Mg²⁺ concentration of 1.06 +/- 0.66 ppm, Ca²⁺ concentration of 8.59 +/- 5.65 ppm, and K⁺ concentration of 1.01 +/- 0.20 ppm.

Cation concentrations for JD 25 were similar to the intermediate or shallow wells. JD 25 had a Mg^{2+} concentration of 8.93 ppm, Ca^{2+} concentration of 65.91 ppm, and a K⁺ concentration of 8.05 ppm. Interestingly, JD 25 had the highest levels of Na⁺ with a concentration of 546.91 ppm. The signature of the pond samples was distinct with a mean Na⁺ concentration of 59.24 +/- 1.10 ppm, Mg^{2+} concentration of 17.04 +/- 0.11 ppm, Ca^{2+} concentration of 26.08 +/- 0.65 ppm, and K⁺ concentration of 3.97 +/- 0.08 ppm. Additional cations and REE were reported in Appendix B.

Placement on a trilinear plot of the ions highlighted the dominant ions (Figure 2.7). Springs had high levels of HCO₃⁻ but varied across the other ions. Shallow wells also varied across the anions with a slight shift towards HCO_3^- . In particular, GW J had a mixed signature, similar to the pond samples. The intermediate wells had higher levels of Na⁺ and lower levels of HCO_3^- compared to the shallow wells. Deep wells had the highest levels of Na⁺ and higher levels of HCO_3^- than the intermediate wells. Finally, JD 25 was dominated by SO_4^{2-} and Na⁺.

We calculated charge balance and charge balance error to determine the accuracy of our geochemical results (Table 2.5). Most of the samples fell within 5% error with adjustments such as the addition of various anions or substituting a calculated HCO_3^- concentration for DIC. For the samples calculated with DIC, we assumed a charge of -1 because the pH of the wells indicated the carbon in this system was dominantly HCO_3^- . The samples with >5% error were GW 16 (15.82% error), a shallow well with high levels of Na⁺, and SW 3 (-12.14% error), a spring with low levels of Na⁺. Additionally, SI were estimated with Aqion (Table 2.5). Samples with >5% error based on charge balance calulcations and pond samples were not included in the Aqion calculations or models. The wells had positive SI for calcite indicating calcite saturation. Shallow wells ranged from 0.188-0.567, intermediate wells ranged from 0.044-0.503, deep wells ranged from 0.462-0.654, and JD 25 was 0.415. Interestingly, GW J had a negative calcite SI along with the springs indicating ongoing calcite dissolution.

Table 2.5 Charge balance calculations and estimated calcite saturation indices (SI) from Aqion v.7.4.2 (https://www.aqion.de/).

	Sample Name	Cations (mol/l)	Anions (mol/l)	CBE (%)	Additional Anions	Calcite SI	pCO ₂
Shallow	GW 2*	9.42E-03	8.57E-03	4.74	+F,NO3,Br	0.21	2.25
	GW 6*	8.14E-03	7.73E-03	2.59	+F,NO3	0.188	2.02
	GW 14	6.93E-03	6.96E-03	-0.20	+NO3	0.567	2.46
	GW 16	1.35E-02	9.80E-03	15.82	(F,NO3,Br)	-	-
	GW J*	1.22E-02	1.29E-02	-2.52	-	-0.295	1.57
Intermediate	GW 35*	1.16E-02	1.15E-02	0.55	-	0.044	2.55
Intermediate	GW OD	1.62E-02	1.62E-02	-0.02	+F	0.503	2.46
	GW 23	4.06E-03	3.94E-03	1.44	+F,NO3	0.462	4.1
Deep	GW 22	7.44E-03	7.72E-03	-1.89	-	0.654	3.02
	GW 25	6.39E-03	6.15E-03	1.91	+NO3	0.49	3.6
	SW 1	6.29E-04	6.36E-04	-0.61	+NO3	-3.56	2.21
	SW 2	3.26E-03	3.37E-03	-1.65	-	-0.691	1.95
Santa a	SW 3	3.03E-04	3.86E-04	-12.14	(-)	-	-
spring	SW 4	2.59E-03	2.43E-03	3.13	+F,NO3	-1.28	2.02
	SW 5	2.59E-03	2.43E-03	0.83	+F,NO3	-1.86	1.83
	SW 6	1.65E-03	1.66E-03	-0.28	-	-2.81	1.62
Л	JD 25	2.80E-02	2.87E-02	-1.28	-	0.415	3.01
Dond	P1	5.31E-03	5.32E-03	-0.11	-		
FOID	P2*	5.36E-03	5.37E-03	-0.02	+F,NO3		

*Uses HCO3⁻ (calculated from carbonate alkalinity using Geochemists Workbench) instead of DIC

2.4.6 Statistical analyses

T-tests results based on environmental parameters showed significant differences between the springs and Summit wells. P-values were 0.00066 for pH, 0.039 for temperature, 0.00014 for electrical conductivity, and 0.00047 for alkalinity.



Figure 2.8 Results of principal component analysis showing groupings of wells by relative depths (shallow, intermediate, deep) and potential mixing.

Results of PCA confirmed the differentiation among the Summit wells. Component 1 separated the shallow and deep wells, while Component 2 distinguished the intermediate wells.

2.5 DISCUSSION

In this study, we used field parameters, carbon and ion concentrations, and various isotopes to identify sources of carbon and water, evaluate the evolution of carbon through the subsurface, and interpret aquifer properties. Here we interpreted that the springs were 1) undergoing calcite dissolution, 2) sourced from snow-dominated, high elevation areas, and 3) evolved in alkali-rich environments. Additionally, we found that the wells accessed aquifers that were 1) evolved from sources similar to the springs, 2) calcite saturated to the point of precipitation, and 3) weathering basalts by dissolving plagioclase and pyroxene minerals.

2.5.1 Sources of water

 δ^{18} O and δ^{2} H values of the groundwater samples were more negative along the GMWL, Boise LMWL, and Reynolds LMWL indicating a snow-dominated area of recharge (Figure 2.5). Based on the climate gradient in RCEW, these samples were recharged in the higher elevations. Consistent with our findings, previous groundwater studies in semi-arid regions, such as Eastoe and Wright (2019), interpreted samples with more negative $\delta^{18}O$ and $\delta^{2}H$ values as predominantly recharged at higher elevations by winter precipitation. Three groundwater samples collected by Radke et al. (2019) from wells at Reynolds Mountain East (RME), the highest elevation in the basin, displayed similar negative values consistent with our interpretations of the recharge sources.

We found that the springs plotted along the Reynolds LMWL meaning the spring waters were similar to the source precipitation. This would indicate the springs emerged from shallow, less evolved aquifers. Additional RCEW springs analyzed by Warix (Personal communication, 2020) and streams analyzed by Lohse (personal communication, 2021) followed this trend by plotting along the LMWL. The shallow wells (depths <31m) evolved from sources similar to the springs (Figure 2.9). Interestingly, GW J plotted closer to the pond samples than the shallow well samples. This supports our hypothesis that the irrigation pond is influencing the GW J geochemical signature. The deviation of the pond and GW J samples from the LMWL could be attributed to evolution from surface waters— 11.8% evaporated (Figure 2.9).



Figure 2.9 Plot of δ^{18} O and δ^{2} H values for shallow wells and springs alongside potential sources from the Reynolds Creek basin including additional springs (Warix, Personal communication, 2020), pond samples, stream waters, and Reynolds Mountain East (RME) wells (Radke et al., 2019).

The intermediate and deep wells had a distinct, more negative signature compared to the shallow wells. Divergence from the Reynolds LMWL was interpreted as the influence of paleowaters. When compared to paleowaters identified by Schlegel et al. (2009) in the nearby

Idaho Batholith, we found that the intermediate and deep wells had a similar signature and followed a similar slope (Figure 2.10). The placement of JD 25 could be interpreted as modern or paleowater and therefore, will be discussed further in Chapter 3.

With a changing climate, sources will transition from snow-dominated to become raindominated with implications for the signature of the springs and shallow aquifers (Oki and Kanae, 2006; Klos et al., 2014). Because the shallow aquifers were recharged in higher elevations leading to negative isotopic ratios, we predict the waters will shift towards less negative values in response to the climate transition. As seen with GW J, shallow aquifers are vulnerable to anthropogenic influence (Bates et al., 2011). If agricultural practices in RCEW increase the use of irrigation ponds, more wells could be impacted leading to a positive shift in δ^2 H and δ^{18} O. Deeper wells, supplied by paleowaters, are disconnected from the climate and therefore, exempt from these influences but not renewable for use. These interpretations will be further discussed in Ch. 3.



Figure 2.10 Plot of δ^{18} O and δ^{2} H values for deep and intermediate wells alongside known paleowaters reported in Schlegel et al. (2009). Dotted blue line shows trendline for paleowaters projected out to Summit well samples.

2.5.2 Carbon evolution

As expected, spring samples expressed low DIC and δ^{13} C-DIC values (Figure 2.6, Figure 2.11) indicating ongoing calcite dissolution. More negative δ^{13} C-DIC values relative to well samples indicate evolution under open-system conditions and interaction with the vadose zone.

Based on δ^{13} C-DIC values, the main source of DIC in the springs was from soil CO₂, but waters had begun to react with solid carbonates in a shallow, unconfined aquifer (Han et al., 2012).

In contrast, well samples had high DIC concentrations and pH values (Figures 2.6 and 2.11) which were interpreted as saturated in calcite based on the relationship between calcite dissolution and water pH (Eq. 2.3). Less depleted δ^{13} C-DIC indicates development under closed-system conditions in a fully saturated, confined aquifer (Han et al., 2012). While the δ^{13} C-DIC and δ^{13} C-DOC values indicate some of carbon was originally sequestered by C3 plants, the majority of the inorganic carbon was sourced from weathering of soils and bedrock with values <19‰ (Clark and Fritz, 1997; Pearson and Hanshaw, 1970; Cartwright et al., 2020).

With increasing atmospheric temperatures, groundwaters recharged by modern waters will become warmer, increasing soil and bedrock weathering (White and Blum, 1995). In response, springs would display a shift towards calcite saturation, and shallow aquifers could reach supersaturation leading to an increase in the precipitation of calcite.



Figure 2.11 Comparison of dissolved inorganic carbon (DIC) concentrations and isotopes depicts degree of carbon evolution by estimating system conditions.

2.5.3 Aquifer properties

Based on characteristics defined by Piper (1944), ion concentrations of groundwater samples portrayed alkali-rich to mixed environments. Springs evolved in alkali-rich environments under open-system conditions suggesting an unconfined, shallow aquifer. Shallow wells accessed aquifers that evolved in mixed environments. Because of a slight alkaline signature, high levels of DIC, and positive calcite SI (Figures 2.6, 2.7, and 2.11), we interpreted that the shallow aquifer continued evolution after calcite saturation under closed-system conditions. Intermediate and deep wells presented alkali-rich to saline aquifers with high levels of Na⁺ and carbon (Figure 2.7). Intermediate wells showed more of a mixed signature compared to the deeper wells. JD 25 represented a unique aquifer with high levels of SO_4^{2-} and Na^+ . While distinct from the Summit wells, this signature was closest to that of the intermediate wells (Figure 2.7). We compared our results to Rattray (2015) who examined the geochemical signature of groundwaters in eastern Idaho (Figure 2.12). Interestingly, one deep well was similar to our deep well samples with high levels of Na^+ , HCO_3^- , and SO_4^{2-} . Gastmans et al. (2016) found samples with similar signatures in basaltic aquifers and interpreted as a higher degree of weathering (Figure 2.12).



% meq/kg

Figure 2.12 Piper (1944) diagram displaying aquifer characteristics based on relative ion levels of groundwater samples alongside relative levels reported in previous studies (Rattray, 2015; Gastmans et al., 2016).

We propose deep groundwater can result in substantial bedrock weathering (Rattray, 2015; Gastmans et al., 2016). In response to climatic changes, temperatures of shallow aquifers, recharged by modern waters, are predicted to increase which could lead to an increase in bedrock weathering (Oki and Kanae, 2006; White and Blum, 1995). Additionally, as agricultural practices respond to the changing climate, shallow aquifers are vulnerable to anthropogenic influence. Similar to GW J, inputs from irrigation ponds would cause an increase in contaminants such as nitrates, salts, and various metals (Böhlke, 2002; Bates et al., 2011).

2.5.4 Geochemical modeling

Combining our newfound understanding of the aquifer's geochemistry and previous knowledge of dominant minerals in the basalt, we ran various geochemical models with NETPATHXL to determine which minerals were likely driving the geochemical evolution through dissolution or precipitation (Appendix C). In the Summit area, we found that the aquifers were likely precipitating calcite and various clays (Ca-mont, Mg-mont) and dissolving plagioclase and pyroxene (Gastmans et al., 2016). This is consistent with previous studies that found the geochemical evolution of basaltic aquifers was driven by bedrock weathering, specifically the dissolution of plagioclase and pyroxene minerals (Gastmans et al., 2016). When modeling the geochemical evolution from the springs to the Summit wells, we found that the clays were dissolving while calcite was precipitating in small amounts. These results provide further evidence of the evolution from unconfined aquifers undergoing calcite dissolution towards the confined aquifers saturated in calcite. Finally, we ran multiple models to test sources of and mixing within intermediate wells and found both wells were a mix of the shallow and deep signatures. Consistent with PCA results, the deep aquifers contributed more to GW 35 while the shallow aquifer supplied more to GW OD.

2.5.5 Future work

Sampling was limited by the wells still intact and running since drilling in the 1960s. Further drilling and sampling in RCEW are required, specifically towards the lower basin at intermediate depths to expand our dataset and improve our understanding of the intermediate signature. Additionally, sampling throughout the year would allow for examination of seasonal variation. Continued collection and analysis of precipitation samples, especially snow samples, would further define the Reynolds LMWL.

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2.6 CONCLUSIONS

Consistent with our hypotheses, we found the springs emerged from shallow aquifers undergoing calcite dissolution under open-system conditions. Wells accessed calcite saturated aquifers that evolved under closed-system conditions by weathering plagioclase and pyroxene minerals in the basalt while precipitating calcite. While shallow wells were recharged by modern waters, intermediate and deep wells reflected a paleo signature. We predict the changing climate will affect shallow aquifers by increasing temperatures leading to a change in the type of source precipitation and an increase in bedrock weathering. Additionally, shallow aquifers are vulnerable to anthropogenic influence such as agricultural contaminants. Disconnected from the climate, deeper aquifers will not be affected by the changing climate but are not sustainable for use. Groundwaters, especially deeper aquifers, are sequestering carbon, precipitating calcite, and could aid in the mitigation of climate change if not overused.

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Chapter 3: Mapping the spatial and temporal flow of groundwater in a semi-arid basin: A geophysical and geochemical approach

3.1 ABSTRACT

Understanding the spatial and temporal flow of groundwater through the subsurface is critical to predict the areas vulnerable to the effects of climate change. In this study, we analyzed groundwater samples from wells along a longitudinal transect and springs throughout the basin for environmental and age tracers including carbon concentrations (DIC, DOC) and various isotopes (δ^{13} C-DIC, δ^{13} C-DOC, ³H, ¹⁴C-DIC). We found that the springs had the shortest residence times (<30 years) evident from detectable tritium. Wells accessed aquifers that ranged from tritium-rich (4.1 TU) to tritium-dead (0.08 TU). Geophysical borehole logs-fluid temperature, fluid conductivity, gamma, and calipers— confirmed three distinct flowpath depths along the well transect as well as a hydrothermal gradient beginning at 20m depth. Deep wells accessed two deep, older flowpaths— tritium-dead with low percent modern carbon (<57 pmc) and high temperatures (>16.5°C). In comparison, the shallow wells accessed a single, younger flowpath with detectable tritium. Finally, the intermediate wells accessed the shallow flowpath allowing for tritium detection and one of the deeper flowpaths resulting in low percent modern carbon. In comparison to the shallow aquifers accessed by the springs and shallow wells, the deeper aquifers are temporally variable and large stores of carbon due to longer residence times.

3.2 INTRODUCTION

Groundwater is a major reservoir for freshwater and carbon especially in semi-arid regions (Stephenson and Zuzel, 1981; Clark and Fritz, 1997; Meredith et al., 2017). Globally, an estimated 22.6 million km³ of water (Gleeson et al., 2015) and 1404 Pg C (Monger et al., 2015) are stored in aquifers. Storage and fluxes of water and carbon in groundwater systems remain

uncertain because residence times, the length of time the water or carbon is in the subsurface, can vary a few to tens of thousands of years (Monger et al., 2015). In addition, with a changing climate, temperatures are rising and precipitation inputs are changing (Oki and Kanae, 2006). In particular, snow-dominated catchments, like the Snake River Plain, are projected to transition to rain-dominated by 2050 (Klos et al., 2014). This transition from snow to rain will alter the timing and amount of precipitation with implications for recharge to groundwater (Taylor et al., 2013; Lindquist et al., 2019). Finally, aquifers with shorter residence times are more sustainable for daily use but vulnerable to climatic changes (Salahat et al., 2014). Determining the residence times and evolution of groundwater and carbon is essential to further develop our understanding of the flow of water and carbon through the subsurface (Viviroli et al., 2011). Understanding the architecture of the subsurface and timing of groundwater recharge allows for prediction of vulnerable areas.

Groundwater flow is defined by the architecture of the subsurface, specifically the type and length of flowpath (Markovich et al., 2019). Preferential flowpaths depend on sources, recharge rate, lithology, fracture density, and other aquifer properties (Johnson et al., 2000). Shallow aquifers with shorter residence times generally flow along local flowpaths. Local flowpaths often emerge as springs or as an input to surface waters because of intersection with faults, geologic contacts, or a change in geomorphology such as the exposure of a fractured layer (Springer and Stevens, 2009). Intermediate flowpaths describe deeper and older aquifers. The deepest aquifers with the longest residence times are known as regional flowpaths. Because of the longer residence times, regional flowpaths are often the most equilibrated geochemically with bedrock (Johnson et al., 2000). To map the subsurface flowpaths and enhance interpretations of geochemical data, previous studies used geophysical imaging and borehole

logging (Clair et al., 2015; Radke et al., 2019). For example, geophysical measurements and geochemical analyses have been used to evaluate the storage and flow of deep groundwater in sub-humid to sub-arid regions (White et al., 2019). Additionally, geophysical techniques are used to identify sites with geothermal potential (Kessler et al., 2017; Lachmar et al., 2019).

Previous studies have used carbon isotopes and other environmental tracers to estimate residence time and system conditions (Bates et al., 2011; Brown et al., 2011; Carlson et al., 2011; Meredith et al., 2017). Groundwater age dating methods produce a single age which can be interpreted as a proxy for residence time, but this age often does not accurately reflect the system (Bethke and Johnson, 2008). Aquifers can consist of a mixture of waters from different sources, such as modern recharge mixing with paleowaters (Clark and Fritz, 1997; Bethke and Johnson, 2008; Han and Plummer, 2016). Age dating techniques— radiocarbon (¹⁴C), tritium (³H), and chlorofluorocarbons (CFCs)— each have advantages and errors associated with the calculations and assumptions (Bethke and Johnson, 2008). Because of the spatial and temporal variability of carbon and groundwater in semi-arid to arid regions, there is a high degree of uncertainty in residence time calculations, especially with ¹⁴C (Love and Zdon, 2018). Han and Plummer (2016) reviewed models for calculating ¹⁴C ages and developed a graphical method (Han et al., 2012) to choose a model to accurately calculate ¹⁴C ages based on system conditions.

Many studies use a combination of environmental and age tracers to investigate evolution of carbon in groundwater (Han et al., 2012; Meredith et al., 2016; Meredith et al., 2017). Combining ¹⁴C and ³H with carbon concentrations and isotopes allows for interpretation of system conditions of aquifers undergoing calcite dissolution (Cartwright et al., 2013). In semiarid climates, dissolved carbonates and residence times often correlate with aquifer depths (Bates et al., 2011). Age tracers (¹⁴C, ³H, and CFCs), stable isotopes of water, and ionic concentrations

can distinguish modern waters vulnerable to anthropogenic influence and deeper, nonrenewable paleowaters (Vengosh et al., 2002; Schlegel et al., 2009; Brown et al., 2011; Currell et al., 2012).

In this study, we aimed to evaluate the movement of carbon through the subsurface using geochemical and geophysical techniques to develop a conceptual model of the architecture of the subsurface groundwater environment and calculating groundwater residence times. We conducted this study in a semi-arid basin, the Reynolds Creek Experimental Watershed (RCEW) and Critical Zone Observatory (CZO), located in Owyhee County in southwest Idaho, USA (Figure 3.1).



Figure 3.1 Map of Reynolds Creek basin with bedrock geology (Bonnichsen and Godchaux, 2006) and well locations.

The focus of RCEW and research by the USDA Agricultural Research Service (ARS) has been to monitor and study the cycles of water and carbon, yet their residence times— the length of time in the subsurface— remain uncertain. Stephenson (1965, 1973) created a map of the piezometric surface using water levels and well depths describing groundwater flow direction as east to west in the northeast region of RCEW. Stephenson and Zuzel (1981) studied the characteristics of recharge in the basaltic aquifer and found recharge varied spatially and temporally; they calculated the mean groundwater recharge rate to be about 2.4 m/yr during ideal conditions such as high precipitation. To our knowledge, no studies in RCEW have used geochemical tracers to understand the groundwater subsurface or estimate residence times of water and carbon.

We sought to fill the gap in knowledge of the carbon bible through the subsurface, specifically temporal variation by collecting and analyzing groundwater samples from research wells and springs for geochemical tracers as well as performing borehole geophysical logging. Wells were sampled along a hypothesized east-west flowpath in the northeastern portion of the basin. Springs were sampled at higher elevations across the basin. We analyzed the groundwater for a variety of environmental and age tracers to interpret and understand the evolution and residence time of water and carbon through the groundwater. Geophysical borehole logs were used to visualize the subsurface by identifying fractured layers and depths of inflow. We hypothesized that the springs would evolve in relatively young, unconfined aquifers and vary in geochemistry reflecting the dominant bedrock. We also hypothesized that the groundwater wells would access multiple aquifers, flowing along highly fractured layers of basalt, that would vary in age and bedrock source based on depth. Deeper wells would access older, confined aquifers

that evolved over the course of a few hundred years and in contact with the granitic basement rock.

3.2.1 Geochemistry background

Aquifers with longer residence times reflect the geochemical signature of the bedrock while shorter flowpaths correspond to the source (Johnson et al., 2000). Environmental tracers, such as strontium (⁸⁷Sr/⁸⁶Sr) and uranium (²³⁴U/²³⁸U) isotopes, are used to evaluate these waterrock relationships, identify dominant bedrocks, and ascertain flowpaths (Clark and Fritz, 1997; Johnson et al., 2000; Santoni et al., 2016). For example, basaltic aquifers have ⁸⁷Sr/⁸⁶Sr values around 0.705 while granitic aquifers have ⁸⁷Sr/⁸⁶Sr values around 0.707 (Shoemaker and Hart, 2002; Benford et al., 2010). While less commonly used, ²³⁴U/²³⁸U isotopes are important for assessing geochemical evolution and distinguishing flowpaths because activity ratios are influenced by ages, rock type, and geochemical reactions (Roback et al., 2001; Grabowski and Bem, 2012). For example, ²³⁴U/²³⁸U isotopes identify preferential flowpaths when correlated with depth (Roback et al., 2001).

Environmental age tracers are used to estimate residence times and recharge rates in groundwaters (Bethke and Johnson, 2008; Cartwright et al., 2017; Cartwright et al., 2020). Because ¹⁴C is radiogenic and decays, with a half-life of around 5700 +/- 30 years, carbon ages can be calculated and used as proxies for relative groundwater age based on the measured ¹⁴C levels, estimated initial ¹⁴C, and the isotopic ratios ¹³C/¹²C reported in δ notation (δ ¹³C) (Eq 3.1) (Han et al., 2012).

Eq 3.1
$$\delta^{13}C_{sample} = \left(\frac{\binom{(1^3C/1^2C)_{sample}}{(1^{13}C/1^{12}C)_{reference}}} - 1\right) \times 1000 \% V - PDB$$

As the half-life of ¹⁴C is large, ³H and CFCs are used to estimate ages and residence times of younger waters. Starting in 1951, large amounts of ³H were released into the atmosphere from nuclear bomb testing (Clark and Fritz, 1997). Because of its short half-life of 12.32 years, water ages are calculated based on the levels of detectable tritium in the water. CFCs are anthropogenic contaminants that have been released since the 1940s and accumulated in the atmosphere (Clark and Fritz, 1997). Similar to ³H, CFCs are used to estimate water ages based on the concentration levels (Clark and Fritz, 1997).

3.2.2 Site description

The RCEW was established in 1960 to monitor and investigate the soil, vegetation, and water within the basin (Kormos et al., 2018; Seyfried et al., 2018). The Reynolds Creek runs north through the 238 km² basin and across an elevation gradient of 2244 m to 1100 m. The Reynolds Creek Critical Zone Observatory (CZO) was established in 2014 in collaboration with the ARS with a special interest in the movement of carbon through the critical zone (Seyfried et al., 2018). The ARS had monitored over a hundred precipitation and climate stations and stream gauges throughout the basin and compiled extensive data collected since 1960 including mean annual precipitation (ranging from 200mm in the low elevations to 1140mm in the high elevations) and mean annual temperature (7.8°C) (Kormos et al., 2018). The dominant geology is comprised of volcanic rocks, specifically olivine-rich basalts, andesite tuffs, and granitic basement rock (McIntyre, 1972).

3.3 METHODS

3.3.1 Sampling design overview

The northeastern portion of RCEW, the lower basin and Summit sub-basin has a unique east to west flow direction. Groundwater flow direction was established based on 41 wells drilled

in the 1960s by creating a piezometric surface from water table elevations using ordinary kriging in ArcGIS Pro with a spherical model (Figure 3.2). The elevation of the water table was determined from modern depth to water measurements using a Solinst (Georgetown, Ontario, Canada) flat taped water level meter and original water levels obtained from drill logs.



Figure 3.2 Piezometric surface mapped using ordinary kriging method in ArcGIS Pro v. 2.8 (ESRI, California, USA) with static water level measurements from sampled Summit wells in 2019 overlain on bedrock geology (Bonnichsen and Godchaux, 2006). Additional static water levels were obtained from original drill logs for private, Idaho Department of Water Resources (IDWR), and additional Summit wells (Stephenson, 1965, 1973).

Because of the western flow direction, we chose to sample wells along an ideal east-west transect. We chose to sample seven monitoring wells, one artesian well, and two domestic wells (Figure 3.3). Springs were sampled in the higher elevations to understand the evolution of groundwater from hypothesized source waters towards the lower elevation Summit wells. Six flowing springs were identified by satellite imagery and ground truthing (Figure 3.3). Finally, JD 25 was sampled to provide insight into groundwater in other regions of the basin.



Figure 3.3 Map of sampling sites with bedrock geology (Bonnichsen and Godchaux, 2006).

3.3.2 Groundwater sampling

Groundwater samples were collected during the summer and fall of 2019 from seven research wells, one artesian well, two domestic wells, six springs, and the shallow JD well (JD 25) (Figure 3.3). We measured water level for each of the research wells using a Solinst (Georgetown, Ontario, Canada) flat taped water level meter. We determined the total depth of wells using original drill logs, water level meter, and caliper logs (Table 3.1).

	Sample Name	Sample Date	Easting	Northing	Elevation (m)	Well Depth (m)	Depth to Water (m)	Casing Depth (m)	Pump
Shallow	GW 2	7/25/19	523614	4788933	1266	27.02	8.16	9.4	1
	GW 6	7/24/19	523221	4788699	1238	7.86	3.15	7.86	1
	GW 14	7/23/19	522772	4788238	1219	9.98	5.62	9.98	1
	GW 16	7/22/19	521692	4788269	1167	13.5	4.76	5.5	1
	GW J	9/6/19	520324	4788320	1130	30.5	11.84	30.5	-
Intermediate	GW 35	9/5/19	520851	4788402	1140	63.50	9.44	1.4	2
	GW OD	7/24/19	520568	4788394	1131	123	3.90	123	-
Deep	GW 23	10/3/19	523800	4788268	1286	171.06	4.17	5	2
	GW 22	7/22/19	521393	4788114	1157	236.43	0	236.43	-
	GW 25	10/17/19	520902	4788394	1140	192.68	20.46	85	2
Spring	SW 1	8/5/19	512226	4788145	1734	-	-	-	-
	SW 2	8/5/19	515853	4782301	1516	-	-	-	-
	SW 3	8/6/19	519811	4768306	2056	-	-	-	-
	SW 4	8/6/19	521321	4772133	1851	-	-	-	-
	SW 5	8/6/19	521451	4771901	1882	-	-	-	-
	SW 6	8/6/19	524206	4775866	1780	-	-	-	-
Л	JD 25	10/8/20	518217	4774475	1498	25	2.78	25	3

Table 3.1 Sampling locations and well descriptions

¹Geotech (Denver, CO, USA) 1.66 Reclaimer (positive air displacement pump)

²Hallmark Industries (Streamwood, IL, USA) 3.3" Deep Well Submersible Pump

³Proactive Environmental Products (Hamilton, NJ, USA) Stainless Steel Monsoon XL Pump

Wells were purged three pore volumes with a deep well submersible pump (Table 3.1). Assuming everyday use, we only purged the domestic wells one pore volume. No purging was necessary for the artesian well and springs. We purged JD 25 once a week for over a month before sampling to allow the aquifer to re-equilibrate after the well installation. Pore volumes were calculated using the radius of the well casing and the height of water in the well (Eq 3.2).

Eq 3.2 Pore Volume
$$(m^3) = \pi * (Radius(m))^2 * (Height of Water (m))$$

The radius of the well was calculated by reviewing the original drill logs and measuring the diameter of the casing at ground level. Height of water was calculated by subtracting water level from the total depth of the well.

While purging the wells, we monitored environmental parameters, including pH, temperature, and electrical conductivity. The pH and temperature were measured with an Oakton (Vernon Hills, Illinois, US) Handheld pH and Temperature Meter. The meter uses a 3-point calibration (4.01, 7.00, 10.00) to obtain a +/- 0.01 pH accuracy. Electrical conductivity was measured with YSI (Yellow Springs, Ohio, US) Model 30 Handheld Conductivity and Temperature Meter. The meter was calibrated with a 500 μ S/cm solution to ensure +/- 0.5% accuracy. The meters were calibrated before purging the wells.

After field characteristics stabilized, we collected three and a half liters of sample to be refrigerated immediately and filtered within 24 hours. Additionally, we collected two 500 mL samples in new or pre-conditioned clear HDPE bottles for tritium analysis. Sampling bottles were pre-conditioned by leaching with MilliQ deionized water for 24 hours. When sampled, each bottle was rinsed three times with the sample before being filled with no headspace and refrigerated. Within 24 hours of collection, samples were measured for alkalinity using a Hanna Instruments (Woonsocket, Rhode Island, US) Total Alkalinity Mini Titrator and filtered for analyses. The alkalinity titrator has a +/- 1 mg/L accuracy after calibration with Total Alkalinity Calibration Standard (HI 84531-55). In brief, the Titrator calculates alkalinity based on the amount of Total Alkalinity Titrant (HI 85531-50) needed to acidify the sample.

3.3.3 Environmental tracers

Samples were analyzed for a range of environmental tracers including 87 Sr/ 86 Sr, 234 U/ 238 U, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), 513 C-DIC, and

δ¹³C-DOC. ⁸⁷Sr/⁸⁶Sr, and ²³⁴U/²³⁸U were hand filtered through 0.45µm Whatman Puradisc nylon syringe filters and analyzed on an IsotopX Limited (Middlewich, Cheshire, UK) Phoenix X62 Thermal Ionization Mass Spectrometer at the Isotope Geology Laboratory at Boise State University. 50mL samples for Sr and U analysis were preserved with 6 drops of concentrated nitric acid. Isotopic ratios were reported with one and two sigma errors.

DIC and DOC samples were hand filtered through 0.45µm Whatman Puradisc nylon syringe filters, and δ^{13} C samples were hand filtered through 0.2µm Whatman Puradisc nylon syringe filters. DIC and DOC concentrations were measured by the Lohse Soil and Biogeochemistry Laboratory (LSB) at Idaho State University (ISU) using a Shimadzu Corporation (Kyoto, Japan), TOC-V CSH. Percent error was less than 2% for Shimadzu. Additional DIC samples were analyzed at the Arizona Laboratory for Emerging Contaminants at the University of Arizona using a Shimadzu Corporation (Kyoto, Japan) TOC-L, and additional DOC samples were analyzed at the Environmental Analytical Agency at Brigham Young University in Provo, UT. All samples were reported as mg/L with standard deviation. ¹³C-DIC was measured using a Thermo Scientific (Bremen, Germany) GasBench system interfaced to a Delta V Plus IRMS and ¹³C-DOC was measured using a Xylem Analytics (College Station, Texas, US) O.I. Analytical Model 1030 TOC Analyzer at the Stable Isotope Facility (SIF) at University of California, Davis. ¹³C values were reported in per mille (‰) relative to the international standard, Vienna PeeDee Belemnite (V-PDB). SIF reported long-term standard deviation of 0.1 for 13 C-DIC and an accuracy of +/- 0.4‰ for 13 C-DOC.

3.3.4 Geologic and geophysical techniques

To further our understanding of the system, we used field observations, such as ground truthing the geologic boundaries and collecting rock samples, to develop a longitudinal and

elevational transect and begin mapping the subsurface groundwater environment. In addition, we used geophysical borehole logging techniques to investigate the physical characteristics of the aquifers. Borehole logging provided geophysical measurements that were used to interpret aquifer characteristics such as permeability and porosity of the bedrock (Hearst et al., 2000). We use a Mount Sopris Instruments (Denver, Colorado) MATRIX QL40 data acquisition system with a 500 m winch to collect all geophysical measurements. To estimate the depth of inflow, we measured fluid temperature and conductivity with a Mount Sopris Instruments (Denver, Colorado) QL40-FTC probe and spectral gamma with a Mount Sopris Instruments (Denver, Colorado) QL40-SGR probe. To find highly fractured layers, we used borehole caliper logs measured with a Mount Sopris Instruments (Denver, Colorado) QL40-Cal probe to highlight the true diameter and condition of the wells. We used WellCAD Reader (Version 5.3) to visualize and interpret geophysical borehole logs. Finally, we compared rock descriptions and inflow depths to historic drill logs to confirm our findings and generate a conceptual cross section of the subsurface groundwater environment.

3.3.5 Age tracers

To estimate residence times, samples were analyzed for ³H and ¹⁴C-DIC. Due to the turbulent pumping, we did not analyze samples for CFCs or ³He. ³H concentrations were analyzed by the Dissolved Gas Lab at the University of Utah and reported in tritium units (TU) with 1 sigma error. Samples for ¹⁴C-DIC analysis were hand filtered through 0.2µm Whatman Puradisc nylon syringe filters. ¹⁴C-DIC analyses were completed by the University of Arizona AMS Laboratory. Percent modern carbon (pmc) was calculated as a weighted average from multiple machine-runs to reduce overall error.

Models used to calculate ages were chosen based on the Han-Plummer graphical method (Figure 3.4, Table 3.2) (Han and Plummer, 2016). The Tamers model can be used for any values but has the least accuracy because it assumes a simple 50-50 mixing of solid carbonates and soil CO₂ (Tamers, 1967, 1975; Tamers and Scharpenseel, 1970). While Tamers is easy to calculate assuming an initial ¹⁴C of 50 pmc, this ideal mixing ratio does not accurately reflect most groundwater systems (Han and Plummer, 2016). The Pearson model allows for different levels of carbon mixing by incorporating initial soil and solid carbonate values (Ingerson and Pearson, 1964; Pearson and White, 1967; Pearson and Hanshaw, 1970; Pearson et al., 1972; Pearson and Swarzenki, 1974). Because δ^{13} C varies with system conditions (Han et al., 2012), Mook and Eichinger models incorporate enrichment factors. Mook is ideal for carbon exchange with soil CO₂ under open-system conditions (Mook, 1972, 1974, 1976, 1980; Clark and Fritz, 1997), while Eichinger is ideal for exchange with solid carbonates under closed-system conditions (Eichinger, 1983).



Figure 3.4 Han-Plummer graphical method (Han et al., 2012; Han and Plummer, 2016) for interpreting system conditions and choosing radiocarbon (¹⁴C) age dating model. Graphs (I) and (II) show theoretical evolution with calcite dissolution towards calcite saturation.

We used the Han-Plummer graphical method (Figure 3.4) to compare DIC concentration, δ^{13} C, and ¹⁴C to interpret the evolution of carbon in groundwater systems and indicate appropriate models for calculating ¹⁴C ages (Han et al., 2012; Han and Plummer, 2016). Graph I plots the reciprocal of DIC concentration and δ^{13} C (‰), Graph II plots the reciprocal of DIC concentration and ¹⁴C (pmc), and Graph III plots δ^{13} C and ¹⁴C. The graphs are separated into regions for interpretation using initial ¹³C (½ δ^{13} C_o) and ¹⁴C (½ ¹⁴C₀) values of the soil from the recharge area as well as the 1/[DIC] value of a sample that plots close to the intersection of the regions in Graph III. Based on where the samples plot on the graphs, we can interpret if the system is evolving under open or closed-system conditions and if the system is calcite saturated. Using the distribution of points in Graph III, we can evaluate which samples have viable ¹⁴C ages and which models would give the most accurate ages for our samples (Table 3.2).

3.3.6 Residence time calculations

Sample ³H levels were plotted based on the known decay rate alongside atmospheric ³H levels overtime in the continental US (Michel et al., 2018). Residence time is also calculated in years before sampling based on measured ³H levels and the initial atmospheric ³H level (Eq 3.3).

Eq 3.3
$$t = 17.77*\ln(^{3}H/^{3}H_{0})$$

Ages were calculated assuming an initial ³H concentration (³H₀) between 5.9 and 8.1 TU.

 14 C ages (t) are calculated based on their known rate of decay from the estimated initial 14 C (14 C₀) and measured 14 C (14 C_{DIC}) as unnormalized values using (Eq 3.4).

Eq 3.4
$$t = -8267 * ln \frac{{}^{14}C_{DIC}}{{}^{14}C_0}$$

Initial ¹⁴C is estimated based on the single-sample-based model chosen through the Han-Plummer method, system conditions, and δ^{13} C values (Table 3.2). These take into account the concentration of CO_{2(aq)} (C_a), HCO₃⁻ (C_b), and total DIC (C_T), as well as the isotopic composition of soil dissolved CO₂ (a1), solid carbonate (s), and soil gas CO₂ (g). Temperature is reported in °C. For models with multiple options for d¹³C_s, we averaged the final ages (t_s). Enrichment factors and initial variable estimates, such as Tamers point, were taken from Han and Plummer (2016) based on known environmental conditions. All viable ¹⁴C ages are averaged from calculations based on four models (Table 3.2) and reported in years before present (BP) with standard deviation. The resulting ¹⁴C age is used as a proxy for groundwater age and therefore, relative residence time.

Table 3.2 Radiocarbon (14 C) age dating models with associated assumptions and errors (Han and Plummer, 2016).

Model	Equation	Initial conditions	Assumptions/Error	References
Tamers	$\label{eq:constraint} \begin{split} ^{14}C_0 &= \left(\frac{C_a}{C_T}\right){}^{14}C_{a1} + 0.5 \left(\frac{C_b}{C_T}\right){}^{14}C_{a1} \\ & + 0.5 \left(\frac{C_b}{C_T}\right){}^{14}C_s \end{split}$ Simplified: ${}^{14}C_0 = 50$	$C_a = 0, C_b = C_T,$ ${}^{14}C_s = 0$ ${}^{14}C_{a1} = {}^{14}C_g =$ 100	Assumes ¹⁴ C _{DIC} is from 50% solid carbonates and 50% soil CO2.	Tamers, 1967, 1975; Tamers and Scharpenseel, 1970
Pearson	${}^{14}C_0 = \frac{{}^{14}C_g - {}^{14}C_s}{\delta^{13}C_g - \delta^{13}C_s} \times (\delta^{13}C_{DIC} - \delta^{13}C_s)$ Simplified: ${}^{14}C_0 = \frac{100}{-26 - \delta^{13}C_s} \times (\delta^{13}C_{DIC} - \delta^{13}C_s)$	$\label{eq:constraint} \begin{split} ^{14}C_g &= 100 \\ \delta^{13}C_g &= -26 \\ ^{14}C_s &= 0 \\ \delta^{13}C_s &= 0, \ 2.5 \\ \text{Averaged final } t_s \end{split}$	$\delta^{13}C_g$ = soil CO ₂ at equilibrium $\delta^{13}C_s$ = potential isotopic composition of solid carbonate Allows for varying ratio of carbon mixing.	Ingerson and Pearson, 1964; Pearson and White, 1967; Pearson and Hanshaw, 1970; Pearson et al., 1972; Pearson and Swarzenki, 1974
Mook	$ \begin{split} ^{14}C_0 &= {}^{14}C_i + \left({}^{14}C_g - 0.2\varepsilon + {}^{14}C_i \right) \\ & \times \frac{(\delta^{13}C_{DIC} - \delta^{13}C_i)}{\delta^{13}C_g - \varepsilon - \delta^{13}C_i} \\ \text{Simplified:} \\ ^{14}C_0 &= 50 + \left(50 - 0.2\varepsilon_{g/b} \right) \times \frac{\delta^{13}C_{DIC} + 12.5}{-13.5 - \varepsilon_{g/b}} \\ \varepsilon_{g/b} &= -\frac{9483}{T + 273.15} + 23.89 \end{split} $	$\label{eq:14} \begin{array}{l} {}^{14}C_i = 50 \\ {}^{14}C_g = 100 \\ {}^{\delta^{13}}C_i = -12.5 \\ (Tamers \ point) \\ {}^{\delta^{13}}C_g = -26 \end{array}$	Allows for carbon exchange with the soil under open- system conditions. <u>Takes into account</u> temperature (T) for the enrichment factor (ε).	Mook, 1972, 1974, 1976, 1980 Clark and Fritz, 1997
Eichinger	$ \begin{split} ^{14}C_0 &= \frac{\delta^{13}C_{DIC} - \delta^{13}C_E}{\delta^{13}C_i - \delta^{13}C_E} \times {}^{14}C_i \\ \delta^{13}C_E &= \delta^{13}C_s - \varepsilon_{s/b} \\ &= \delta^{13}C_s - \left(-\frac{4232}{T+273.15} + 15.1\right) \end{split} $		Allows for carbon exchange with solid carbonates in the bedrock under closed-system conditions.	Eichinger, 1983

3.4 RESULTS

3.4.1 Field measurements

Table 3.3 Environmental parameters measured in the field after reaching stable conditions during purging and before sampling of wells— pH, temperature (°C), electrical conductivity (μ S/cm)— and within 24 hours of sampling— alkalinity (mg/L).

	Sample Name	pН	Temperature (°C)	Electrical Conductivity (µS/cm)	Alkalinity (mg/L)	
	GW 2	7.6	16.1	675	222.6	
Shallow	GW 6	7.46	15.4	697	273.6	
	GW 14	7.9	14.3	614	198	
	GW 16	7.64	17	1295	261.1	
	GW J	7.03	13.2	1124	291.9	
Intermediate	GW 35	7.9	18.1	953	216.1	
	GW OD	7.88	15.6	1576	243.5	
Deep	GW 23	9.27	16.5	377.8	158.3	
	GW 22	8.45	17.6	634	151.9	
	GW 25	8.9	17.73	505	197	
	SW 1	6.31	11	34.8	<30.0	
	SW 2	7.09	12.4	258.8	152.5	
Samina	SW 3	5.35	6	21.1	<30.0	
Spring	SW 4	6.99	10.3	148.7	142.5	
	SW 5	6.64	15.3	115.1	86.5	
	SW 6	6.07	16.5	97.1	68.2	
JD	JD 25	8.2	18.9	1224	204.8	

Spring waters differed significantly from well waters in their environmental parameters, with springs being more variable and generally lower than wells (Table 3.3, Figure 3.5). Two-sample t-tests, assuming unequal variance, generated p-values <0.05 indicating a significant difference between spring and well samples. Springs' pH ranged from 5.35-7.09 (mean of 6.41 +/- 0.648), whereas pH in wells ranged from 7.03-9.27 (mean of 8.0 +/- 0.682) (p-value of 0.00066). Temperatures in springs ranged from 6-16.5°C (mean of 11.92 +/- 3.772°C), while wells ranged from 13.2-18.1°C (mean of 16.2 +/- 1.572°C) (p-value of 0.039). Electrical conductivity was much lower in springs (p-value of 0.00014) ranging from 21.1-258.8 μ S/cm, while wells ranged from 377.8-1124 μ S/cm. The alkalinity of springs ranged from 151.9-291.9 mg/L (p-value of limit (<30.0 mg/L) to 152.5 mg/L, and well samples ranged from 151.9-291.9 mg/L (p-value of 0.0002).

value of 0.00047). The JD well had a signature similar to the Summit wells with a pH of 8.2, temperature of 18.9°C, electrical conductivity of 1224 μ S/cm, and alkalinity of 204.8 mg/L.

Summit wells were further distinguished according to depth. Shallow wells (<30.5 m depth) had low pH values (7.03-7.9) and temperatures (13.2-17°C), as well as mixed electrical conductivity (614-1295 μ S/cm) and alkalinity values (198-291.9 mg/L). Intermediate wells (63.5-123 m) had pH values of 7.88-7.9, temperatures of 15.6-18.1°C, electrical conductivity of 953-1576 μ S/cm, and alkalinity of 216.1-243.5 mg/L. Deep wells (>171 m depth)



Figure 3.5 Variations in field parameters across the Summit transect and the basin. (A) pH, (B) temperature, and (C) electrical conductivity were measured after reaching stable conditions during purging of the wells before sample collection. (D) Alkalinity was measured within 24 hours of sample collection.

3.4.2 Environmental tracer analysis



Figure 3.6 Plot of ⁸⁷Sr/⁸⁶Sr and ²³⁴U/²³⁸U values with approximate bedrock ratios (Benford et al., 2010, Shoemaker and Hart, 2002) showing partial mixing with unknown ²³⁴U/²³⁸U source labelled ?.

Comparison of known ⁸⁷Sr/⁸⁶Sr and ²³⁴U/²³⁸U values for the dominant bedrocks (Benford et al., 2010, Shoemaker and Hart, 2002) with groundwater samples showed variation in ⁸⁷Sr/⁸⁶Sr values according to source but presented mixing with an unknown ²³⁴U/²³⁸U source (Figure 3.6, Table 3.4). While springs varied in ⁸⁷Sr/⁸⁶Sr (0.70519-0.70690) following the bedrock at the site of emergence, ²³⁴U/²³⁸U values were less variable in springs (mean of 8.18×10^{-5} +/- 1.87×10^{-5}) compared to wells. Shallow wells had a mean ⁸⁷Sr/⁸⁶Sr ratio of 0.70519 +/- 2.9×10^{-4} and ²³⁴U/²³⁸U ratio of 7.83x10⁻⁵ +/- 1.50×10^{-5} . Intermediate wells were the most consistent in ⁸⁷Sr/⁸⁶Sr with a mean of 0.70503 +/- 1.3×10^{-4} and had a mean ²³⁴U/²³⁸U ratio of 8.49×10^{-5} +/-

2.09x10⁻⁵. Finally, the deep wells had a similar mean 87 Sr/ 86 Sr ratio of 0.70489 +/- 4.1x10⁻⁴, but the 234 U/ 238 U ratios were substantially higher with a mean of 1.39x10⁻⁴ +/- 5.35x10⁻⁵. While the deep wells had a similar mean 87 Sr/ 86 Sr ratio of 0.70489 +/- 4.1x10⁻⁴, the 234 U/ 238 U ratios were substantially higher with a mean of 1.39x10⁻⁴ +/- 5.35x10⁻⁵ leading to the use of an additional end-member.

Table 3.4 Summary of environmental and age tracers, including dissolved carbon concentrations (reported in mg/L) and isotopes (reported in ‰) discussed in Chapter 2.

	Sample Name	⁸⁷ Sr/ ⁸⁶ Sr	²³⁴ U/ ²³⁸ U	DIC (mg/L)	DOC (mg/L)	$\delta^{13}C\text{-}DIC$	δ ¹³ C-DOC	³ H (TU)	¹⁴ C (pmc)
Shallow	GW 2	0.70545	7.26E-05	37.524	12.31	-14.18	-23.35	0.46	92.96
	GW 6	0.70503	1.00E-04	56.774	14.79	-14.23	-23.7	0.47	96.96
	GW 14	0.70476	8.70E-05	67.245	10.93	-13.12	-23.66	1.32	99.77
	GW 16	0.70534	6.85E-05	55.304	13.22	-12.03	-23.53	0.43	95.27
	GW J	0.70537	6.33E-05	68.316	2.64	-15.54	-24.78	4.1	81.69
Intermediate	GW 35	0.70527	7.74E-05	49.303	0.97	-12.1	-23.825	0.14	37.58
	GW OD	0.70445	1.68E-04	65.754	14.34	-13.89	-24.37	0.92	40.71
	GW 23	0.70493	1.72E-04	36.141	0.4	-13.06	-24.306	0.08	56.23
Deep	GW 22	0.70512	7.01E-05	60.964	6.46	-12.86	-24.29	0.08	40.09
	GW 25	0.70493	9.97E-05	46.049	0.5	-10.94	-22.78	0.08	13.18
Spring	SW 1	0.70622	9.49E-05	6.66	3.97	-20.12	-25.8	4.88	86
	SW 2	0.7069	5.48E-05	38.53	8.71	-15.34	-24.39	2.37	84.26
	SW 3	0.70616	8.98E-05	4.16	1.45	-21	-23.8	3.88	82.78
	SW 4	0.70519	1.06E-04	28	5.82	-12.03	-24.28	1.38	66.27
	SW 5	0.70527	7.63E-05	22.41	5.83	-13.7	-25.05	3.58	90.94
	SW 6	0.70519	6.91E-05	18.6	5.22	-16.86	-25.32	4.51	97.26
JD	JD 25			38.18	71.06	-13.41	-28.165	0.01	45.59

3.4.3 Inflow intervals and fractured layers

Caliper borehole logs, fluid temperature and conductivity profiles, and spectral gamma values showed a steady rise in fluid temperatures with depth as well as revealed layers with high fracture density and flowing water. Fluid temperatures rose about 1°C every 15 m across all wells greater than 20 m depth, most notable in deep wells (Figure 3.7). For example, the deepest well (GW 22) rose to about 29°C at 236 m (Appendix D). Fluid conductivities also increased

slightly with depth (Appendix D). Caliper logs showed fractured layers and changes in the slope of fluid profiles indicated inflow depths. Shallow wells reach a fractured layer between 10-15 m below the ground surface and showed peak inflow at about 11 m deep. Intermediate wells accessed two fractured layers and two distinct inflow points. The caliper borehole log and field parameter profiles for GW 35 showed inputs from 20-25 m and from 50-60 m depths (Appendix D). In lieu of geophysical imaging, historic drill logs for GW OD identified two perforated sections in the casing from 42.5-67 m and 103.5-110 m that indicated inflow of water. While depths match those of the deep wells, geochemical analyses from Ch. 2 show GW OD resembled a mixture of the shallow and deep waters and therefore, grouped as intermediate. Geophysical borehole logs for the deep wells (GW 23, GW 22, GW 25) displayed two depths of inflow at around 70 m and 160 m below the surface.



Figure 3.7 Compilation of fluid temperature profiles showing an increase in temperature after about 20 m below ground surface.

3.4.4 Age tracer analysis



Figure 3.8 Plot of age tracers, tritium (³H) and radiocarbon (¹⁴C), compared to alkalinity showing shallow aquifers, including springs, were younger (>0.43 TU and >66 pmc) while deeper aquifers were older (<0.08 TU and <57 pmc). Intermediate wells (63.5-123 m deep) had detectable levels of ³H (>0.08 TU) and ¹⁴C (<41 pmc).

Springs had substantially higher ³H than most wells whereas ¹⁴C (pmc) was higher in springs and shallow wells compared to deep and intermediate wells (Figure 3.8, Table 3.4). Springs had high mean ³H values of 3.43 ± 1.33 TU (ranging from 1.38 ± 3.48 TU) and a high mean percentage of modern carbon of $84.59 \pm 10.41\%$ (ranging from 66.27 ± 97.26 pmc). Shallow wells had high levels of modern carbon ranging from 81.69 ± 99.77 pmc (mean of 93.33 ± -6.96 pmc) and detectable ³H ranging from 0.14 ± 4.1 TU (mean of 1.356 ± -1.58 TU). The three deepest wells had low levels of modern carbon ranging from 13.18 ± 56.23 pmc (mean of 36.50 ± -21.75 pmc) and were ³H dead (0.08 TU). The two intermediate wells, GW OD and GW 35, had detectable ³H with a mean of 0.53 ± -0.55 TU and low levels of modern carbon with a mean of 39.15 ± 2.21 pmc indicating mixing of modern and paleo waters. Additionally, JD 25 was ³H-dead (0.01) with 45.59 pmc.

3.5 DISCUSSION

In this study, we used environmental parameters, various isotopes, geophysical borehole logs, and age tracers to distinguish aquifers, map the architecture of the subsurface groundwater environment, and calculate residence times. We combined our understanding of the geochemical evolution and the geophysical borehole logs to interpret distinct aquifer types accessed by springs and wells as well as distinguish flowpaths within the Summit area by depth. Here we 1) map the flowpaths, 2) interpret recharge by modern or paleo-waters, and 3) estimate residence times based on geophysical and geochemical analyses.

3.5.1 Distinguishing flowpaths

Isotopic ratios of ⁸⁷Sr/⁸⁶Sr for our groundwater samples to relative isotopic ratios for granite and basalt indicated a dominantly basaltic aquifer with some granitic mixing (Figure 3.5). We found that the springs varied in ⁸⁷Sr/⁸⁶Sr depending on the lithology, while the Summit wells were more consistent. The slight variation in ⁸⁷Sr/⁸⁶Sr in the Summit wells suggests some mixing with the granitic basement rock, likely closer to the source of recharge (Figure 3.5). In fact, the ⁸⁷Sr/⁸⁶Sr isotopic ratios decreased with distance along the transect and depth by shifting towards the basaltic signature. This is consistent with the results from Johnson et al. (2000) who found that slower, evolved aquifers were more equilibrated with the isotopic ratios of the bedrock.

High ${}^{234}\text{U}/{}^{238}\text{U}$ values found in the deep wells indicated another source of uranium beyond the basalt and granite sources. While ${}^{234}\text{U}/{}^{238}\text{U}$ values typically decrease with depth owing to more reducing conditions (Hem, 1985), our deepest wells— GW 22 and GW 25— had the highest ${}^{234}\text{U}/{}^{238}\text{U}$ values. The high ${}^{234}\text{U}/{}^{238}\text{U}$ ratios suggest an additional source of uranium in

the deeper aquifers and mixing with other wells. One potential explanation for this high uranium signature is hydrothermal alteration (Grabowski and Bem, 2012). This is supported by the geophysical data that showed an increase in fluid temperature after about 20m depth. Similarly, Roback et al. (2001) discovered high isotopic ratios in deep, thermal wells attributed to extended water-rock interactions resulting in dissolution and ion exchange. While other studies have documented geothermal activity in the Snake River Basin (Roback et al., 2001; Nielson et al., 2012; Neupane et al., 2014; Nielson and Shervais, 2014; McLing et al., 2016; Kessler et al., 2017; Lachmar et al., 2019), this study is the first to identify hydrothermal activity in RCEW (Figure 3.7).

Combining geophysical well logs with geochemical interpretations indicated three distinct flowpaths along the longitudinal transect with mixing occurring within the intermediate and deep wells (Figure 3.9). The shallow wells accessed a single, shallow flowpath while the deep wells accessed two deeper, older flowpaths. The intermediate wells accessed the shallow flowpath and one of the deeper flowpaths. While the geophysical borehole logs could be used to argue the intermediate wells accessed a single, mixed flowpath rather than mixing within the wells, this would not support the high 234 U/ 238 U values in deeper wells or the geochemical signatures discussed in Ch. 2. Instead, as the topography flattens out when we reach the lower basin and arkosic unit, the groundwater continues to flow downward, following the fractured layers in the basalt.



Figure 3.9 Conceptual flowpath diagram of longitudinal transect generated from geophysical borehole logs, geochemical analyses, and historic drill logs.

3.5.2 Relative ages



Figure 3.10 Graph of atmospheric tritium (³H) levels over time with measured ³H levels of groundwater and spring samples. Additional spring ages were estimated using chlorofluorocarbons (CFC-12) (Warix et al., 2021).

In partial support of our hypotheses, calculated ³H and ¹⁴C ages revealed the shortest residence times for the springs and the longest residence times for the deeper aquifers. However, we found longer residence times than expected, especially for the deep and intermediate wells. Residence times of springs were estimated by calculation of ³H ages (Figure 3.9) and comparison to CFC ages. The mean calculated ³H age of the springs was 13.60 +/- 8.50 years before sampling (ranging from 5.88-28.34 years). Because atmospheric ³H varied overtime, we also estimated the ³H ages graphically. Using the appropriate ³H curve for RCEW (Figure 3.10) and

the known rate of decay, we projected the samples back through time to estimate the initial ³H level and the associated age. Because of the high degree of variation in ³H overtime, samples can intersect with the curves multiple times suggesting multiple ages or mixed waters.

Detectable ³H in the shallow and intermediate wells allowed us to estimate ages analytically and graphically (Figure 3.9). Shallow wells had a mean tritium age of 36.45 +/-17.44 years (ranging from 8.97-49.15 years) with minimal mixing. In particular, GW J, the westernmost well, was the youngest of the Summit wells indicating substantial recent recharge from the surface. Based on ground truthing and additional geochemical analyses, GW J had inputs from the shallow flowpath and an irrigation pond. Following the Han-Plummer method (Han et al., 2012; Han and Plummer, 2016), none of the shallow wells had viable ¹⁴C ages, but all were calcite saturated (Figure 3.11). Intermediate wells had a mean tritium age of 52.04 +/-23.32 years (35.55-68.53 years) with signs of mixing— multiple graphical ages. Additionally, the intermediate wells had viable ¹⁴C ages and were saturated in calcite (Figure 3.11). GW 35 had a mean age of 1866 +/- 366 years BP and GW OD had a mean age of 2520 +/- 998 years BP (Figure 3.12). The detectable ³H and viable ¹⁴C ages in the intermediate wells are indicative of mixing of older, paleowaters with younger, ³H-rich waters, which suggests the older components may be older than the calculated ¹⁴C ages.


Figure 3.11 Use of the Han-Plummer (Han et al., 2012; Han and Plummer, 2016) graphical method to interpret system conditions and viability of radiocarbon (¹⁴C) age calculations from dissolved inorganic carbon (DIC) concentrations and isotopes.

Deep wells accessed older, ³H-dead waters (0.08 TU) that increased in age moving west along the transect according to ¹⁴C values. Unfortunately, the ¹⁴C age for GW 23, the easternmost well, could not be calculated because the sample contained more than 50pmc. The other deep wells had viable ¹⁴C ages of 2146 +/- 336 years BP for GW 22 and 9440 +/- 1395 BP for GW 25 (Figure 3.12). Similar to the deep wells, JD 25 was ³H dead but had a viable ¹⁴C age of 1404 +/- 591 years BP.



Figure 3.12 Summary of radiocarbon (¹⁴C) age calculations using Tamers, Pearson, Mook, and Eichinger models.

In Chapter 2, stable isotopes of water of the intermediate and deep wells indicated recharge by paleowaters, and in this study, we further demonstrate that the deeper aquifers have longer residence times. Consistent with these findings, Vengosh et al., (2002) described unsustainability of using deep groundwater resources due to longer residence times, especially when recharged by paleowaters. Previous works (Table 3.5) found springs and shallow wells accessing basaltic aquifers were recharged by modern waters (Brown et al., 2011; Georgek et al., 2018; Love and Zdon, 2018; White et al., 2019). Paleowaters, from 1.8-45 ky BP, evolved in deeper, often basaltic and granitic, aquifers (Bates et al., 2011; Brown et al., 2011; Love and Zdon, 2018; Schlegel et al., 2019). While Bates et al. (2011) dated groundwaters evolving along mixed lithologies such as sandstone and coals, they found deeper wells accessed aquifers with longer residence times. Focused in semi-arid to arid regions, Love and Zdon (2018) found emerging springs recharged by paleowaters that evolved in deep, dominantly sedimentary

bedrocks. In contrast, Georgek et al. (2018) found emerging springs recharged by young, shallow aquifers in a high-elevation, arid to semi-arid region.

Flowpath type	Groundwater Ages	Age Tracer	Lithology	Location	Reference
Paleowaters (groundwater wells)	2-9 ky	14C	Basalt	SW Idaho	This study
Modern waters (groundwater wells)	8-68 yrs	3H	Basalt	"	"
Modern waters (springs)	5-28 yrs	3H	Basalt, some granite/mixed	"	"
Paleowaters (groundwater wells)	10-45 ky	14C	Sandstone, coals, etc.	SE MT-NE WY	Bates et al., 2011
Paleowaters (groundwater wells)	33-16 ky	14C	Basalt	SE WA	Brown et al., 2011
Mixed	<0.08-8.3 TU	3H	Basalt	"	"
Modern waters	20-38 yrs		Basalt	"	"
(groundwater wells)					
Modern waters (springs)	3-115 yrs	3H and CFC	Limestone, sandstone, etc.	N Colorado, USA	Georgek et al., 2018
Modern and paleowaters (springs)	1.8-15.5 ky	14C	Sed rocks, some volcanics	SE California, USA	Love and Zdon, 2018
Modern and paleowaters	Modern-28 ky	14C	Volcanics	SW Idaho	Schlegel et al., 2009
Mixed	17-202 yrs 0.6-2 ky	3H, 14C	Volcanics	New Mexico	White et al., 2019

Table 3.5 Review of groundwater age studies in semi-arid to arid regions.

Overall, we found the younger, shallow flowpaths, including springs, were recharged by modern waters and therefore, susceptible to anthropogenic influence. We conclude that recharged by paleowaters, the deep flowpaths are disconnected from the climate and more resistant to contamination, but not sustainable for extensive use.

3.5.3 Future work

Further research is required to confirm our interpretations and complete our understanding of the subsurface groundwater environment. While this study provides a baseline for future groundwater research at RCEW, more wells of varying depths are necessary to expand our findings to the rest of the basin. Specifically, wells of intermediate and deep depths, accessing one or both of the deep flowpaths, need to be drilled, logged, and analyzed. Further studies are also necessary to characterize the high $^{234}U/^{238}U$ signature. Additionally, further geophysical surveys are needed to map the architecture of the subsurface groundwater environment of the full basin.

3.6 CONCLUSIONS

While springs emerged from young, unconfined aquifers, consistent with our hypotheses, the groundwater wells accessed much older waters, including paleowaters. Combining geophysical and geochemical techniques, we created a conceptual cross-section of the subsurface groundwater environment to visualize carbon movement along three distinct flowpaths accessed by the Summit wells. While older than anticipated, the shallow flowpath was recharged by modern waters evident from the detectable ³H. The deep flowpaths were ³H-dead, calcite saturated, and recharged by paleowaters indicating a disconnect from the climate; therefore, the deeper flowpaths are large stores of carbon spatially and temporally. Additionally, we found high ²³⁴U/²³⁸U ratios and warmer temperatures in deeper waters highlighting a previously undiscovered geothermal activity. The mixing of the younger, shallow flowpath with the deeper, paleowaters within the intermediate wells offers a unique aquifer with modern recharge. We conclude that repeated use of deeper waters would result in depreciation of these paleowaters and amplification in its vulnerability as well as remove a substantial store of carbon.

3.7 WORK CITED

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Chapter 4: Appendices

Appendix A: Stable isotopes of water for all precipitation samples at three sampling sites— high (Reynolds Mountain East (RME), elevation of 2043 m), mid (Breaks, elevation of 1585 m), low (Quonset, elevation of 1203 m). Locations listed in Table 2.1.

Site	Date	δ ¹⁸ Ο (‰)	δ ² H (‰)	Site	Date	δ ¹⁸ Ο (‰)	δ ² Η (‰)	Site	Date	δ ¹⁸ Ο (‰)	δ ² Η (‰)
	1/23/2020	-14.84	-111.07		1/23/2020	-14.89	-114.18		2/18/2020	-15.16	-120.21
	2/18/2020	-14.20	-105.63		2/18/2020	-15.65	-119.28		3/18/2020	-9.87	-69.56
	3/2/2020	-20.48	-158.25		3/18/2020	-12.15	-86.50		4/7/2020	-9.76	-78.68
	3/18/2020	-13.35	-97.42		4/7/2020	-13.17	-92.75		4/24/2020	-15.39	-119.30
	4/7/2020	-13.80	-101.45		4/21/2020	-15.07	-109.74		5/28/2020	-8.84	-71.73
	4/21/2020	-16.28	-122.93		5/28/2020	-13.55	-98.17		7/8/2020	-14.70	-120.11
	5/28/2020	-14.48	-108.29		7/8/2020	-15.75	-123.38		7/30/2020	-4.62	-52.93
	7/8/2020	-17.32	-128.81		7/30/2020	-10.93	-81.88	Low	9/3/2020	-8.92	-73.09
TT'_1	7/30/2020	-8.70	-68.77	Mid	8/24/2020	-0.45	-25.71	Quonset	10/13/2020	-10.97	-95.6
High	8/24/2020	-2.30	-25.64	Breaks	9/3/2020	-11.29	-81.67		10/29/2020	-7.11	-56.5
KWL	9/3/2020	-13.69	-96.37		10/13/2020	-11.77	-89.0		11/29/2020	-9.07	-77.7
	9/24/2020	-12.02	-111.69		10/29/2020	-9.19	-66.5		12/3/2020	-17.18	-130.1
	10/13/2020	-13.18	-92.1		12/7/2020	-14.24	-107.5		2/3/2021	-13.08	-101.0
	10/29/2020	-11.67	-80.6		1/6/2021	-13.90	-104.5		3/3/2021	-20.78	-163.4
	12/7/2020	-14.22	-104.9		2/3/2021	-14.88	-114.1		3/30/2021	-14.73	-116.2
	1/6/2021	-13.17	-98.5		3/3/2021	-19.04	-149.5				
	2/3/2021	-14.36	-107.2		3/30/2021	-15.89	-122.2				
	3/3/2021	-17.77	-136.5								
	3/30/2021	-15.38	-114.8								

Туре	Sample ID	7Li	9Be	11B	23Na	25Mg	27Al	29Si	31P	39K	44Ca
	units	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
	GW 2	1.84	0.04	157.5	43510	51760	6.5	16590		2658	67770
	GW 6	0.7	0.12	76.96	28770	41260	5.68	17940		415.3	71080
Shallow	GW 14	0.75	0.06	68.81	42850	23600	5.54	11620		999.8	57100
	GW 16	5.37	0.02	196.9	186100	30880	6.3	9280		1077	60050
	GW J	4.65	0.08	203.5	149700	29960	7.44	9601		1552	76670
Intermediate	GW 35	1.79	0.11	3.43	220500	9364	7.45	5642	45.64	1395	24140
Intermediate	GW OD	4.38	0.13	48.64	249500	17040	6.3	11150		1860	74070
	GW 23	1.47	0.06	78.83	86630	792.5	10.33	13410		1246	3834
Deep	GW 22	1.08	0.03	60.92	106300	1812	5.57	7322		916.6	14830
	GW 25	1.65	0.09	23.88	137200	575.5	11.23	6624	29.22	873.9	7109
JD	JD 25	17.634	0	80.542	546911.56	8931.1	19.104	7404.36		8054.77	65906.88
Dond	P1- inlet	3.62949		103.52	60014.021	17120.4		4758.43	2.6286	4029.62	25619.1
I Ollu	P2- mid	3.66246	0.004	103.76	58465.141	16961.6		4951.48		3912.56	26534.34
	SW 1	0.94	0.01	26.19	5075	929.6	32.46	20400		3709	3011
	SW 2	4.9	0.02	25.43	14170	7179	5.66	7867		2814	39660
Samina	SW 3	1.23	0.06	37.4	3755	315.9	58.05	8923		1409	1351
spring	SW 4	2.73	0.08	203.5	10310	13810	7.9	18400		1742	19250
	SW 5	1.75	0.06	78.83	10420	8371	11.21	17420		1277	13900
	SW 6	0.96	0.09	23.88	9518	5680	7.12	14750		1313	12580

Appendix B: Full suite of cations and rare earth elements

Туре	Sample ID	45Sc	47 Ti	51V	52Cr	55Mn	57Fe	59Co	60Ni	65Cu	66Zn
	units	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
	GW 2	5.08	1.2	39.14	0.57	0.14	244.6	0.13	1.24	3.03	12.83
	GW 6	5.8	1.61	23.72	0.09	0.11	255	0.13	1.08	1.61	12.19
Shallow	GW 14	3.71		14.09	0.25	0.4	194.7	0.1	0.74	2.77	12.43
	GW 16	2.93		13.13	0.43	0.51	218	0.12	1.02	1.63	14.56
	GW J	2.99		2.37	0.16	67.02	284.2	0.17	2.57	3.02	23.61
Intormodiate	GW 35	1.73		3.59	0.14	6.61	130.7	0.1	0.59	2.06	16.93
	GW OD	3.4	0.63	1.94	0.1	112.4	278.8	0.15	1.24	4.2	23.98
	GW 23	4.14	1.06	15.2	0.97	2.95	26.49	0.04		1.77	15.6
Deep	GW 22	2.25		1.08	0.04	34.74	139.9	0.03		1.01	12.19
	GW 25	1.92	0.28	1.07	0.28	10.74	56.39	0.03		1.93	33.7
JD	JD 25	1.233	392.48	4.693	0.133	2317.2	265.24	1.801	2.294	7.67	20.839
Dond	P1- inlet	0.5247	142.08	5.5848		5.2805	57.98	0.4934	2.8086	2.849	
ronu	P2- mid	0.719	142.5	4.8175		7.339	75.302	0.3786	2.6786	2.6232	
	SW 1	6.15	4	1.31	0.09	4.89	57.8	0.11		1.66	75.49
	SW 2	2.52	0.23	3.35		0.16	144.1	0.07	0.61	2.47	16.71
Spring	SW 3	2.95	4.14	0.22	0.02	0.83	41.72	0.05	0.34	0.98	33.33
opring	SW 4	5.94	3.53	4.23	0.93	0.08	103.1	0.07	1	1.95	18.4
	SW 5	5.36	3.83	5.36	0.35	51.3	83.42	1.1	6.13	3.12	189.8
	SW 6	4.41	2.42	2.18	0.29	3.06	68.4	0.12	0.95	2.17	15.75

Туре	Sample ID	69Ga	72Ge	75As	82Se	85Rb	88Sr	89Y	90Zr	93Nb	95Mo
	units	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
	GW 2	0.36	0.12	2.31	3.81	2.38	332.9	0.04	0.06	0.07	1.99
	GW 6	0.18	0.09	1.07	1.9	0.7	174.4	0.09	0.04	0.09	0.95
Shallow	GW 14	0.11	0.05	0.47	0.22	0.89	98.14	0.06	0.03	0.02	0.77
	GW 16	0.52	0.04	2.01	8.92	0.14	113.9	0.08	0.06	0.01	4.36
	GW J	0.59	0.06	0.28	0.57	2.5	301.4	0.02	0.06	0.08	4.76
Intermodiate	GW 35	1.27	0.12	0.9	1.45	2.38	104.9	0.02	0.07	0.01	2.31
Intermediate	GW OD	1.44	0.16	0.9	2.76	2.83	208.8	0.02	0.07	0.09	2.74
	GW 23	3.3	0.29	0.41	1.7	1.27	21.59	0.02	0.05	0.02	1.57
Deep	GW 22	0.27	0.05	0.01		2.06	25.42	0.01	0.02	0.05	1.57
	GW 25	0.48	0.13	0.36	1.34	1.52	21.85	0.13	0.07	0.03	3.34
JD	JD 25	0.06	0.33	5.246	4.761	5.895	1797.5	0.029	0.111		28.467
Dond	P1- inlet			2.3849	0.0778	1.0525	248.26	0.0718			
ronu	P2- mid	0.002		2.2658		0.9939	260.78	0.0211			
	SW 1	6.47	0.09	0.09		7.41	15.64	0.81	0.15	0.03	0.11
	SW 2	3.64		0.38		0.13	166.3	0.07	0.02	0.02	0.61
Spring	SW 3	0.81	0.02	0.53	0.69	3.36	6.85	0.74	0.12	0.04	0.23
opring	SW 4	0.61	0.03	2.12		4.06	102.3	0.03	0.06	0.04	0.53
	SW 5	7.81	0.06	1.32	0.06	0.86	71.28	0.06	0.05	0	0.47
	SW 6	1.29	0.06	0.07		0.84	58.17	0.06	0.04	0.01	0.39

Туре	Sample ID	101Ru	107Ag	111Cd	118Sn	121Sb	125Te	133Cs	137Ba	139La	140Ce
	units	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
	GW 2	1.08	0		0.1	0.06	0.1	0.02	10.63	0	0.01
	GW 6	1.09		0		0.06	0.13	0.01	5.79	0.01	0.01
Shallow	GW 14	1.11	0.01		0.01	10.44	0.11	0.01	3.01	0.01	0.01
	GW 16	1.13	0.01	0.03		0.03	0.01	0.03	15.83	0.01	0
	GW J	1.03	0.01	0.03	0.18			0.07	18.86	0.01	0.01
Intormodiate	GW 35	1.02	0.01		0.03		0.26	0.05	36.19	0.01	0.02
Intermediate	GW OD	1.05	0.02	0.03	0.45	0.15	0.08	0.07	43.89	0.01	0.01
	GW 23	1.05						0.03	102.3	0.01	0.02
Deep	GW 22	1.18	0	0.02			0.15	0.05	6.97	0	0.01
	GW 25	1.06	0	0				0.06	11.65	0.03	0.06
JD	JD 25				1.506			0.033	92.037	0.004	0.006
Dond	P1- inlet			0.0212				0.0243	45.062	0.0202	0.0475
rona	P2- mid			0.0141	0.1098			0.0433	39.549	0.007	0.006
	SW 1	1.15	0.01	0.02				0.03	200.4	0.29	0.61
	SW 2	1.2	0	0.01				0.01	107.1	0.02	0.02
Spring	SW 3	0.98	0.02	0.02	0.02	0.22	0.09	0.06	23.55	0.23	0.32
spring	SW 4	1.01	0.01	0.01	0.06	0.07	0.11	0.07	18.9	0.02	0.01
	SW 5	1.03	0.01	0.02	0.06	0.13		0.01	232.5	0.02	0.04
	SW 6	1.04	0	0.19				0.01	38.88	0.02	0.02

Туре	Sample ID	141Pr	146Nd	147Sm	153Eu	157Gd	159Tb	163Dy	165Ho	166Er	169Tm
	units	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
	GW 2	0	0.01	0.01	0				0	0	0
	GW 6	0	0.02	0	0		0	0.01	0	0	0
Shallow	GW 14	0	0.01		0			0	0	0	0
	GW 16	0	0	0	0		0	0.01	0	0	0
	GW J	0	0		0.01	0.01		0	0	0	0
Intermediate	GW 35	0.01	0.01	0.02	0.01	0.01	0	0.01	0.01	0.01	0
Intermediate	GW OD	0.01	0.02	0	0.01			0	0	0	0
	GW 23	0.01	0	0	0.02	0.01		0.01	0.01	0.01	0
Deep	GW 22	0	0.01		0	0	0		0		0
	GW 25	0.01	0.04	0.02	0.01	0.01	0	0.02	0.01	0.01	0
JD	JD 25				0.013	0.013		0.005		0.009	
Dond	P1- inlet	0.0091	0.0222		0.0071	0.0101		0.0182			
Fonu	P2- mid				0.0081	0		0.002		0.002	0.002
	SW 1	0.09	0.43	0.13	0.05	0.12	0.02	0.13	0.03	0.1	0.01
	SW 2	0.01	0.02	0	0.02		0		0	0	
Spring	SW 3	0.11	0.48	0.19	0.02	0.15	0.03	0.15	0.04	0.11	0.03
spring	SW 4	0.01	0.02	0.03	0.01	0.01	0	0.01	0.01	0.01	0.01
	SW 5	0.01	0.02	0.02	0.06	0.01	0	0.01	0	0.01	0
	SW 6	0.01	0.02	0.01	0.01	0.01		0.01	0.01	0.02	0.01

Туре	Sample ID	172Yb	175Lu	178Hf	181Ta	182W	205Tl	208Pb	232Th	238 U
	units	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
	GW 2	0	0	0.06	0.03	0.16	0	0.05		7.16
	GW 6	0.01	0	0.03	0.04	0.03		0.01		4.72
Shallow	GW 14	0	0	0.01	0.06	0.02		0.03		3.48
	GW 16	0	0	0.02	0.01	0.1		0.02		14.92
	GW J	0	0	0.01	0.02	0.1		0.02		5.17
Intermediate	GW 35	0.01	0.01	0.04	0.04	0.31		0.02		1.67
	GW OD			0.06	0.06	0.21	0.1	0.73	0.03	0.04
	GW 23	0.01	0.01		0.01	0.69		0.04		1.36
Deep	GW 22			0	0.02			0.01		0.02
	GW 25	0.02	0.01	0.02	0.01	0.46		0.02		0.03
JD	JD 25	0.003	0.001	0.006			0.012	0.293		11.781
Dond	P1- inlet	0.003					0.1122	0.1577		1.8097
FOIL	P2- mid		0.002				0.6022	0.3142		1.8398
	SW 1	0.09	0.02					0.06		0.05
	SW 2							0.25		1.84
Spring	SW 3	0.14	0.03	0.02	0.04	0.32	0.06	0.1		0.06
spring	SW 4	0.01	0.01	0.01	0.04	0.19		0.02		0.1
	SW 5	0.01	0	0.01	0.02	0.17		0.05		0.09
	SW 6	0	0		0.01	0.05		0.02		0.02

Appendix C: NETPATH Results

Shallow wells (GW 14)-M	lixing of GW 2 and GW 6
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(I Display th	gnoring em <a>11	126 models chee 3 models four 1 dissolution/p at once, <retur< th=""><th>cked nd precipitation rn> for each,</th><th>constraints) or <n>one.</n></th></retur<>	cked nd precipitation rn> for each,	constraints) or <n>one.</n>
Init 1 Init 2 ANORTH Ca-MONT CALCITE GOETHITE Mg-MONT	MODEL + F + F + ·	1 0.98748 0.01252 -1075.95838 929.88302 920.53738 -0.00085 -6.31360	(Constraint	ignored)
Init 1 Init 2 AUGITE Ca-MONT CALCITE GOETHITE Mg-MONT	MODEL + F + F +	2 0.98748 0.01252 -777.38831 -3650.97363 920.53738 544.17096 3717.70223	(Constraint	ignored)
Init 1 Init 2 AUGITE Ca-MONT CALCITE MAGNETIT Mg-MONT	MODEL + F + F +	3 0.98748 0.01252 -777.38831 -3650.97363 920.53738 181.39032 3717.70223	(Constraint	ignored)
No more mo	dels, hit	t <enter> to com</enter>	ntinue	

Display th	em <a>11	126 models checked 9 models found at once, <return> for each, or <n>one.</n></return>	Init 1	MODEL + F	6 0.73529 0.26471
Init 1 Init 2 ALBITE	MODEL + F + F +	1 0.51766 0.48234 1.66867 0.10175	ANORTH Ca-MONT CALCITE Mg-MONT NA-MONT	+ F +	0.20471 0.73166 -6.25912 0.27835 -0.15434 5.78547
CALCITE GOETHITE Mg-MONT	MODEL	-0.17185 -0.07167 -0.72485	Init 1 Init 2 ANORTH Ca-MONT GOETHITE	MODEL + F + F +	7 0.60074 0.39926 0.88951 -5.89258 -0.00027
Init 1 Init 2 ALBITE Ca-MONT CALCITE GOETHITE Mg-MONT	+ F + F +	0.59890 0.40110 1.75845 -0.54825 -0.00380 -0.00028 -0.20641	Mg-MONT NA-MONT Init 1	MODEL + F	-0.20571 5.33480 8 0.60074
Init 1 Init 2 ALBITE Ca-MONT CALCITE	MODEL + F + F +	3 0.73529 0.26471 1.44289 -1.87795 0.27835	Init 2 AUGITE Ca-MONT GOETHITE Mg-MONT NA-MONT	+ F +	0.39926 0.64268 -2.10551 -0.45015 -3.28441 5.33480
Mg-MONT NA-MONT Init 1	MODEL + F	-0.15434 1.41306 4 0.60074	Init 1 Init 2 AUGITE CALCITE GOETHITE Ma-MONT	MODEL + F + F +	9 0.32796 0.67204 0.87389 -0.56428 -0.61256 -4.49615
Init 2 ALBITE Ca-MONT GOETHITE Mg-MONT NA-MONT	+ F +	0.39926 1.75421 -0.56615 -0.00027 -0.20571 0.01903	NA-MONT	odels, h	4.42120 4.42120 it <enter> to continu</enter>
Init 1 Init 2 ALBITE CALCITE GOETHITE Mg-MONT NA-MONT	MODEL + F + F +	5 0.54266 0.45734 1.88856 -0.12013 -0.00039 -0.22788 -0.58262			

Deep wells (GW 25)— Mixing of GW 23 and GW 22

MODEL 1 Init 1 + F 0.83344 Init 2 + F 0.16656 AUGITE + 0.00383 Ca-MONT -13.52554 CALCITE 3.49731 Mg-MONT 9.13050 NA-MONT 4.39469	
MODEL 2 Init 1 + F 0.81542 Init 2 + F 0.18458 Ca-MONT -13.58244 CALCITE 3.51141 GOETHITE 0.00269 Mg-MONT 9.18554 NA-MONT 4.39688	
MODEL 3 Init 1 + F 0.81542 Init 2 + F 0.18458 Ca-MONT -13.58244 CALCITE 3.51141 MAGNETIT + 0.00090 Mg-MONT 9.18554 NA-MONT 4.39688	

Summit wells (GW 2)— Mixing of SW 4 and SW 6

Appendix D: Geophysical borehole logs

GW 23







GW 25



GW 35

