ISOTOPES, GEOCHEMISTRY, CITIZEN SCIENCE AND LOCAL PARTNERSHIPS AS TOOLS TO BUILD UPON A FRACTURED UNDERSTANDING OF THE HYDROLOGY OF THE NORTHERN PATAGONIA MOUNTAINS

By

Sean Schrag-Toso

A Thesis Submitted to the Faculty of the

DEPARTMENT OF HYDROLOGY AND ATMOSPHERIC SCIENCES

In Partial Fulfillment of the Requirements
For the Degree of:

MASTER OF SCIENCE
WITH A MAJOR IN HYDROLOGY AND WATER RESOURCES

In the Graduate College

THE UNIVERSITY OF ARIZONA

2020

THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

As members of the Master's Committee, we certify that we have read the thesis prepared by: Sean Schrag-Toso

titled: Isotopes, Geochemistry, Citizen Science, and Local Partnerships as Tools to Build Upon a Fractured Understanding of the Hydrology of the Northern Patagonia Mountains

and recommend that it be accepted as fulfilling the thesis requirement for the Master's Degree.

Jennifer C Mcintosh — Date: May 27, 2020

Kristine Uhlman — Date: May 27, 2020

Thomas Meixner

Thomas Meixner — Date: May 27, 2020

Final approval and acceptance of this thesis is contingent upon the candidate's submission of the final copies of the thesis to the Graduate College.

I hereby certify that I have read this thesis prepared under my direction and recommend that it be accepted as fulfilling the Master's requirement.

Jennifer C Mcintosh
Thesis Committee Chair
Hydrology and Atmospheric Sciences — Date: May 27, 2020

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ACKNOWLEDGEMENTS

This research revolves around groundwater, one of the most precious resources in the arid West. In the course of developing an understanding of this resource, I seek to acknowledge the many groups of people who have accompanied me through the learning process: the community of Cerro Pita, in Panama, who hosted me for two years during my Peace Corps service which planted the seed for a career in water resources; the professionals who have devoted their lives to advancing the field of hydrology; and, the citizens of the Town of Patagonia, who are feeling the effects of uncertainty around this precious resource. I am grateful for your influence and for the lessons you have taught me.

Kristine Uhlman, with decades of experience, voluntarily chose to mentor and advise me throughout this research. Thank you, Kristine, for your guidance and dedication to mentoring the next generation of water resources professionals and for the bowls of phở. Thank you, Dr. Jennifer McIntosh, for patiently advising me throughout this research. I have been inspired by your attention to detail, calm leadership, and patience in teaching.

Numerous other individuals have volunteered their time and expertise to this research. Thank you Floyd Gray, James Callegary, and Chris Eastoe, for responding to my many emails, providing expertise and for meeting to discuss the project and its goals. From Patagonia, I would like to thank Dave Ellis and Carolyn Shafer for your enthusiasm and leadership in the Patagonia area. To Howard from the Audubon Society, thank you for enduring a day of sampling as we drove around the Patagonia Mountains in my car that lacked air conditioning and tends to backfire. To Dr. McIntosh's research group: Chandler, for answering my impromptu questions and advice on writing, Alyssa, for the encouragement and exchange of ideas, and the rest of the research group for their feedback and guidance. To the Department of Hydrology and Atmospheric Sciences: thank you Tim for the help in the lab and for sharing decades of knowledge on the hydrology of Southern Arizona, and to Thomas, Kathy, Sarah, and Anna for the help with grants. Thank you, Terrie, for the unsolicited snacks that power the student body in Harshbarger.

Additionally, I want to thank my friends in the hydrology department, in particular: Amy, Garrett, Cara, Ammon, Neha, and Charlie for being an endless source of laughter, encouragement, and knowledge.

Funding for this project was provided by a 104b grant through the United States Geological Survey (USGS), the Climate and Society (CLIMAS) Fellowship, funded through the National Oceanic and Atmospheric Administration (NOAA), and in-kind contributions from partners and advisors. Lastly, thank you, Georgia Ehlers for directing the Peace Corps Coverdell Fellow program which allows for continued service, balanced work, and financial support for returned Peace Corps Volunteers throughout graduate school.

Contents

Tables

Figures

Abstract

The rural Town of Patagonia in Southeastern Arizona is facing uncertainty around the future availability of groundwater resources in the area. This uncertainty is due to extended drought and increased groundwater extraction by the mining industry in the Northern Patagonia Mountains, which are located south of the Town. To address this uncertainty, and advance the hydrologic understanding of the area, this two-phase project was formulated with partner groups working in the Patagonia area.

The first phase was analysis of isotope ratios and geochemistry of springs and wells in the Northern Patagonia Mountains to better conceptualize groundwater movement within the mountain's fracture system and determine the hydrologic connectivity between the mountains and the Sonoita Creek alluvial aquifer. The results indicate that major mapped faults within the mountain block, including the Harshaw Creek Fault, appear to be conduits of groundwater movement. The Mountain Front Fault, which separates the mountains from the basin, appears to obstruct groundwater flow, resulting in distinct water chemistry and Pleistocene-aged groundwater in select areas northwest of the fault. Southeast of the fault, most mountain springs and wells produce water recharged from modern precipitation. Fossil water was found within the mountains, however, the quantity of fossil water in the mountains is unknown. Mountain front recharge and focused mountain block recharge via Harshaw Creek partially recharge the Sonoita Creek alluvial aquifer from which the Town of Patagonia pumps for its municipal water source. The results of this research indicate that drought is the primary concern for springs in the study area and the secondary concern is the resultant impact on groundwater flow in stream channel sediments around Harshaw Creek and its tributaries.

This improved conceptual understanding of groundwater flow informed the second phase of this research: education on groundwater movement by means of a well owner training and recommendations for monitoring steps. Regular collection of data by the citizen science group or other stakeholder groups working in the area will allow for monitoring of groundwater resources by residents living in the watershed. Monitoring also will contribute to future hydrologic studies within the basin and will aid in making management decisions around water use by the Town Council.

Introduction

The following research has been conducted to build upon existing knowledge of the groundwater hydrology of the Northern Patagonia Mountains in Southeastern Arizona. It is intended to advance not only the understanding of groundwater movement in the mountains by the scientific community, but also build upon the basic understanding of groundwater movement by residents within the Patagonia area. This thesis was planned with residents living within the Sonoita Creek Watershed and is intended to address some of the questions and concerns of those residents that were present at the time of the study's genesis. The thesis is in part a traditional scientific project, by means of sample collection, analysis and interpretation; and, in part, a partnership that attempts to include existing social and political groups in the scientific process by means of inclusion and consideration in the formation, execution and interpretation of the research.

Hydrologic Motivations

1. The potential impact of drought, climate change, and mining activities in the mountain block on the local riparian area and basin aquifers.

In the Basin and Range province of the Southwestern United States, the mountain ranges and alluvial basins are hydrologically connected. Due to the orographic effect, mountains often receive higher levels of precipitation, at colder temperatures, than the neighboring lowlands. Runoff after storms and surface flow in washes, sustained by snowmelt and springs, flow from the mountains into the low-lying basins, where it recharges the basin-fill aquifer systems. This relationship between precipitation in the mountain block and overland flow that leaves the mountain system and recharges the alluvial lowlands is called mountain front recharge (MFR) and until recently was widely accepted to be the principal hydrologic relationship between the basin and range (Markovich, et al. 2019). Recent research indicates a second recharge mechanism, embedded within the definition of MFR. This mechanism is called mountain block recharge (MBR). MBR is the result of mountains storing some of the precipitation that falls in the mountain system within its system of faults and fractures. The mountains act like water towers, slowly releasing groundwater stored in the systems of faults and fractures to the basin via springs or diffuse recharge. In MBR the groundwater is released to the basin either diffusely across the mountain front (diffuse MBR) or is focused around mountain stream sediments and discrete faults and fractures (focused MBR) (Markovich, et al. 2019). Recent hydrologic studies worldwide indicate that MBR is responsible for between 5-50% of recharge in the adjacent low-lying alluvial basins. (Markovich, et al. 2019). The combination of MFR and MBR are recognized as the main groundwater recharge component in many arid and semi-arid basins (Ajami, et al. 2011). Having recognized the significance of MFR and MBR on groundwater supply in alluvial basins, the two mechanisms are difficult to characterize or quantify, due to limited data, particularly within mountain blocks that lack accessible wells or other windows into the subsurface (Markovich, et al. 2019).

The Town of Patagonia's location in the alluvial basin next to two mountain ranges (the Patagonia Mountains and the Santa Rita Mountains) exemplify the societal dependence on groundwater recharged from the mountains. Extended drought, varying intensity of precipitation, and an increase in demand on groundwater resources has already decreased the availability of groundwater in the southwest (Gonzalez, et al. 2018). This trend towards a more arid climate coupled with increased pumping of groundwater by proposed industrial mining activities in the mountain block could directly impact MFR and MBR from the Patagonia Mountains to the Sonoita Creek alluvial aquifer, and thus impact base flow in Sonoita Creek and the aquifer around the Town of Patagonia.

A decline in regional water tables can have resounding effects on the ecosystem and livability of an area. As groundwater levels decline, discharge from aquifers to gaining streams and creeks can decline. As a result, streamflow can diminish, and once perennial creeks and streams can disappear underground. Recent modeling of the impact of volumetric streamflow from groundwater declines, show a 10 – 50% decline in stream flow due to groundwater extraction across the western United States (Condon and Maxwell 2019). As basins around the world are experiencing a decline in surface water flow due to groundwater extraction (de Graaf, et al. 2019, Condon and Maxwell 2019), understanding the connectivity of groundwater in the basin to recharge from the mountains is key to protecting future surface water and groundwater availability in basin aquifers, and protecting riparian areas. The Patagonia Mountains and their proximity to a municipality and perennial creek make them a unique study site to advance the understanding of MFR and MBR and the implications of changing conditions (drought and groundwater extraction) in the mountain system on the low-lying basin.

2. Need for improved hydrologic understanding of groundwater movement in fractured bedrock and the resultant vulnerability of springs in the mountain system.

Because the Patagonia Mountains are composed of primarily fractured rock, flow is channeled through faults and fractures, discharging to the land surface as springs that sustain base flow in mountain creeks. Due to the heterogeneity of fracture systems, hydrologic modeling of groundwater flow in fractured bedrock is challenging. Resultantly, empirical data can be useful in understanding groundwater flow in these mountain systems. However, obtaining groundwater samples from bedrock can be challenging because of the high expense associated with bedrock wells and the typically low yield associated with those wells. There are very few wells completed in the bedrock of the Patagonia Mountains (Montgomery & Associates 1999). As a result, data from springs can provide insight into groundwater movement in this complicated and data-limited region.

Studies in adjacent basins have seen that groundwater chemistry and isotopic signatures at the mountain front can be similar to the chemistry and isotopic signature of groundwater produced at springs in the mountain system (Markovich, et al. 2019). Resultantly, the productivity of the springs in the mountain system can be an integral component to recharge to adjacent alluvial aquifers. These recharge mechanisms are dependent upon the geology at the edge of the mountain block and the hydrologic connectivity of the alluvial aquifer to the mountain block.

Societal Motivation

Residents and wildlife within the Sonoita Creek Watershed are highly dependent upon groundwater. The Town of Patagonia's municipal water source draws from the local alluvial aquifer and the Sonoita Creek, which runs through the Town of Patagonia, depends on ample shallow groundwater to sustain base flow. Through use of sulfate isotopes, base flow in the Sonoita Creek was determined to be composed of approximately 15-25% recharge from the Patagonia Mountains (A. Gu 2005). The Sonoita Creek is integral to the work of over 30 stakeholder groups in the area (NextGen Engineering 2017, A. Gu 2005). Within the mountain block numerous ranchers and residents depend on groundwater resources for their drinking water supply. Cattle, wildlife, and numerous plant species depend on springs as their water source during times of drought. The discussed changing conditions within the watershed, notably extended drought, and the return of mining operations to the area within the last decade, have sparked concern among these stakeholder groups about the future availability of groundwater in the watershed. Recent research indicates that the majority of residents living within the Sonoita Creek Watershed have a high level of concern about water quality and water scarcity (Petrakis, Norman and Pritzlaff 2020). Local stakeholder groups, discussed below, have already begun to address these societal concerns, and this research complements their efforts.

Local Partnerships

The Sonoita Creek Watershed which includes the Town of Patagonia and the Northern Patagonia Mountains is not located within an Arizona Department of Water Resources (ADWR) Active Management Area (AMA) and thus well owners and industry do not have to operate under the laws of the Groundwater Management Act (GMA) [1]. Resultantly, there are very few laws that apply to groundwater extraction in the Patagonia area. However, in the winter of 2014, the Town Manager of Patagonia issued a "water alert" on the front page of the Town's local paper *The Patagonia Regional Times*. The "alert" was due to having to drop the Town's municipal supply pump nearly 20 feet (Reibslager 2014) to sustain demand. The decline was attributed to drought and the water table has since rebounded. In response to these changing conditions, and recognizing the limited oversight of groundwater extraction, residents living within the area have organized to better understand and manage their groundwater resources.

As a researcher working in a remote study site, it is important to recognize that often "environmental issues have been treated as the purview of experts, [even though,] local people know best what their problems are and how to solve them" (Austin 2004). Resultantly a key motivation of this study was to collaborate with, engage, and educate residents within the Patagonia area to increase the project's utility. As a result, a partnership with the local water advisory committee, the Flood and Flow Committee (F&F Committee) and a local citizen science group, Patagonia Area Water Study (PAWS) was established, with the hope of including these groups in the research and passing on any future monitoring and scientific inquiry. Ultimately, the findings of this research will be used by these groups to better understand and manage groundwater resources in the area.

The Town of Patagonia's Flood and Flow Committee [2]

The Town of Patagonia's Flood and Flow Committee makes recommendations to the Patagonia Town Council with respect to best practices within its jurisdiction to manage erosion; to enhance water flow, and to create optimal flood mitigation; and, to promote the long-term health of the riparian corridor. The Committee promotes the interests of 30 identified stakeholder groups within the greater Patagonia area that are intimately tied to and dependent upon the water in the creeks and aquifers (NextGen Engineering 2017). With this mission in mind, the Flood and Flow Committee depends on data and analysis to make management decisions within the watershed. For that reason, these stakeholders have a keen interest in how

[1] Prior to 1980, the high population centers of Arizona were experiencing symptoms of low groundwater levels. These conditions in high population zones led to the unprecedented collaboration among industries and stakeholders and produced the Groundwater Management Act of 1980 (GMA) and established a new progressive law to replace antiquated water law. The laws created by the GMA, in general, are limited to Active Management Areas (AMAs), which are focused around these high population centers. The area outside of the boundaries of AMAs are not required to adhere to most of the strict policies laid out in the GMA, besides providing ADWR with a notice of intent (NOI) to drill and an overall rule of exempt and non-exempt wells. Exempt wells are private wells that are limited to pumping rates below 35 gallons per minute. (Megdal 2012)

[2] Web address: https://patagonia-az.gov/flood-and-flow-committee-meeting-agendas/

climate change and groundwater pumping will affect water quantity and quality within the basin. Stakeholders are actively working to compile existing data and characterize water resource vulnerability. A partnership with the F&F Committee was also established to help circulate the findings of this research and to facilitate meetings and trainings.

Patagonia Area Water Study

A citizen science group, Patagonia Arizona Water Study (PAWS), was formed in 2017 to advance the local contribution to understanding the Watershed. In 2018 the group began working with the Arizona Department of Environmental Quality (ADEQ) to bolster the existing database of surface water quality and create a "pre-mining" dataset for the Watershed. In reality, historic mining and drought conditions had already impacted the Sonoita Creek Watershed with reported break-outs of acid rock drainage (ARD) following intense precipitation events (Dean 1982). However, continued drought and pumping of groundwater from deep wells within the mountain block by mining companies could further impact water availability and quality in the watershed. Resultantly, PAWS plans to expand their efforts to monitor springs that may be vulnerable to dewatering or decrease in supply. A key motivation of this study is to guide PAWS in selecting vulnerable springs and identify the potential drivers for the drying-up of selected springs. The impact of decreased supply at springs would immediately impact wildlife and ranchers that work and live in the Patagonia Mountains, could decrease flow in ephemeral and intermittent streams that originate as springs, and could impact groundwater supply in the basin (Markovich, et al. 2019).

Objectives

Recognizing the hydrologic connectivity between groundwater in the Sonoita Creek alluvial basin and groundwater in the Northern Patagonia Mountains, alongside the time sensitive societal concerns, the following objectives were formulated working with local partners:

Hydrologic objectives

1. Determine the recharge elevation and seasonality of groundwater sampled from springs and wells;
2. Conceptualize groundwater flow path and residence times, and assess hydrologic connectivity of groundwater recharge in the mountains to alluvial aquifers in the Sonoita Creek basin, specifically around the Town of Patagonia;

3 Discuss the potential impact of drought conditions and groundwater extraction in the mountains on mountain springs and groundwater availability in the alluvial basin;

Societal objectives

4 Educational outreach and dissemination of findings within the greater Patagonia area to improving public understanding of groundwater movement in the mountains; and,
5 Provide guidance for further studies, monitoring and management.

Background

Study Area

In the Southwestern United States, approximately 60 miles (100 km) southeast of the city of Tucson, Arizona, the Patagonia Mountains rise from the southern border of the Town of Patagonia and extend into Northern Mexico. The study area is limited to the northern portion of the mountains and includes the Harshaw Creek sub-watershed and Alum Gulch-Flux Canyon sub-watersheds (Alum-Flux) and the greater area that supports groundwater flow within those sub-watersheds. The Harshaw Creek sub-watershed comprises most of the study area and drains into Sonoita Creek just north of the Town of Patagonia, while the Alum-Flux watershed drains into Sonoita Creek south of the Town (Figure 1). The Sonoita Creek drains into Lake Patagonia approximately 5 miles (8 km) south of the Town of Patagonia, which ultimately drains into the Santa Cruz River. While the study area is focused around watersheds, this is a groundwater study and samples were taken outside of these watersheds due to the assumed connectivity of groundwater outside of watershed boundaries. The Arizona Department of Water Resources (ADWR) defines the groundwater basin that includes the study area as the Cienega Creek Groundwater Basin, which extends well beyond the boundaries of the Sonoita Creek watershed to the north. Previous studies indicate a portion of groundwater originates in this central portion of the Cienega Creek Groundwater Basin (A. Gu 2005). The study area was chosen due to the proximity to the Town of Patagonia; its accessibility; the availability of historic data for comparison; the inclusion of current and historic mining activity; and, due to its utility in addressing current concerns of partner organizations.

Climate

Previous studies include data on the climate of the Town of Patagonia (A. Gu 2005, Ben-Asher 1981). Due to the lack of access to a weather station in the mountains, data from those reports were used to describe the modern climate of the study area. However, in general, the study area is located at elevations higher than the Town, and resultantly the study area receives higher precipitation and lower temperatures than the reported conditions, however the climatic trends are assumed to be similar.

The Town of Patagonia is located at an elevation of 4060 ft (1240 m) and has a semi-arid climate, with mild winters, hot summers, and low humidity. Precipitation ranges from approximately 10 in (254 mm) to 30 in (762 mm) per year, with an average of around 18 in (450 mm) (A. Gu 2005). About two-thirds of this precipitation occurs during convective monsoon storms occurring in the late summer, however frontal systems in the winter can last several days with less intense precipitation (A. Gu 2005). Temperatures range from 27 °F (-2.9 °C) as a low in January to 95 °F (34.9 °C) as a high in June (A. Gu 2005). Mean annual evapotranspiration varies depending on location within the watershed. Perennial reaches of the Sonoita Creek can have evapotranspiration rates has high as 6 ft/yr (1,830 mm/yr), with an average rate in the basin of approximately 1 ft/yr (305 mm) within the greater Sonoita Creek Watershed (Ben-Asher 1981). Previous studies indicate that evaporation of surface water is common both in summer and winter as seen by analysis of stable water isotopes that fall to the right of the Global Meteoric Water Line (GMWL) in neighboring mountain systems (Eastoe and Wright 2019, Gray 2018).

Geology

The study area is in the Basin and Range physiographic province with north to northwest trending mountain ranges separated by alluvial valleys. A geologically older, southwest to northeast extension lineament is present in the region that runs nearly perpendicular to the major north-northwest-trending Harshaw Creek Fault, the most prominent structure in the area (Chaffee, et al. 1980). The Town of Patagonia sits in the basin on top of Holocene and Pleistocene unconsolidated deposits bordered by the Santa Rita Mountain Range to the north and the Patagonia Mountain Range to the south. A generalized geologic map of the Patagonia Mountains, which included major faults, is presented in Figure 2.

The geology of the Patagonia Mountains is complex and is composed of volcanic, sedimentary, metamorphic and intrusive igneous bedrock that range in age from the Precambrian biotite quartz monzonite and hornblende diorite to quaternary and tertiary gravels (Chaffee, et al. 1980). The mountains were formed by the deposition of Paleozoic limestone, followed by uplift, faulting, and intrusion of volcanic rocks (Dean 1982). The northern portion of the range is characterized by its high concentration of pyrite, andesite, welded and non-welded rhyolite and latite tuff, as well as volcaniclastic sandstone and breccia

(Graybeal, et al. 2015). A geologic map of the mountains is provided by the United States Geological Survey (USGS) (Graybeal, et al. 2015) and contains compiled surface geologic information from numerous previous studies (Figure 3A). Also included in the USGS map is a geologic cross section (Figure 3B). Units for the map and cross section are presented in Figure 3C.

Hydrogeology

Two principal hydrogeologic units are present within the study area: fractured bedrock and porous media. These two umbrella units are broken into more specific hydrogeologic components below. Visual representation of some of the hydrogeologic features are presented in Figure 2 and Figure 4.

(1) Fractured bedrock
  - Mapped systems of large faults
  - Mine shafts within the bedrock
  - Fracture matrix
  - Subsurface (Paleozoic) limestone layer that may contain karst features

(2) Porous media flow
  - Stream channel sediments within the mountain system
  - Sonoita Creek alluvial aquifer

Fractured Bedrock

Bedrock, which is intrinsically impermeable, is made porous due to fracturing, faulting, and the excavation of mine shafts. Groundwater flow in this unit is directed through these openings in the rock system known as fractures. Additionally, a limestone layer, which can have unique hydrogeologic properties due to the creation of solution cavities, has been reported below the surface and is an important component of the hydrogeologic setting of the mountains.

Mapped system of large faults

Major northwest striking faults separate rock formations within the mountains. The Harshaw Creek Fault is the dominant feature within the mountains, trending north-northwest, and showing more than 4 miles (6.4 km) of displacement at its southernmost end (Scalamera 2003). The southwest reach of Harshaw Creek flows along the Harshaw Creek Fault for about three miles, until it branches north, and crosses the fault (Dean 1982). Smaller faults run in the east-west direction and divide the area into a complicated array of geologic blocks. In general, the formations dip in a north to northwest direction (Simons 1972). The geologically older Mountain Front Fault separates the Patagonia Mountains from the Sonoita Creek alluvial basin. Many of the older fault and fracture systems have been filled with mineral deposits during mountain building and now obstruct water flow (Montgomery & Associates 1999). The faults and fractures that have not yet been filled act as conduits for groundwater flow in rock systems.

Mine shafts

Further complicating the hydrogeologic setting is anthropogenic alteration due to extensive historic mining activity. Valuable ore bodies are often contained in fissure-veins and as replacement deposits along fault lines. To access these bodies, the Patagonia mountains were mined extensively throughout the last two centuries. With these relatively small mining operations closing in the mid-20th century, mine shafts are now abandoned and act as strong conduits for groundwater flow.

Fracture Matrix

Much of the exposed geology in the study area is fractured volcanic rock and is highly heterogeneous (Chaffee, et al. 1980). Igneous and metamorphic rocks range in hydrologic conductivity from 1 ft/100,000 years (0.3m/100,000 years) to 300 ft/day (91m/day) (Artiola, Uhlman and Hix 2017) depending on the concentration and size of fractures, as well as alteration and mineralization of volcanic and sedimentary rocks. Springs sampled for this study and previous studies, as well as wells drilled in the fractured bedrock, have low discharge rates indicating the fractured bedrock likely stores small quantities of groundwater (Montgomery & Associates 1999).

Paleozoic Limestone

A review of deep well logs from the mine's property (Table 1), as well as published geologic maps (Figure 3B) indicate a limestone layer below the igneous and metamorphic volcanic strata visible at the surface. Well logs indicate that the limestone layer occurs approximately 1000 ft – 1800 ft (300 m - 550m) below the surface and extends past the depth of the wells, some of which extend below sea level such as well 920498 in Table 1. Paleozoic limestone is also found at the surface throughout the study area (Simons 1972). The presence of a deep and expansive limestone layer complicates the hydrogeology, particularly due to several of the wells from the mine have apparently been completed in this deep limestone layer. Hydrologic conductivity in limestone is generally higher than fractured bedrock with values of 0.1 ft/year (0.03m/year) to 3 ft/day (1m/day) (Artiola, Uhlman and Hix 2017), however hydrologic conductivity is dependent upon solution cavities in the limestone also known as karst features.

Porous Media Flow

Porous media is the result of weathering of bedrock and the redistribution of the sediment by wind or water. Unconsolidated to moderately consolidated deposits of gravel, sand, silt and clay build up overtime within channels due to this sediment transport. The accumulation of these sediments allows for groundwater to be stored in the space between sediments and has unique hydrogeologic properties from bedrock fracture flow. Often hydrologic conductivity, or rate of groundwater flow, is higher in porous media than fractured bedrock and groundwater yield and productivity of wells is generally much higher (Artiola, Uhlman and Hix 2017).

Stream Channel Sediments

A thin veneer of stream channel sediments is present in the mountains, focused around Harshaw Creek. These quaternary alluvial deposits present a unique hydrogeologic unit within the mountain system. This hydrogeologic unit allows for greater groundwater availability within the mountains, with numerous wells drilled in this unit. Lee's Well (site 11, ADWR Wells 55-540425) was drilled in this hydrogeologic unit. Review of the ADWR well log indicates that the alluvium around site 11 extends 36 ft (11 m) before hitting bedrock, and at the time of drilling the water table was 18 ft (5.5 m) below the surface.

For approximately 3 miles (4.8 km) Harshaw Creek parallels major lineaments in the area, and presumably flows along fracture lines, before draining into the Sonoita Creek. Resultantly, groundwater released from fractures likely contribute to flow in the alluvial sediments.

Sonoita Creek alluvial aquifer

The Sonoita Creek alluvial aquifer is composed of two porous media units, defined by their age and level of consolidation, however both are erosional deposits. The first is basin fill, which is older and deeper in the basin. On top of this unit, is alluvial fill. Most of the wells in the area are completed in the basin fill or the alluvial fill hydrologic units (Montgomery & Associates 1999).

Quaternary and Tertiary age basin fill deposits in the Sonoita Creek aquifer are estimated to extend 2950 ft (900 m) below the surface before hitting bedrock (Menges 1981). While basin fill deposits are also able to transmit large quantities of water, their transmissivity is likely lower than the localized Quaternary alluvial fill deposits (Montgomery & Associates 1999).

Alluvial deposits composed of unconsolidated silt, sand and gravel are present at a depth of up to 88 ft (27 m) in the streambed and old floodplains of the Sonoita Creek (Nassereddin 1967). The rate of hydrologic conductivity varies greatly, depending on the type of alluvial fill, be that clay, silt, sand or gravel (Freeze and Cherry 1979, Artiola, Uhlman and Hix 2017). Previous studies of the area indicate that the transmissivities of these aquifers range from 8,000 to 260,000 gpd/ft at a 1:1 hydraulic gradient (Nassereddin 1967).

Hydrology

Overland Flow

The Patagonia Mountains are composed of steep slopes, with various degrees of incline, with most slopes ranging from 10 to 60 percent (Dean 1982) which contribute to rapid surface runoff after precipitation events. During base flow conditions, springs maintain perennial flow in reaches of the Alum-Flux watershed and Harshaw Creek. Based on field observations from the Patagonia Mountains and observations of previous researchers, springs are the sole source of flow during these baseflow conditions (Scalamera 2003).

Water Table and Groundwater Recharge

Groundwater levels in the Patagonia Mountains are unpredictable and vary by location. Three artesian wells were reported to the author, Hale Ranch (site 6), Flowing Well in Humbolt Canyon (site 21), and Flux Canyon Flowing Well (site 20). The high level of variance in groundwater levels is due to the fractured nature of the mountains as well as the system of faults and mine tunnels. Perched water tables are common (Dean 1982). Over the past many decades, groundwater levels in the Patagonia Mountains have reportedly dropped (Dean 1982). Previous reports attribute this decline to pumping for mining purposes, stock water, and domestic purposes as well as ground cover depletion and changes in climate (Dean 1982).

Mechanisms of groundwater recharge can be informed by studies done in neighboring basins. Similar basins in the southwest indicate that basin recharge is a mix of MBR, MFR and direct recharge into the basin from precipitation (Markovich, et al. 2019). Recharge patterns seen in the mountain block of the Santa Catalina Mountains, about 60 miles (100 km) north of the Patagonia Mountains, indicate that high elevation catchments, which receive higher precipitation and have lower temperatures, contribute to deep aquifer recharge and fractured bedrock storage, and are a major contributor to MBR (Ajami, et al. 2011). In these neighboring catchments lower elevation rain falls on steeper slopes, with less soil and often recharges the basin alluvial aquifer through MFR, or infiltrating into stream channel sediments (Ajami, et al. 2011). While the Patagonia Mountains do not rise to the same elevation as the Santa Catalina Mountains, similar topographic conditions are present in the Patagonia Mountains, and these neighboring catchments can act as a baseline conceptual model for groundwater recharge of the Patagonia Mountains.

With regards to seasonality of recharge, isotopic studies in the nearby Upper San Pedro basins indicate higher MFR and MBR contribution to the adjacent alluvial basins during the winter months (65% ± 25%) than summer months (35% ± 25%) (Wahi., et al. 2008), however only from precipitation falling in the wettest months (Eastoe and Wright 2019).

Springs

In bedrock aquifers, springs can be useful groundwater sampling sites due to lack of access to wells. Springs occur when the water table breaches the land surface. Because the water source for springs is local groundwater, springs are often perennial. However, the recharge location for many springs can be challenging to deduce because the potential of complicated flow paths. Springs can produce water from adjacent, shallow, or atmospheric sources, or long-traveled, deep, regional aquifers (Springer, Boldt and Junghans 2017), or from water that was recharged in distant regions and transported via fault and fracture systems. Monkey Spring, a spring located approximately 6 miles (10 km) north of the Town of Patagonia is reported to have produced 400 GPM (Feth 1954), and was hypothesized to gather water in the Permian Limestone distant from the discharge of the spring itself. The water is hypothesized to follow an ancient drainage below the surface and then discharge when it hits a dammed fault and is pushed up to the surface (Feth 1954). Springs in the study area produce much smaller quantities of water, with several seeps and fracture springs located within the study area.

Acid Rock Drainage/Pyrite Oxidation

Acid rock drainage (ARD) or pyrite oxidation can originate in natural settings, however, is often associated with areas that that contain current or historic mines. Acid rock drainage is commonly associated with the mineral pyrite (FeS_2). There are numerous pyrite zones in the Patagonia Mountains (Figure 4). The most common setting that produces ARD is water collecting in underground mine workings directly from precipitation, or seepage through faults, or percolating through overlaying soils or rocks where that water encounters the atmosphere. The process of acidification requires oxygen and contact with pyrite for the iron sulfide to be oxidized. The resulting H^+ increases acidity and increases metal solubility. The overall process is summarized below (Moran and Wentz 1974):

$$FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O = Fe(OH)_3 + 2SO_4{}^{2-} + 4H^+$$

Mining activity in the Patagonia Mountains has resulted in abandoned mine tunnels and acid mine drainage, often occurring after heavy precipitation events. Due to the historic mining activity and the presence of pyrite in the mountains, groundwater samples in the study area can contain sulfate concentrations above 250 mg/L (Wanty, et al. 2001, Montgomery & Associates 1999), and thus exceed the EPA secondary drinking water standard. This high concentration of sulfate resulting from ARD and isotopic signature of pyrite oxidation is useful in tracking the movement of groundwater from the Patagonia Mountains after it leaves the fractured bedrock and enters the adjacent basin.

Methods

Field Methods

Groundwater samples were collected from a total of 15 sites, including 10 springs, 4 wells and one surface water sample in the study area. Study site locations and sources of data are listed in Figure 5. Samples were collected in the spring and fall of 2019. Care was taken to assure samples were not contaminated with rainwater, and each sampling event occurred at least two weeks after a precipitation event. The surface water sample (Middle Harshaw, site 12) was collected by residents living in the Harshaw Creek Watershed and the sample was collected as the mine upstream was reportedly conducting a pump test of wells screened in the deep aquifer. The Middle Harshaw sample was taken out of protocol, however given the rare presence of assumed flow from the mine's wells, the 'opportunity sample' was used for radiocarbon dating.

Due to a lack of wells in the fractured bedrock, springs were chosen as sampling sites for groundwater in the Patagonia Mountains. All known and accessible springs in the study area were sampled. Spring locations were identified using the Springs Institute database, USGS maps and from local knowledge of the area. Spring water is assumed to be representative of groundwater for this study. Well sampling locations were chosen to give better spatial representation to the entirety of the studied area. Sample locations were collected using a Global Positioning System Garmin eTrex 10©.

Field parameters (pH and temperature) were collected at each sample site. The meter was calibrated using 3-point slope calibration with 4.1, 7.0 and 10 buffer solutions on the morning of the day of sampling.

Spring water was collected at the spring source and, when possible, water was drained from the spring to allow for new spring water to accumulate prior to collection. Groundwater from wells was collected at the faucet closest to the well, prior to any water treatment or storage tanks. The faucet was turned on, and once temperature and pH had stabilized, and field parameters were recorded, the samples were collected. Spring water samples were collected using a sterile syringe and filtered through a 0.45 µm nylon filter, apart from tritium, radiocarbon, sulfate isotopes and trace metals, which were not filtered. Sample aliquots for alkalinity, anions, and cations were collected into precleaned 30mL high-density polyethylene (HDPE) bottles with no headspace. Two drops of ultra-pure nitric acid were added to the cation aliquot to pH<2. Sample aliquots for stable water isotopes ($\delta^{18}O$ and δD) were collected using 10-mL glass vials with no headspace. Aliquots of tritium were collected in 1-L HDPE opaque bottles with no headspace. Sulfate isotope aliquots were collected in 1-L HDPE amber HDPE bottles with no headspace. Radiocarbon samples were collected in two 1/2-L glass amber bottles with no headspace and sealed with parafilm. All samples were stored on ice in the field and refrigerated in the laboratory to remain below or at 4 °C prior to analysis.

Laboratory Methods

Alkalinity and $\delta^{18}O$ and δD analysis were performed at the University of Arizona's Department of Hydrology and Atmospheric Sciences. Alkalinity was measured using the Gran-Alk titration method as described by Gieskes and Rogers (1973) (precision ±0.6%) and was completed within 24 hours of sampling. Stable water isotopes (^{18}O and D) were analyzed using a Los Gatos Research Laboratory Isotopes Analyzer model LWIA-24d with 4th generation cavity enhance absorption (precision < 0.08 ‰ and <0.9 ‰, respectively).

Cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Fe_{total}) were analyzed using an Elan DRC_II Inductively Couples Plasma-Mass Spectrometer (IPC-MS) at the University of Arizona Laboratory for Emerging Contaminants (ALEC). Anions (F^{-}, Cl^{-}, Br^{-}, NO_3^{-}, SO_4^{2-}) were analyzed using a

ThermoFisher Scientific Dionex ICS-6000 ion chromatography with chemical suppression of eluent conductivity method as reported in method 4110 B. from Standard Methods for Examination of Water and Wastewater, 22nd Edition (Eaton 1992) also at ALEC.

Tritium, $\delta^{34}S$ of dissolved sulfate ($\delta^{34}S$-SO_4) and $\delta^{18}O$ of dissolved sulfate ($\delta^{18}O$-SO_4) were analyzed at the University of Arizona's Department of Geosciences Environmental Isotope Laboratory (EIL). Tritium was analyzed using a Quantulus 1220 Spectrometer in an underground counting laboratory using electrolytic enrichment and liquid scintillation decay counting methods. Samples were enriched by a factor of about nine and subsequently mixed 1:1 with an ULTIMA Gold Low Level Tritium Cocktail and counted for 1,500 minutes. Standardization is based on international standard OGS-1. The detection limit for tritium was 0.5 TU.

Sulfur isotopes of sulfate ($\delta^{34}S$-SO_4) were analyzed (precision ±0.15‰) using a ThermoQuest Finnigan Delta Plus XL instrument. $BaSO_4$ was precipitated out of the samples, which were subsequently combusted at 1030°C with O_2 and V_2O_2 using an elemental analyzer coupled to the mass spectrometer. Standardization is based on international standards OGS-1 and NBS123 and several other sulfide and sulfate materials that have been compared between laboratories. Oxygen isotopes of sulfate ($\delta^{18}O$-SO_4) were analyzed (precision ±0.40‰) using a Thermo Electron Delta V instrument. Samples were combusted with excess carbon at 1350 °C using a thermal combustion elemental analyzer coupled to the mass spectrometer. Standardization is based on international standard OGS-1.

Radiocarbon samples were measured at the University of Arizona's Accelerator Mass Spectrometer (AMS) Laboratory. Samples were analyzed (detection limit – 0.2 pmc) using a National Electrostatics Corp. tandem accelerator mass spectrometer. Carbon dioxide was extracted from the samples by acid hydrolysis and was then reduced to graphite that was made into targets for accelerator mass spectrometry. Lab reports from the AMS lab contain uncorrected radiocarbon ages.

Radiocarbon Age Corrections

Radiocarbon or carbon 14 (^{14}C), is a radioactive isotope of carbon and has a half-life of 5730 years and is useful for dating groundwater (Clark and Fritz 1997). Because ^{14}C enters water when the water is in contact with the atmosphere and during recharge; once it is beneath the water table, and out of contact with the atmosphere, the ^{14}C beings to decay. Resultantly, groundwater can be dated to approximately 35,000 years old using ^{14}C methods. However, there are multiple water-rock interactions in the subsurface, such as dissolution of fossil carbonate minerals that can decrease ^{14}C amounts by addition of "dead" carbon into the groundwater and thus increase the apparent ‘uncorrected’ radiocarbon age. The equation used for dating groundwater using ^{14}C methods is:

$$t = -8267 * \ln\left(\frac{a_t{}^{14}C}{q * a_0{}^{14}C}\right)$$

When using radiocarbon to date groundwater, $a_t{}^{14}C$ is measured, and is the percent modern carbon (pmc) at the time of analysis, however the original value of ^{14}C ($a_0{}^{14}C$) is assumed to be 100, which is not often the cause due to addition of carbon while in the subsurface. In the above equation “q” is the correction coefficient and must be solved for. Numerous correction models exist to calculate “q” and thus correct ^{14}C ages. The relatively simple δ^{13}C mixing model reported by Clark and Fritz (1997) and first introduced by Pearson (1965) was used for this research, as carbonate dissolution appears to be the primary process adding dead carbon to groundwater in the Patagonia Mountains.

The δ^{13}C mixing model uses carbon stable isotopes, (δ^{13}C) of dissolved inorganic carbon (DIC) as a tracer for various sources of DIC in groundwater, including dissolution of CO_2 (assumed to have 100 pmc ^{14}C) during recharge and carbonate derived DIC (assumed to have 0 pmc ^{14}C). The δ^{13}C mixing model provides a process to correct for this addition of carbon and solves for “q” using the following equation:

$$q_{\delta 13C} = \frac{\delta^{13}C_{DIC} - \delta^{13}C_{carb}}{\delta^{13}C_{recharge} - \delta^{13}C_{carb}}$$

δ^{13}C-DIC of groundwater samples was measured alongside ^{14}C at the AMS laboratory. δ^{13}C of carbonate minerals ($\delta^{13}C_{carb}$) was estimated to range from 1-3 ‰ (Veizer 1967) resulting in a range of corrected ages. To quantify the introduction of DIC into the sample during recharge ($\delta^{13}C_{recharge}$) the following equations must be solved.

$$\delta^{13}C_{recharge} = \delta^{13}C_{soil} + \varepsilon * \delta^{13}C_{DIC-CO_{2(soil)}}$$

$$\varepsilon * \delta^{13}C_{DIC-CO_{2(soil)}} = mCO_{2(aq)} * \varepsilon^{13}C_{CO_2(aq)-CO_2(g)} + mHCO_3 * \varepsilon^{13}C_{HCO_3-CO_2(g)}$$

δ^{13}C for CO_2 gas in soil was assumed to be -23 ‰ (Clark and Fritz 1997). Recharged water was assumed to be dominated by HCO_3 and the enrichment factor ($\varepsilon^{13}C_{HCO_3-CO_2(g)}$) was taken from by Clark and Fritz (1997) and ranged from 7-9-8.65. The enrichment factor is based on the temperature of the sample at the time of recharge, which cannot be known and thus the large assumption of the temperature at the time of sampling being indicative of temperature at the time of recharge was made.

For the Harshaw Creek surface water sample (site 12), a correction coefficient of 0.75 was used because pH and temperature were not taken at the time of sampling. If the well sample was pumped from the deep limestone layer, as hypothesized, a correction coefficient of 0.75 is characteristic of Karst systems (Clark and Fritz 1997), however confidence in the precision of the age of this sample is low, because the sample is likely a mix of recent precipitation with deep aquifer groundwater, as discussed previously.

Previous Works used for Comparison

Due to the availability of high-quality historic data, data from previous studies were used to complement newly collected data. While numerous reports with relevant hydrologic data and insights were available for comparison (A. Gu 2005, Wanty, et al. 2001, Montgomery & Associates 1999, Dean 1982, Ben-Asher 1981, Nassereddin 1967, Feth 1954), the below listed studies were selected due to their relevance to the present study's objectives, completeness of the data presented, and the study location of each report. Previous studies used for comparison in the discussion and in figures are discussed below. Data used from previous reports are provided in Table 3, Table 5, Table 7, and Table 10.

1. Gu, Ailiang, Floyd Gray, Christopher Eastoe, Laura Norman, Oscar Duarte, and Austin Long. 2005. *Isotope and Chemical Compositions of Groundwater and Surface Water near Patagonia, Arizona: Sources of DIssolved Sulfate, and Implication for the Origin of Base Flow in Sonoita Creek.* PhD Disseration, Tucson: University of Arizona.

Ailiang Gu's PhD dissertation includes detailed information on sulfate sources as well as water chemistry from the Patagonia Mountains and the Sonoita Creek alluvial aquifer. The dissertation quantified the percentage contribution to the Sonoita Creek from three distinct sources, one of which is the Patagonia Mountains. Temporal trends are discussed in the dissertation; however, those trends are not further explored in the present thesis. Data from the dissertation was used directly for comparison. Sample sites were selected based on completeness of data for the site as well as location. The current study relies heavily on the data presented in Gu's dissertation to compare Patagonia Mountains groundwater to the Sonoita Creek basin.

2. Wanty, Richard B., Wayne C. Shanks III, Paul Lamothe, Al Meier, Fred Lichte, Paul H. Briggs, and Byron R. Berger. 2001. *Results of Chemical and Stable Isotopic Analyses of Water Samples Collected in the Patagonia Mountains, southern Arizona.* USGS.

The USGS collected and published the results from numerous samples in the Patagonia Mountains. The results are unique due to their location within the mountain block and include surface water and groundwater isotopic and water quality data. Three groundwater samples were used from the report and were selected based on the location and the completeness of the data set for the given location.

Results

The following results section discuss the results from samples collected by the author, with occasional comment on previously published data for comparative purposes. Results reported by Gu et al. (2005) and Wanty et al. (2001) are used for comparison in figures and are discussed in greater detail in the Discussion section of the present report.

The symbology used in the figures is based on the hydrogeologic unit the sample was collected from and the source of the data. Samples collected from the mountain system are reported in blue. Samples from the Sonoita Creek alluvial aquifer are reported in orange. The Town of Patagonia, because of its interest to the present study, is symbolically separated from the basin samples and reported in red. Samples collected by the author are presented as squares in figures and samples reported by others are presented as circles. The following Results section focuses on the samples represented by squares in figures, or the samples collected by the author.

Field Parameters

Measured field parameters (temperature, pH) can help determine flow paths of the sampled groundwater, and geochemical trends in the aquifer system (Markovich, et al. 2019). The temperature of samples varied widely, with a low temperature of 51 °F (10.6 °C) and a high of 74.7 °F (23.7 °C) and an average of 61.3 °F (16.3 °C), comparable to the average temperature in Patagonia of approximately 62°F (16.5 °C). Deviations from this average could be indictive of geothermal activity, if hotter, or recent precipitation, if colder. pH values ranged from neutral to acidic, with a high pH of sampled water of 7.74 at Farrell spring to highly acidic water with a pH of 2.84 at Humbolt Spring (site 4). The average pH for all sampled water was slightly acidic at 5.82.

Alkalinity

Alkalinity is an indicator of water's resistance to change in acidification, and is often the dominant anion (HCO_3, CO_3) present in natural waters from carbonate and silicate weathering reactions (Freeze and Cherry 1979). Alkalinity values remained relatively low throughout the study area, indicating low resistance to acidification and lack of significant carbonate mineral dissolution, consistent with the relatively low pH of sampled water. The maximum measured alkalinity was 4.87 meq/kg, at Red Mountain spring (site 7). Numerous samples had no resistance to acidification (sites 2, 4, 10, 15), thus returning negative alkalinity values (reported as 0 meq/kg alkalinity). The average alkalinity of the sampled waters was 1.42 meq/kg. Alkalinity was assumed to be dominated by HCO_3, based on the pH range of samples with detectable alkalinity.

Major Ions

The dominant water type based on major ion chemistry of sampled water can be useful in determining geochemical reactions controlling water chemistry and help determine flow paths and mixing relationships (Gray 2018). Throughout the study area the dominant water type is Ca-SO_4. However, three sample sites (sites 1, 5, and 6) plot as Ca-HCO_3 water as seen in the Piper Diagram presented in Figure 6 . HCO_3 dominant waters are found in in the southern region of the study area. Flux Canyon Flowing well (site 20) is the only sample that plots as Na-HCO_3 type water. Anion analysis highlights the dominance of SO_4 in the sampled water, with numerous samples well above the EPA drinking water limit of 250 mg/L for SO_4. Ca is the dominant cation for all samples, however numerous samples (sites 1, 4, 14, and 15) demonstrate higher levels of Na, while remaining Ca-SO_4 type water.

Trace Elements

Trace elements can help in determining flow paths and trace past water-rock reactions of the sampled groundwater (Balistrieri, et al. 2007). Many of these trace metals are potentially toxic to humans and animals and are often found in elevated concentrations in mountainous regions (Balistrieri, et al. 2007). The analyzed trace elements were detected in quantities below EPA drinking water standards. Results are presented in Table 8. Several trace elements, including As, Cr, Pb, Se, and Ag were not detected in any of the samples. Barium (Ba) was present in Paymaster Spring (site 2) with a concentration of 0.72 mg/L, and Farrell Spring (site 5) had a concentration of 0.14 mg/L. Upper Harshaw Spring (site 3) and Red Mountain Spring (site 7) each had low levels of boron (B) with 0.1 mg/L and 0.12 mg/L, respectively. Cadmium (Cd) was present in three springs, Paymaster, Upper Harshaw and Humbolt (sites 2, 3, and 4), with levels of 0.0023 mg/L, 0.016, 0.0025 mg/L, respectively. Zn was the most prevalent trace metal detected, however all levels were below the EPA's drinking water standard of 5 mg/L. Zn was detected with levels of 1.7 mg/L in Paymaster Spring, 3.7 mg/L in Upper Harshaw Spring, 0.44 mg/L in Humbolt Spring, 0.6 mg/L in Flux Canyon Spring, 0.04 mg/L in Chinaman Spring, 0.12 mg/L in Lee's well and 0.4 mg/L in Alum Gulch well (sites 2, 3, 4, 8, 9, 11 and 14). Samples from Hale Ranch, Chinaman SW, Harshaw Creek and Iron Well (sites 6, 10, 13, and 15) were not analyzed for trace elements.

Stable Water Isotopes

Stable water isotopes can be helpful in determining elevation, seasonality and age of recharged water at a sample site (Springer, Boldt and Junghans 2017, Eastoe and Wright 2019). Figure 7 includes long-term stable water isotopic data from precipitation, adjusted for altitude, from the Tucson Basin, approximately 60 miles (100 km) north of the Town of Patagonia, as reported by Eastoe and Wright (2019). Precipitation data is split into four endmembers: summer and winter precipitation and for both summer and winter precipitation the data is split between all the precipitation fell over those 30 years and the largest 30% of storms; all at 5250 ft (1600 m) (Eastoe and Wright 2019). Alongside the precipitation data, Figure 7 also plots $\delta^{18}O$ and δD values from groundwater sampled by the author with $\delta^{18}O$ and δD values reported by previous studies.

Samples from the mountains generally plotted above the Global Meteoric Water Line (GMWL), with a distinct evaporation trend, Including data reported by others, samples from the basin generally plotted below, with samples taken from sites 14 and 20 having significantly lower $\delta\,^{18}O$ and δD values than other samples from the mountains and the basin. The lowest measured $\delta^{18}O$ and δD values were observed at sites 14 and 20 with values of and -10.21 ‰ and -10.5 for $\delta^{18}O$ and 72.82 ‰ and -73 ‰ for δD, respectively.

The average $\delta^{18}O$ value for all groundwater samples taken by the author was -8.10 ‰ with most sample values clustered around -8 ‰ to -9 ‰. The average δD value was -55.92‰, with most values being in the -50 ‰ to -60 ‰ range. The highest $\delta^{18}O$ and δD values were measured at Paymaster spring (site 2) with values of -5.75 ‰, and-45.47 ‰, respectively. Numerous high elevation springs (sites 2, 4 and 5) plot below the GMWL along an evaporation trend with a slope of 3.4.

Stable Isotopes of Sulfate

Stable Isotopes of SO_4 ($\delta^{34}S$ and $\delta^{18}O$) have a distinct isotopic signature for the Patagonia Mountains due to pyrite oxidation and ARD as seen in Figure 8. Most of the samples fall within the range of $\delta^{34}S$-SO_4 values from -0.5 to -10.7‰ , and δ18O-SO_4 values from -2.2 to 6.1‰. However, there is one anomalous sample, Miller Spring (site 1), which has a $\delta^{34}S$-SO_4 value of 10.1 ‰ and a $\delta^{18}O$-SO_4 value of 12.8 ‰. Samples taken from the basin generally plot in the filed of gypsum dissolution, with three samples (sites 14, 15 and 20) plotting in the pyrite oxidation field. In general, samples from the basin have higher $\delta^{34}S$ and $\delta^{18}O$ values than samples from the mountains, with most $\delta^{34}S$ and $\delta^{18}O$ values ranging from 10.3‰ to 13.8‰ and 9.8‰ to 13.7‰, respectively. Two samples from the Town of Patagonia Well plot between the two identified sources of sulfate: gypsum dissolution and pyrite oxidation.

Age Tracers

Tritium is a useful age tracer and the occurrence of tritium indicates the sample has interacted with precipitation than has fallen within the last 70 years and is considered modern water (Freeze and Cherry 1979). Tritium values ranged from 3.4 Tritium Units (TU) to numerous samples below the detection limit (BDL) of the instrument used (0.5 TU). From the Sonoita Creek basin, samples from sites 14 and 15 both contained non-detect tritium. In the mountains, most samples contained tritium levels between 1 and 3 TU, with Paymaster (site 2) and Upper Harshaw (site 3) being the only two samples containing above 3 TU. Red Mountain Spring (site 7) and Hale Ranch well (site 6) were the only samples from the mountain block containing below detection limit for tritium. Figure 11 includes tritium values mapped across the study site.

Radiocarbon is an age tracer used to date groundwater. ^{14}C samples were taken at sites that reported non-detect levels of tritium and corrected using the $\delta^{13}C$ mixing model (Pearson 1965), and are presented in Figure 9. The age ranges reported are produced from varying the $\delta^{13}C$ value of carbonate minerals from 1 ‰ to 3 ‰. The lowest percent modern carbon (pmc) measured was in the groundwater from the Alum Gulch well (site 14), which contained 9.54 pmc and had a $\delta^{13}C$ value of -12.8 ‰ for dissolved inorganic carbon (DIC), which translates to a corrected ^{14}C age of 18,200-18,400 years old. Water from the well at Hale Ranch (site 6) contained 34.00 pmc and had a $\delta^{13}C$-DIC value of -10.4 ‰, translating to a corrected ^{14}C age of 6,500-6,800 years old. Water from Red Mountain spring (site 7) contained 56.82 pmc and had a $\delta^{13}C$-DIC value of -8.7 ‰, translating to a corrected ^{14}C age of 500–1,100 years old. It is important to note that the 'corrected' ^{14}C age depends on the ^{14}C correction model used and assumed values of parameters in the model. In addition, the 'corrected ^{14}C age' represents the mean age of water.

The highest ^{14}C value reported was Middle Harshaw. The sample contained 65.68 pmc, with a $\delta^{13}C$-DIC value of -5.9 ‰. When corrected, this sample appears to be approximately 1,100 years old. As mentioned, this surface water sample was taken out of protocol and was determined to be an 'opportunity sample' due to the assumption that it was representative of water pumped from the deep aquifer. At the time of sampling the mine was reportedly doing a pump test and discharging the groundwater into Harshaw Creek. If the mine was pumping from their deepest wells, the sample is potentially from a replacement skarn deposit, as seen in the cross section of Figure 3B (Graybeal, et al. 2015). The sample, having spent time in Harshaw Creek as surface water, could have interacted with the atmosphere resulting in exchange of CO_2. This would result in a $\delta^{13}C$-DIC value closer to -7 ‰, which would mean the initial $\delta^{13}C$ value was even more positive. This process would also add atmospheric ^{14}C to the sample, making the sample appear more modern.

Hydrologic Discussion

To discuss the results of this research, the original objectives will be reviewed and responses to those objectives will be provided. Use of the data produced by this research alongside previously published data will either corroborate or contradict past hydrologic insights and provide new evidence-based answers to the original objectives.

Objective 1: Determine the recharge elevation and seasonality of groundwater sampled from springs and wells

Substantive past research has been done on the effect of elevation and seasonality on stable water isotope ratios, $\delta^{18}O$ and δD in precipitation. Global trends show $\delta^{18}O$ and δD values in precipitation generally decrease as elevation increases (Freeze and Cherry 1979). With regards to seasonality, variation between $\delta^{18}O$ and δD in winter precipitation and summer precipitation is consistently significant in the Southwestern United States with summer precipitation having higher average values for $\delta^{18}O$ and δD than winter precipitation (Eastoe and Wright 2019). Through analysis of stable water isotopes from groundwater you can infer the seasonality and elevation of the precipitation that recharged the groundwater that is emergent at the sample site. Figure 7 includes $\delta^{18}O$ and δD values from the study site plotted alongside average precipitation values from the nearby Tucson Basin.

Groundwater from the Patagonia Mountains generally have higher $\delta^{18}O$ and δD values relative to groundwater from the Sonoita Creek alluvial aquifer and resultantly plot above the GMWL, while samples from the Sonoita Creek alluvium plot below. This trend of higher stable water isotope values in the mountains, at higher elevations, is the opposite of global precipitation trends. This deviation from observed global trends likely indicates greater percentage of recharge from snowmelt. Samples with low $\delta^{18}O$ (<-9 ‰) and high δD values, relative to the GMWL, are characteristic of water recharged from snowmelt, due to sublimation or snow-metamorphic process that shift isotopic values (Clark and Fritz 1997, Eastoe and Wright 2019).

Stable water isotope values from the Patagonia Mountains are located between the average values for "all summer" and "all winter" precipitation (Figure 7). This indicates that groundwater in the mountains is recharged by both summer and winter precipitation and contains recharge from smaller precipitation events. However, given the climate of the Patagonia area, a greater fraction of precipitation falls in the summer than winter, resulting in a greater fraction of winter precipitation becoming recharge. In contrast, Sonoita Creek alluvial groundwater appears to contain a significant recharge contribution from precipitation from the 30% wettest storms, as many of the samples plot along the line between 30% wettest summer and 30% wettest winter storms, at the given elevation of 5240 ft (1600 m) likely indicating MFR. Similar trends of MFR have been observed in adjacent basins (Tucci 2018, Eastoe and Wright 2019). Large storms, which produce runoff, flow out of the mountain system and enter the valley, recharging the aquifer in the basin.

Groundwater samples from the mountains, specifically high elevations springs (sites 2, 4, 5) demonstrate an evaporation trend. The observed trend has a slope of 3.4, lower than the GMWL. Evaporation can occur in both the summer and winter months and this trend seems to be localized to sample sites at higher elevations, above 5,000 ft (1524 m). This may be due to the springs being recharged by smaller storm events, allowing for a greater fraction of precipitation to evaporate. An evaporation trend has been seen in the nearby mountains: in the Rincon Mountains, approximately 50 miles (80 km) north of the Patagonia Mountains where springs at comparable elevations demonstrate an evaporation trend with a slope of 3.5; and an in the Santa Rita Mountains, approximately 10 miles (16 km) to the north, with a slope of 4 (Eastoe and Wright 2019).

Stable water isotope values of groundwater from the basin around sites 14, 15, and 20, while isotopically distinct from samples taken from the mountain, also appear to demonstrate an evaporation trend at the time of recharge, as seen in the "unique isotopic signature" label in Figure 7. However, the number of samples for this area are limited, and additional sampling is needed to corroborate this hypothesis.

Objective 2: Conceptualize groundwater flow paths and residence times and assess hydrologic connectivity of groundwater recharge in the mountains to alluvial aquifers in the Sonoita Creek basin, specifically around the Town of Patagonia.

To discuss groundwater flow paths and travel times, the behavior of identified hydrogeologic units seen in Figure 4 will be discussed. A visual aid for this conceptual model is provided in Figure 12.

The Harshaw Creek Fault and surrounding faults appear to be conduits of groundwater flow. Samples taken from the bedrock near Harshaw Creek Fault (sites 2, 3, 4, 8, 9, 10) contain above detection limit tritium levels, suggesting a modern recharge component or recharge that is less than 70 years old (Figure 9, Figure 11). Samples from these same sites along Harshaw Creek Fault are all Ca-SO_4 type water, unlike the Ca-HCO_3 type waters in the surrounding bedrock (Figure 10). The high concentration of springs along this fault system; all with some level of detectable tritium, and the consistent water type along the fault indicate that the Harshaw Creek Fault is a conduit for groundwater flow and moves some amount of recent precipitation along the Harshaw Creek Fault down gradient and towards the basin.

Samples collected from the mountain block at sample sites distant from the Harshaw Creek Fault (sites 5, 6 and 7) contain groundwater with geochemical and isotopic signatures distinct from waters around the fault system. Samples in these areas are Ca-HCO_3 type waters, unlike the Ca-SO_4 type waters that dominate along the Harshaw Creek Fault (Figure 10). Also, unlike the other samples from the mountain block, sites 6 and 7 contain no detectable tritium. Radiocarbon analysis indicates slow movement of pre-modern groundwater around sites 6 and 7 with little mixing with recent precipitation. Based on the unique water type and pre-modern age of these samples, and assuming these samples are representative of the greater mountain block, it can assumed that large portions of the mountain block are hydrologically isolated from the major fault systems and contain pockets of fossil water. The quantity of fossil water in the mountain system is unknown.

The stream channel sediments along Harshaw Creek (sites 3, 11 and 13) contain water from springs in the mountains mixed with some component of modern recharge. Samples in this unit are Ca-SO_4 type waters, with a sulfate isotopic signature of oxidized pyrite, indicative of oxygenated water that has circulated within the sulfide-bearing mountain system. These sample sites are located far from a mapped pyrite zone. The dominance of SO_4 in these samples and sulfate signature of pyrite oxidation, indicate that the water in the stream channel sediments has been circulated in the mountain system, and this alluvial veneer is partially fed by the fractured bedrock. Sites 3 and 11 also contain detectable tritium, indicating the contribution of precipitation that fell within the last 70 years. Resultantly, the thin veneer of stream channel sediments appears to be a conduit of groundwater flow, moving groundwater discharged from the fracture system mixed with recent precipitation towards the Sonoita Creek basin.

The Mountain Front Fault appears to obstruct groundwater flow from the mountains into the basin. This hypothesis is corroborated by numerous trends in the data. Groundwater from sites 14, 15 and 20 all have below detection limit tritium levels and sites 14 and 20 have a stable water isotope signature indictive of recharge under colder climatic conditions. Samples southeast of the fault all contain some level of detectable tritium and stable water isotope signatures consistent with modern precipitation. Water from site 14, acting as the representative sample for the area, is dated to be 18,200-18,400 yrs old, indicating that this fossil groundwater was likely recharged at the end of the last ice age (Late Pleistocene recharge). Late Pleistocene groundwater in alluvial aquifers at the base of mountain systems, have been seen throughout the Southwestern United States (Eastoe and Wright 2019, Tucci 2018). Additionally, site 20 is the only sample site in the study area to express Na-HCO_3 type water. Due to the old age of the water, below detection limit tritium in all sites in this area, the distinct water type, and the distinct isotope signature; it is hypothesized that this area in the alluvial basin, around sites 14, 15 and 20, is hydrologically isolated from the Patagonia Mountains. Groundwater moving down gradient from the Patagonia Mountains towards the alluvial valley likely hits the dammed Mountain Front Fault and does not transfer into the alluvial aquifer. Where the groundwater goes after hitting the fault is unknown. A possible hypothesis is the groundwater is shunted laterally along the fault or deeper into the bedrock and drains more regionally, likely down gradient towards the Santa Cruz River.

Further discussing basin groundwater around sites 14, 15 and 20, this area also appears to be hydrologically isolated from the greater Sonoita Creek alluvial and basin-fill aquifer. Building on the work of Gu et al. (2005), stable isotopes of sulfate have been used to trace the origin of groundwater within the Sonoita Creek alluvial aquifer. Two endmembers exist, either from pyrite oxidation from the Patagonia Mountains or gypsum dissolution from the central Cienega Creek watershed (A. Gu 2005), as seen in Figure 8. All samples from the Sonoita Creek alluvial aquifer plot within the values deemed to be gypsum dissolution, with the exception of sites 14, 15 and 20 which plot within the values deemed to be pyrite oxidation. Also, groundwater in this area does not contain detectable tritium (Figure 9 and Figure 11), while the surrounding alluvial aquifer does. The unique sulfate isotope signature and non-detectable tritium further corroborate the hypothesis that the aquifer in this area is hydrologically isolated from the greater Sonoita Creek alluvial and basin-fill aquifer. The signature of pyrite oxidation indicates that the water likely originated in the mountain system and has made its way into the basin over thousands of years.

Sulfate isotopes from the Town of Patagonia's well (site 17) indicate mixing between pyrite oxidation and gypsum dissolution (Figure 8). The presence of SO_4 isotopes with a pyrite oxidation signature is indicative of groundwater that has circulated within the sulfide bearing Patagonia Mountains. Sulfate concentration in these samples stays consistent, however values for $\delta^{34}S\text{-}SO_4$ vary between the two end members (Figure 8B). To explain this contribution to the Town well, while maintaining the conclusion of the Mountain Front Fault obstructing groundwater flow to the basin, it is assumed that focused MBR from the alluvial veneer aquifer formed by stream channel sediments in Harshaw Creek is likely a key contributor to groundwater recharge around the Town of Patagonia. This alluvial veneer drains directly into the Town of Patagonia, and thus likely is the primary hydrologic unit facilitating this connectivity between the mountains and the alluvial basin. Alongside focused MBR, as previously discussed, MFR from the Harshaw Creek drainage is key to groundwater recharge within the basin.

The anomalous sample of Miller Spring (site 1) is located upgradient and south of the mapped pyrite zone, as seen in Figure 10. Due to the low SO_4 levels and the uncharacteristic $\delta^{34}\text{-}SO_4$ signature (Figure 8B), it is hypothesized that this anomalous sample is composed of primarily precipitation, consistent with the low temperature of the sample, 53 °F (11.7 °C).

Objective 3: Discuss the potential impact of drought conditions and groundwater extraction in the mountains on mountain springs and groundwater availability in the alluvial basin.

All the sampled springs, except for Red Mountain Spring (site 7), contain at least some level of detectable tritium, indicating they are sourced from water that was recharged in the last 70 years. Similar trends, of recent recharge emergent at the springs in the Patagonia Mountains were seen by Gu et al. (2005). The dependence of these springs on recent precipitation make them more vulnerable to drying out due to drought. Compounding this vulnerability is the presence of an evaporation trend in stable water isotopes at high elevations, and a snowmelt recharge component. Continued shift in climatic patterns towards a more arid and hotter climate in the southwest (Gonzalez, et al. 2018) due to global climate change will likely diminish flow of springs in the Patagonia Mountains (Meixner, et al. 2016).

Decreased flow at springs could decrease focused MBR from the Patagonia Mountains to the Sonoita Creek alluvial aquifer. Gu et al. (2005) also observed a decrease in percentage contribution from the Patagonia Mountains to base flow in the Sonoita Creek during times of drought.

Due to the Mountain Front Fault obstructing groundwater flow from the mountains into the basin, direct hydrologic connectivity between the fractured bedrock aquifer the mine is pumping from and the Sonoita Creek alluvial and basin-fill aquifer is unlikely. Impact on groundwater resources due to groundwater pumping by the mine cannot be thoroughly commented upon due to lack of access to the mine's wells at the time of sampling and limited data about the groundwater geochemistry.

Societal Discussion

Objective 4: Educational outreach and dissemination of findings within the Sonoita Creek watershed

Included in this project were regular updates to the F&F Committee and continued work with the PAWS team. The F&F Committee aided in organizing and advertising a well owner training that was presented on February 29, 2020. The well owner training highlighted steps that residents could take to monitor their drinking water supply and presented a basic understanding of the hydrology of the Patagonia area, including preliminary conclusions from this study. The well owner training was well attended and highlighted the high level of interest in the greater Patagonia area in understanding groundwater movement and supply.

The results of this research were planned to be presented on April 22, 2020 in the Town of Patagonia, and at the Science on the Sonoita Plain Conference in late May, 2020. Due to limitations presented by the COVID-19 pandemic, the presentations were canceled and rescheduled for May 14th, 2020. The presentation was organized by the F&F committee, and invitations to participate in the presentation and the following discussion were sent to the USGS, the mine and other interested parties. At the meeting, the results of this research were discussed, and potential future research, partnerships and monitoring steps were outlined. Included below is a list of recommend future research and monitoring.

The results from this research build upon the work of numerous dissertations, thesis, reports and articles, each with insightful findings for the area. Many of these findings and conclusions are not well understood in the Patagonia area. Synthesizing the findings of others and including them besides the findings of present research has been an important tool in building a better understanding of groundwater movement in the Patagonia area.

Objective 5: guidance for further studies, monitoring and management

The original scope of work for this project ended with the Town empowered to better manage groundwater resources in their region. However, it became apparent throughout the project that the legal framework available to rural communities in Arizona to manage groundwater in their surrounding region is weak outside of Active Management Areas (AMAs). If the Town were to try to manage groundwater pumping in the area, strategies would include using federal reserved water rights, if applicable, proving groundwater pumping is damaging the population of a threatened or endangered species, expanding AMA boundaries, or using setbacks or buffers within the Town. Apart from these tangential strategies, given the current governing framework in Arizona, public opinion and the private decisions made by industry and well owners are of more influence than local governance with regards to managing groundwater in the Patagonia Area. Resultantly, public opinion is an important tool for the Town as the Town adapts to new climactic patterns and groundwater use conditions. Public opinion can be informed by continued education of residents in the watershed based on the best available scientific knowledge and continued collaboration with researchers doing work in the area.

Returning to the Diane Austin quote, “environmental issues have been treated as the purview of experts, [even though,] local people know best what their problems are and how to solve them” (Austin 2004). With this idea in mind, continued collaboration between researchers and the local groups will benefit both the researchers and the people local to the Patagonia Area. Researchers and industry working in the Patagonia Mountains should collaborate with the Town, recognizing the efforts of residents of the Town to be stewards of their surrounding area.

This research would have benefited from data from the mine’s wells and access to those wells would have led to more robust results and a better understanding on the part of the author, the mine, the scientific community and residents living within the watershed. The author’s attempt to collaborate with the mine during the research stage were dismissed numerous times by mining officials. There is still opportunity for the mine to collaborate with researchers in the area, and that opportunity should continue to be pursued. Without access to data from the mine’s wells the present research does not have any data to suggest concern for water resources due to pumping. Future research, if it were to include age and geochemistry data from the mine’s wells will allow for a more complete assessment of water resources in the area.

Recommendations for continued research include:

(1) Annual or bi-annual sampling and testing of the Town of Patagonia well for sulfate isotopes (^{34}S and ^{18}O) to monitor the contribution of water from the Patagonia Mountains via Harshaw Creek and stream channel sediments to the Town of Patagonia well. Additional data will build on the work of Gu et al. (2005) and will require professional interpretation;
(2) Monitor vertical gradient and temperature in Harshaw Creek channel sediments using transducers in existing monitoring wells (if available) and temporary piezometers installed in the creek bed to better understand contribution from springs and the fractured bedrock aquifer to this veneer of alluvial sediments;
(3) Further build on present research by collecting age and geochemical data from surface water and groundwater from wells or piezometers at the exit of Harshaw Creek, close to the Town, to better connect groundwater contribution from the Patagonia Mountains to recharge in this area;
(4) Sample the mine's production wells for age and geochemistry, or request such data from the mine, to better understand the hydrologic connectivity between the water the mine is pumping, and water expressed at springs, adits, and wells in the mountain system;

Recommendations for continued monitoring include:

(5) Set up a weather station or gain access to the data from an existing weather station in the mountains. Precipitation data from a weather station is essential for future monitoring of surface water and groundwater resources;
(6) Monitor pressure at Hale Ranch well and the Humboldt Canyon Flowing well (site 6 and 21) to document changes in hydraulic head in these areas;
(7) Monitor spring flow and water quality at Harshaw Creek spring (site 13) and correlate flow with weather data to monitor precipitation and groundwater contribution to the alluvial sediments above the spring, and;
(8) Annual or biannual visits to high elevation springs; Paymaster, Miller, Farrell and Humboldt (sites 1, 2, 4 and 5) to monitor flow as they are most susceptible to drying up due to drought.

Conclusions

Within the study area there are three unique systems with three unique types of groundwater:

(1) Pleistocene groundwater in the Sonoita Creek alluvial aquifer around sites 14, 15, and 20. This area is hydrologically disconnected from the fractured bedrock aquifer in the mountains and the surrounding Sonoita Creek alluvial aquifer.

(2) Water from mountain springs and adits. Water emergent at most springs and adits in the mountains has a modern recharge component which has been circulated in the mountain's system of faults and fractures. The most significant feature moving this groundwater is the Harshaw Creek Fault. Parts of the mountain distant from the major fault systems contain groundwater with a longer residence time and are less likely to contain a modern recharge component. The Mountain Front Fault obstructs groundwater flow from the mountains into the Sonoita Creek alluvial basin. Some of the water stored in the fractured bedrock is discharged from springs or fractures and sustains flow in stream channel sediments in the mountains.

(3) Water in the stream channel sediments around Harshaw Creek. Water in this unit also contains a modern recharge component, mixed with water that has been released from mountain springs or the mountain's fracture system. Groundwater in this system drains to the Sonoita Creek alluvial basin and partially recharges the Sonoita Creek alluvial aquifer through focused MBR.

Based on our results, the primary concern for water resources in the Northern Patagonia Mountains is drought. Groundwater from springs and adits in the mountains express vulnerability to climatic patterns that result in less frequent precipitation events, less snowpack, and higher temperatures. Such patterns are predicted in the southwest due to climate change (Gonzalez, et al. 2018).

The secondary concern is the potential impact on groundwater flow in stream channel sediments around Harshaw Creek and its tributaries. Harshaw Creek and its tributaries appear to partially recharge the basin aquifer and additional monitoring and research could corroborate this conclusion. Apart from the hydrologic connection of Harshaw Creek to the Sonoita Creek alluvial aquifer, the data collected by this research does not indicate concern for water resources in the Sonoita Creek alluvial aquifer from changing conditions in the Northern Patagonia Mountains.

Partnerships and citizen science are two key tools for residents to use in managing and understanding their natural resources. They can lead to greater transparency in data collection and interpretation and allow for local populations to help frame the inquiry done by researchers. The author has found the partnership model to be a multidisciplinary and well-rounded approach to conducting research and addressing pertinent societal questions.

Appendix A: Tables

TABLE 1: WELL DATA FROM THE MINE PROPERTY SHOWING A DEEP LIMESTONE LAYER [1]

ADWR Well ID, 55-	Date Completed	Well Surface (ft)	Latitude	Longitude
920323	2-21-17	5052	31.46203	-110.71810
920370	3-21-17	5144	31.46474	-110.72235
920371	3-21-17	5260	31.46200	-110.72870
920378	4-3-17	5124	31.45936	-110.71811
920392	3-16-17	5136	31.46205	-110.72023
920459	4-9-17	5170	31.46199	-110.71172
920498	5-30-17	5185	31.46473	-110.72447
920500	4-17-17	5053	31.62651	-110.71809
920578	6-7-17	5187	31.46201	-110.71384
227120	10-10-17	5188	31.45402	-110.71176

ADWR Well ID, 55-	Upper Slots	Lower Slots	Water Surface Depth (below surface)	Water Surface	Limestone depth (below surface)	Limestone Occurrence
	(fasl)	(fasl)	(ft)	(fasl)	(ft)	(fasl)
920323	4652	4552			1399	3653
920370	---	---	356	4788	1334	3810
920371	---	---			1835	3422
920378	---	---	190	4934	1325	3799
920392	---	---	190	4946	1793	3343
920459	3416	1500	220	4950	1760	3410
920498	4715	4685			1425	3760
920500	4783	4703	---	---	1778	3275
920578	4787	4760	237	4950	1105	4082
227120	4846	3891	237	4951	1020	4168

[1] Data received ADWR Wells-55 website (https://gisweb2.azwater.gov/WellReg). Fasl = feet above sea level. Latitude and longitude are approximated from Google Earth.

TABLE 2: SAMPLE SITE DETAILS

Site Name	Site number	Sample Source	Hydrogeologic unit [1]	Date Sampled	Latitude	Longitude	Elevation
							ft
Miller	1	Spring	PMG	5/10/2019	31.4100	-110.7155	5545
Paymaster	2	Spring	PMG	5/10/2019	31.4122	-110.7062	5439
Upper Harshaw	3	Spring	PMG	5/27/2019	31.4377	-110.7249	5320
Humbolt	4	Spring	PMG	5/25/2019	31.4644	-110.7453	5230
Farrell	5	Spring	PMG	5/7/2019	31.4383	-110.6976	5148
Hale Ranch	6	Well	PMG	10/16/2019	31.4633	-110.7036	4893
Red Mountain	7	Spring	PMG	5/10/2019	31.4955	-110.7184	4823
Flux Canyon	8	Spring	PMG	5/7/2019	31.4876	-110.7524	4669
Chinaman	9	Spring (adit)	PMG	5/7/2019	31.4842	-110.7377	4555
Chinaman SW	10	Spring	PMG	5/7/2019	31.4837	-110.7386	4549
Lee's Well	11	Well	PMG	5/27/2019	31.4967	-110.6819	4545
Middle Harshaw [2]	12	Surface Water	PMG	12/27/2018	31.4986	-110.6805	4516
Harshaw Creek	13	Spring	PMG	5/7/2019	31.5087	-110.6813	4426
Alum Gulch Well	14	Well	SCAG	5/27/2019	31.5063	-110.7606	4101
Iron Well	15	Well	SCAG	5/29/2019	31.5066	-110.7709	4078

[1] PMG = Patagonia Mountains Groundwater, SCAG= Sonoita Creek Alluvial Groundwater
[2] Sample collected by residents living in the Harshaw Creek Watershed. The sample was collected as the mine upstream was assumed to be conducting a pump test. The sample was taken out of protocol, however given the rare nature of the sample it was used for radiocarbon dating

TABLE 3: SAMPLE SITE DETAILS REPORTED BY OTHERS [1]

Site Name [2]	Site Number	Sample Source	Date Sampled	Hydrogeologic unit [3]	Date Sampled	Latitude	Longitude	Elevation
								ft
Reported by Gu et al. (2005)								
NSS well	16	Well	6/23/1999	SCAG	6/23/1999	31.5443	-110.7406	4100
NSS well	16	Well	4/5/2001	SCAG	4/5/2001	31.5443	-110.7406	4100
NSS well	16	Well	11/14/2003	SCAG	11/14/2003	31.5443	-110.7406	4100
Patagonia Town well	17	Well	7/16/1999	SCAG (TPMW)	7/16/1999	31.5425	-110.7508	4066
Patagonia Town well	17	Well	3/29/2001	SCAG (TPMW)	3/29/2001	31.5425	-110.7508	4066
Patagonia Town well	17	Well	11/6/2002	SCAG (TPMW)	11/6/2002	31.5425	-110.7508	4066
Patagonia Town well	17	Well	12/5/2003	SCAG (TPMW)	12/5/2003	31.5425	-110.7508	4066
Old TNC well	18	Well	10/6/1998	SCAG	10/6/1998	31.5281	-110.7761	3976
Old TNC well	18	Well	1/14/1999	SCAG	1/14/1999	31.5281	-110.7761	3976
TNC well	19	Well	10/8/1998	SCAG	10/8/1998	31.5281	-110.7719	3974
TNC well	19	Well	3/29/2001	SCAG	3/29/2001	31.5281	-110.7719	3974
TNC well	19	Well	12/5/2003	SCAG	12/5/2003	31.5281	-110.7719	3974
Flux Canyon flowing well	20	Well	9/18/1998	SCAG	9/18/1998	31.5137	-110.7844	3960
Flux Canyon flowing well	20	Well	9/24/1999	SCAG	9/24/1999	31.5137	-110.7844	3960
Reported by Wanty et al. (2001)								
Paymaster [4]	2	Spring	Feb-97	PMG	2/1/1997	31.4122	-110.7062	5439
Flowing well in Humbolt Canyon	21	Well	Feb-97	PMG	2/1/1997	31.4647	-110.7447	5150
World Fair Mine Adit	22	Spring (adit)	Feb-97	PMG	2/1/1997	31.4797	-110.7377	4800

[1] Latitude and longitude were not reported by Gu et al. (2005). Google Earth was used to estimate the location and elevation of sites based on site description provided by the authors

[2] NSS = Native Seeds Search. TNC = The Nature Conservancy

[3] PMG = Patagonia Mountains Groundwater, SCAG= Sonoita Creek Alluvial Groundwater, TPMW=Town of Patagonia Municipal Well

[4] Paymaster is the same sample site as site number (2). The same latitude and longitude of the site taken by the author were used for this report, however, they varied slightly from the latitude and longitude reported by Wanty et al. (2001)

TABLE 4: FIELD MEASUREMENTS

Site Name	Site number	Date Sampled	pH	Temperature (°C)
Miller	1	5/10/2019	6.11	11.7
Paymaster	2	5/10/2019	3.45	13.1
Upper Harshaw	3	5/27/2019	5.02	14.8
Humbolt	4	5/25/2019	2.84	10.6
Farrell	5	5/7/2019	7.74	16.3
Hale Ranch	6	10/16/2019	7.20	18.0
Red Mountain	7	5/10/2019	6.77	20.0
Flux Canyon	8	5/7/2019	6.63	15.4
Chinaman	9	5/7/2019	7.05	12.0
Chinaman SW	10	5/7/2019	3.24	19.8
Lee's Well	11	5/27/2019	6.00	18.3
Middle Harshaw [1]	12	12/27/2018		
Harshaw Creek	13	5/7/2019	6.75	14.0
Alum Gulch Well	14	5/27/2019	6.98	23.7
Iron Well	15	5/29/2019	5.80	22.2

[1] Sample collected by residents living in the Harshaw Creek Watershed. The sample was collected as the mine upstream was assumed to be conducting a pump test. The sample was taken out of protocol and no field measurements were recorded.

TABLE 5: FIELD MEASUREMENTS REPORTED BY OTHERS

Site Name[1]	Site Number	Date Sampled	Field pH	Temperature[2]
				(°C)
Reported by Gu et al. (2005)				
NSS well	16	6/23/1999	7.04	28.2
NSS well	16	4/5/2001	7.07	
NSS well	16	11/14/2003	7.05	19.9
Patagonia Town well	17	7/16/1999	6.80	22.0
Patagonia Town well	17	3/29/2001	7.14	22.4
Patagonia Town well	17	11/6/2002	7.14	15.3
Patagonia Town well	17	12/5/2003	7.40	
Old TNC well	18	10/6/1998	4.49	24.0
Old TNC well	18	1/14/1999	4.46	18.7
TNC well	19	10/8/1998	7.19	17.7
TNC well	19	3/29/2001	7.17	20.3
TNC well	19	12/5/2003	7.70	
Flux Canyon flowing well	20	9/18/1998	7.67	24.6
Flux Canyon flowing well	20	9/24/1999	6.91	28.6
Reported by Want et al. (2001)				
Paymaster	2	2/1/1997	6.86	7.3
Flowing well in Humbolt Canyon	21	2/1/1997	3.45	19.3
World Fair Mine Adit	22	2/1/1997	3.07	12.5

[1] NSS = Native Seed Search. TNC = The Nature Conservancy
[2] Spaces were left blank where values were not reported by others

TABLE 6: MAJOR IONS [1]

		Anions [2]						Cations					
Site Name	Site number	F	Cl	Br	NO_3	SO_4	HCO_3	K	Mg	Na	Ca	Fe_{total}	Co
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Miller	1	BDL	3.6	BDL	BDL	19	43	2.2	9	33	53	0.04	BDL
Paymaster	2	0.43	4.8	BDL	BDL	837	0	7.5	35	40	272	3.28	0.21
Upper Harshaw	3	0.10	5.2	BDL	BDL	1231	13	3.7	86	65	524	0.05	0.00
Humbolt	4	0.11	1.9	BDL	BDL	105	0	2.7	5	8	12	0.41	0.03
Farrell	5	BDL	2.8	BDL	BDL	43	157	1.9	16	15	136	0.09	BDL
Hale Ranch	6	BDL	1.6	BDL	0.41	18	157	3.4	15	11	97	0.03	BDL
Red Mountain	7	0.21	5.1	BDL	BDL	1322	297	7.6	184	71	538	1.85	0.01
Flux Canyon	8	0.20	2.8	BDL	BDL	358	99	4.0	38	31	241	0.06	BDL
Chinaman	9	0.16	2.8	BDL	BDL	374	221	3.1	39	58	223	0.10	BDL
Chinaman SW	10	0.40	3.3	BDL	BDL	590	0	5.5	41	38	164	1.03	0.06
Lee's Well	11	0.63	3.5	BDL	BDL	312	143	7.0	47	27	153	21.77	0.03
Middle Harshaw [3]	12												
Harshaw Creek	13	0.13	4.7	BDL	BDL	184	146	3.5	33	38	172	0.02	BDL
Alum Gulch Well	14	0.69	1.6	BDL	BDL	330	65	12.1	17	78	142	2.44	BDL
Iron Well	15	0.48	3.3	BDL	BDL	253	0	5.7	29	58	94	0.13	0.09

[1] BDL = Below Detection Limit (5 µmol/L)
[2] HCO_3 derived from alkalinity measurement. Alkalinity measured as meq/kg and assumed to be dominated by HCO_3
[3] Sample collected by residents living in the Harshaw Creek Watershed. The sample was collected as the mine upstream was assumed to be conducting a pump test. The sample was taken out of protocol and not analyzed for major ions.

TABLE 7: MAJOR IONS REPORTED BY OTHERS [1]

			Anions			Cations			
Site Name [2]	Site Number	Date Sampled	Cl	SO_4	HCO_3	K	Mg	Na	Ca
			mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Reported by Gu et al. (2005)									
NSS well	16	6/23/1999	6	295		1.6	26	11	176
NSS well	16	4/5/2001		300		1.4	24	12	138
NSS well	16	11/14/2003	6	307	205	1.7	30	13	154
Patagonia Town well	17	7/16/1999	7	216		1.7	24	14	141
Patagonia Town well	17	3/29/2001	8	228		2.1	26	18	144
Patagonia Town well	17	11/6/2002	8	252	185	1.9	25	18	148
Patagonia Town well	17	12/5/2003		309					
Old TNC well	18	10/6/1998	10	397		21.5	6	43	67
Old TNC well	18	1/14/1999	27	404		19.2	9	58	69
TNC well	19	10/8/1998	6	269	225	2.0	31	26	141
TNC well	19	3/29/2001	7	222		1.7	27	15	155
TNC well	19	12/5/2003		256					
Flux Canyon flowing well	20	9/18/1998	7	520	78	10.0	4	144	102
Flux Canyon flowing well	20	9/24/1999	10	372		9.5	3		116
Reported by Wanty et al. (2001)									
Paymaster	2	Feb-97	5						
Flowing well in Humbolt Canyon	21	Feb-97	4.7	1700		27	100	11	170
World Fair mine adit	22	Feb-97	10	110		1.9	3	4	6

[1] Spaces were left blank where values were not reported by others
[2] NSS = Native Seed Search. TNC = The Nature Conservancy

TABLE 8: TRACE ELEMENTS [1]

Site Name	Site Number	As	Ba	B	Cd	Cr	Pb	Se	Ag	Zn
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Miller	1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Paymaster	2	BDL	0.72	BDL	0.0023	BDL	BDL	BDL	BDL	1.7
Upper Harshaw	3	BDL	BDL	0.10	0.0160	BDL	BDL	BDL	BDL	3.7
Humbolt	4	BDL	BDL	BDL	0.0025	BDL	BDL	BDL	BDL	0.44
Farrell	5	BDL	0.14	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Hale Ranch	6									
Red Mountain	7	BDL	BDL	0.12	BDL	BDL	BDL	BDL	BDL	BDL
Flux Canyon	8	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.60
Chinaman	9	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.04
Chinaman SW	10									
Lee's Well	11	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.12
Middle Harshaw	12									
Harshaw Creek	13									
Alum Gulch Well	14	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.40
Iron Well	15									
Detection Limit		**0.040**	**0.050**	**0.10**	**0.0020**	**0.030**	**0.040**	**0.040**	**0.010**	**0.040**

[1] BDL= Below Detection Limit. Hale Ranch, Chinaman SW, Middle Harshaw, Harshaw Creek and Iron Well were not analyzed for trace elements.

TABLE 9: ISOTOPES[1]

Site Name	Site Number	Tritium[2]	Tritium Error	δ^2H	$\delta^{18}O$	$\delta^{34}S\text{-}SO_4$	$\delta^{18}O\text{-}SO_4$	^{14}C	^{14}C Error	$\delta^{13}C$-DIC	Uncorrected ^{14}C age (yrs)	Corrected ^{14}C age (yrs)[3]
		TU	TU	‰ (VSMOW)	‰ (VSMOW)	‰ (CDT)	‰ (VSMOW)	(PMC)	(PMC)	‰ (VPDB)		
Miller	1			-54.28	-8.22	10.1	12.8					
Paymaster	2	3.4	0.20	-45.47	-5.75	-10.7	-2.2					
Upper Harshaw	3	3.5	0.26	-56.82	-8.39	-6.9	-2.2					
Humbolt	4	1.4	0.20	-50.42	-6.98	-6.2	0.9					
Farrell	5	1.1	0.19	-49.24	-6.25	-6.4	6.1					
Hale Ranch	6	BDL		-57.42	-8.30	-7.9	5.5	34.00	0.19	-10.4	8,665	6,500-6,800
Red Mountain	7	BDL		-56.06	-7.75	-2.5	0.5	56.82	0.31	-8.7	4,541	500-1,100
Flux Canyon	8	2.5	0.24	-56.40	-8.78	-0.7	3.3					
Chinaman	9	1.6	0.20	-58.12	-8.84	-1.7	0					
Chinaman SW	10	1.0	0.22	-54.12	-8.69	-2.9	-1.9					
Lee's Well	11	1.4	0.25	-55.56	-7.94	-8.4	0.9					
Middle Harshaw[4]	12							65.68	0.44	-5.9	3,377	1,100[5]
Harshaw Creek	13			-53.21	-8.26							
Alum Gulch Well	14	BDL		-72.82	-10.21	-0.5	3.5	9.54	0.13	-12.8	18,880	18,200-18,400
Iron Well	15	BDL		-62.98	-9.01	-1.5	0.8					

[1] Spaces left blank indicate that the sample was not analyzed for the given parameter
[2] BDL = Below Detection Limit (0.5 TU)
[3] The range of ages is the result of $\delta^{13}C$ of the carbonate used during age correction
[4] Sample collected by residents living in the Harshaw Creek Watershed. The sample was collected as the mine upstream was assumed to be conducting a pump test. The sample was taken out of protocol, however given the rare nature of the sample it was used for radiocarbon dating
[5] Corrected using a correction coefficient of .75 for karst systems (Clark and Fritz 1997). This sample is assumed to come from a deep limestone layer. Age is conservative due to the sample likely being a mixture of waters and the sample being collected out of protocol

TABLE 10: ISOTOPES REPORTED BY OTHERS [1]

Site Name [2]	Site Number	Date Sampled	Tritium [3]	δ²H	δ¹⁸O	δ³⁴S SO₄	δ¹⁸O SO₄
Unit			TU	‰ (VSMOW)	‰ (VSMOW)	‰ (CDT)	‰ (VSMOW)
Reported by Gu et al. (2005)							
NSS well	16	6/23/1999	2.3	-59	-8.8	11.7	10.5
NSS well	16	4/5/2001	4.6	-63	-9.1	13.3	12.2
NSS well	16	11/14/2003	1.3	-59	-8.2	13.8	13.7
Patagonia Town well	17	7/16/1999	2.2	-64	-9.0	10.8	10.8
Patagonia Town well	17	3/29/2001	2.6	-61	-8.6	-0.4	5.6
Patagonia Town well	17	11/6/2002	3.5	-59	-8.2	6.9	9.8
Patagonia Town well	17	12/5/2003	1.3	-58	-8.2	12.6	12.8
Old TNC well	18	10/6/1998	BDL	-60	-8.3		
Old TNC well	18	1/14/1999		-58	-8.3		
TNC well	19	10/8/1998	2	-63	-8.8		
TNC well	19	3/29/2001	1.8	-62	-8.8	10.3	10.7
TNC well	19	12/5/2003	1.4	-60	-8.4	11.5	12.8
Flux Canyon flowing well	20	9/18/1998	BDL	-73	-10.5		
Flux Canyon flowing well	20	9/24/1999		-72	-9.2	1.7	3.4
Reported by Wanty et al. (2001)							
Paymaster	2	Feb-97		-56.3	-8.3	-2.4	9.2
Flowing well in Humbolt Canyon	21	Feb-97		-59.4	-8.5		
World Fair Mine Adit	22	Feb-97		-62.2	-8.9	-5.2	1.3

[1] Spaces were left blank where values were not reported by others
[2] NSS = Native Seed Search, TNC = The Nature Conservancy
[3] BDL = Below Detection Limit. Detection limit reported by Gu et al. (2005) was 1 TU

Appendix B: Figures

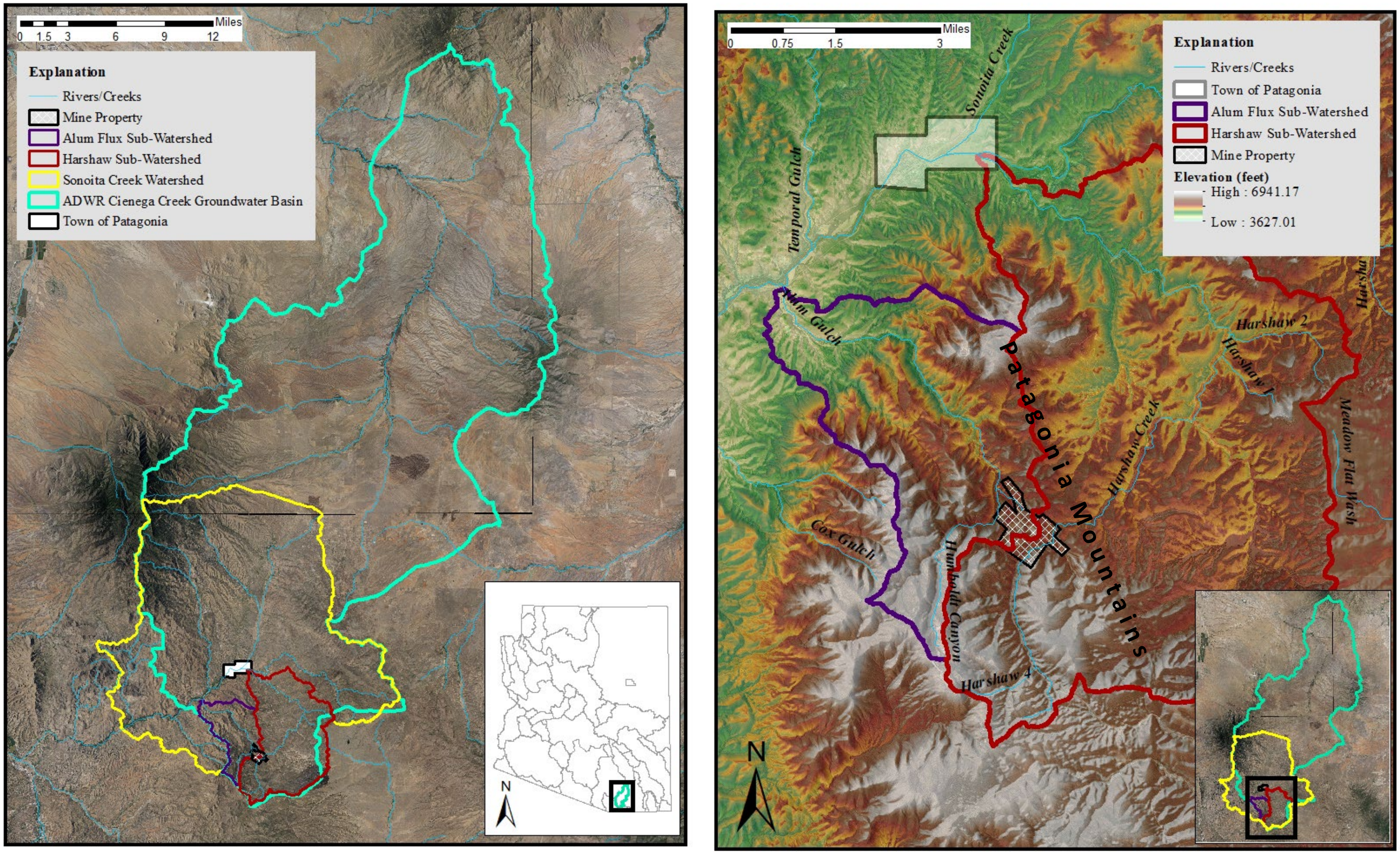

FIGURE 1: STUDY SITE [1]

[1] Boundaries of Town of Patagonia and Mine Property are not representative of the full extent of either the Town or the mine.

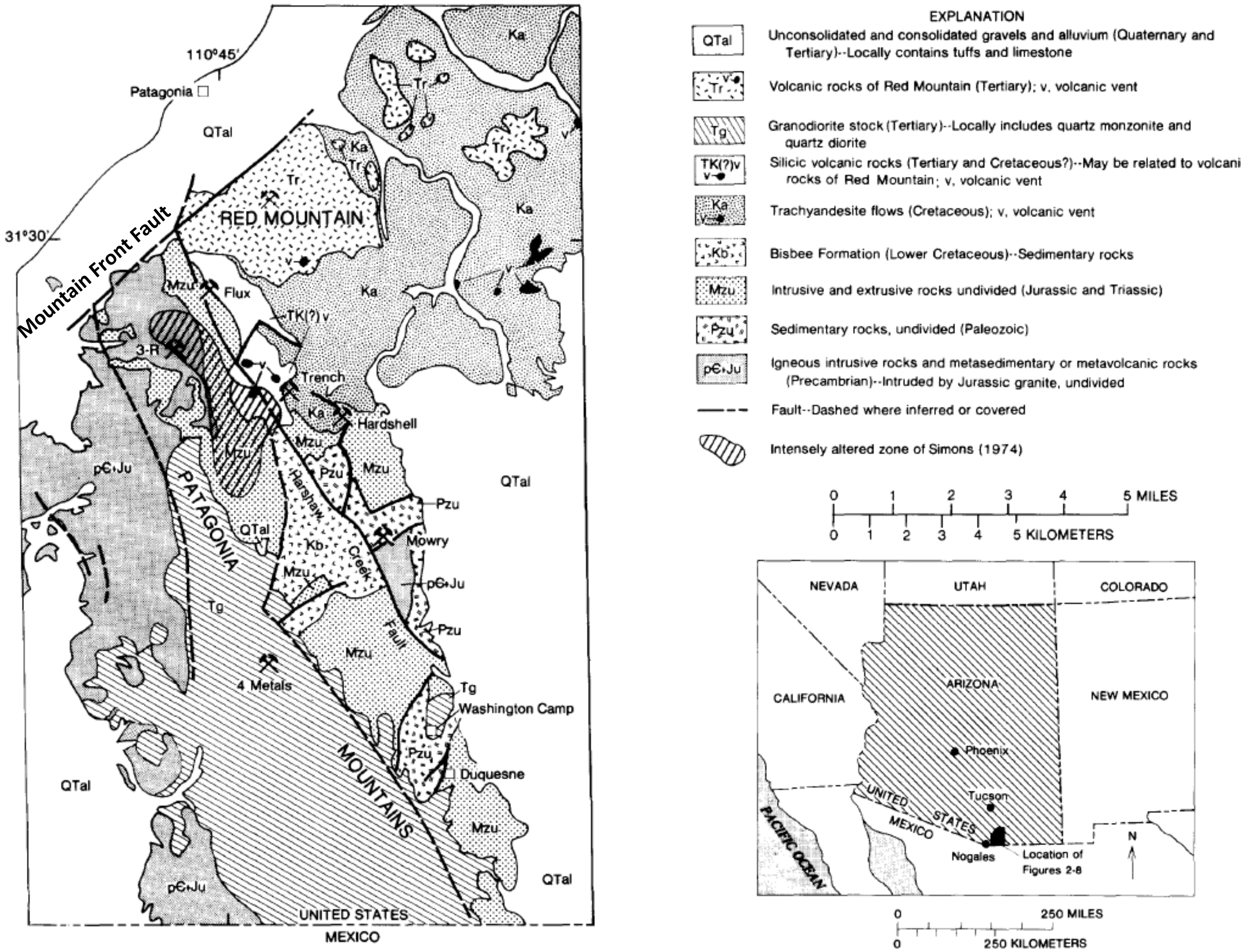

FIGURE 2: GENERALIZED GEOLOGIC MAP OF STUDY SITE [1]

[1] Geologic map from Chaffee (1980).

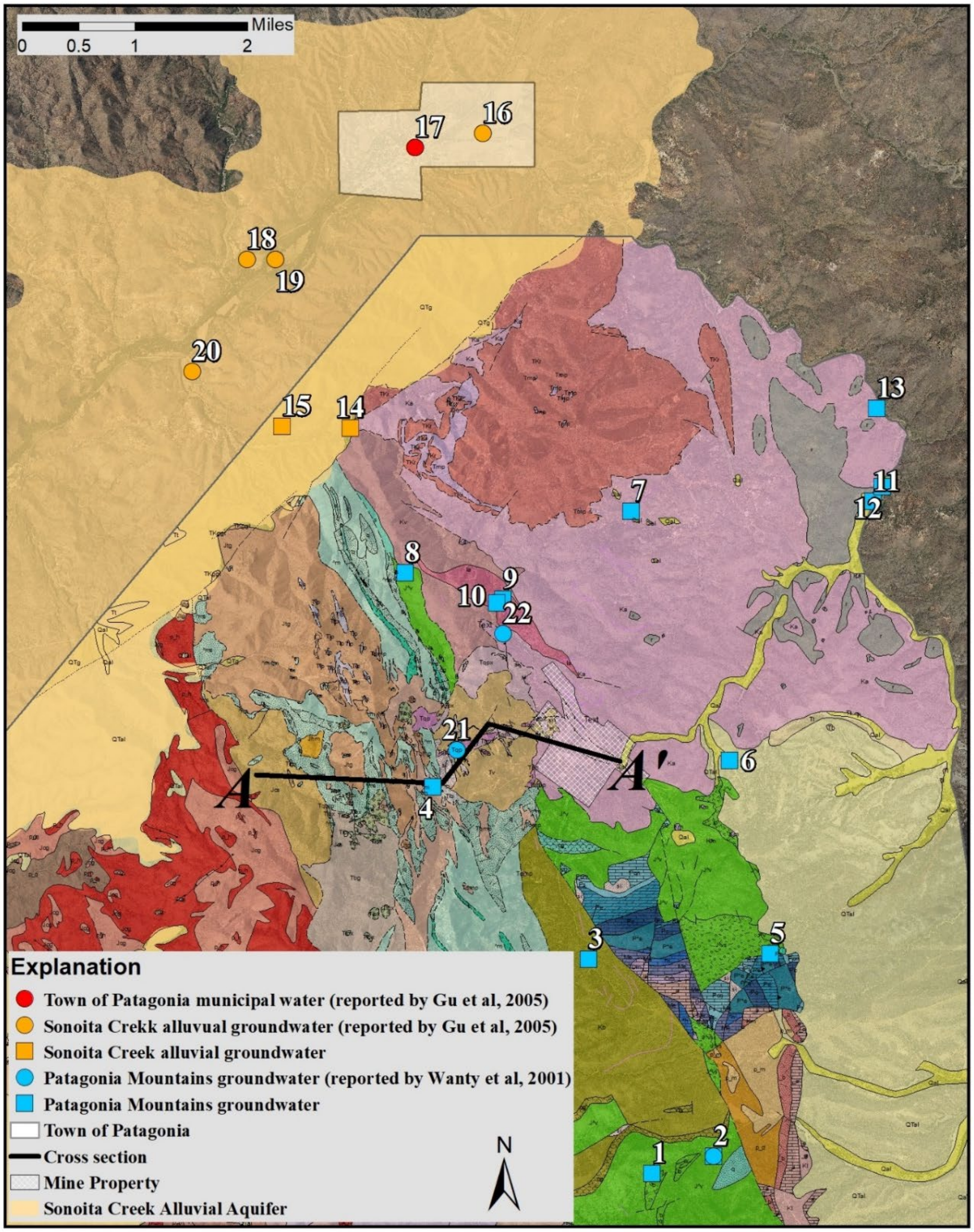

FIGURE 3A: DETAILED GEOLOGIC MAP OF STUDY SITE [1]

[1] Explanation and cross section on following page. Geologic map from Graybeal et al. (2015). Sonoita Creek Alluvial Aquifer approximated from Montgomery and Associates (1999). Boundaries of Town of Patagonia and Mine Property are not representative of the full extent of either the Town or the mine.

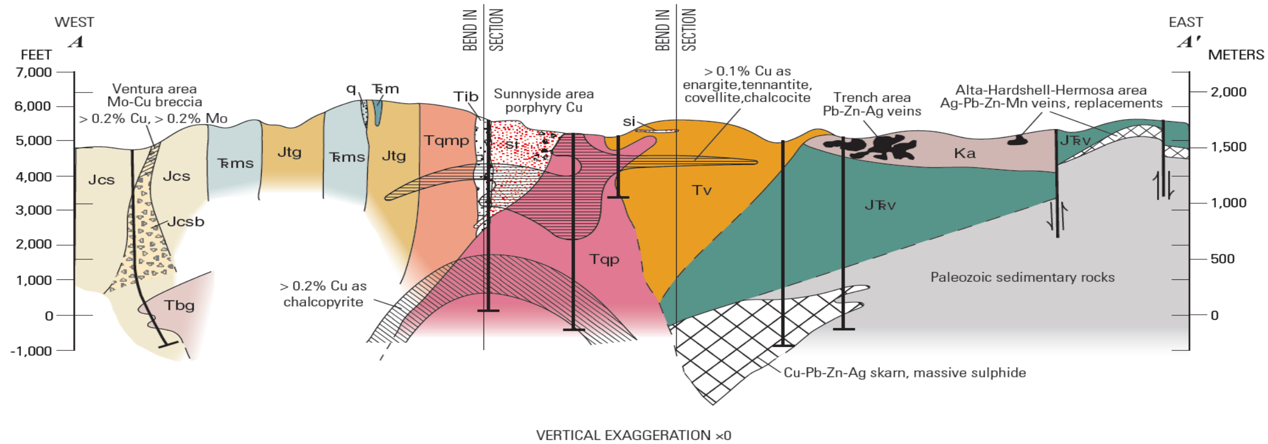

FIGURE 3B: GEOLOGIC CROSS-SECTION [1]

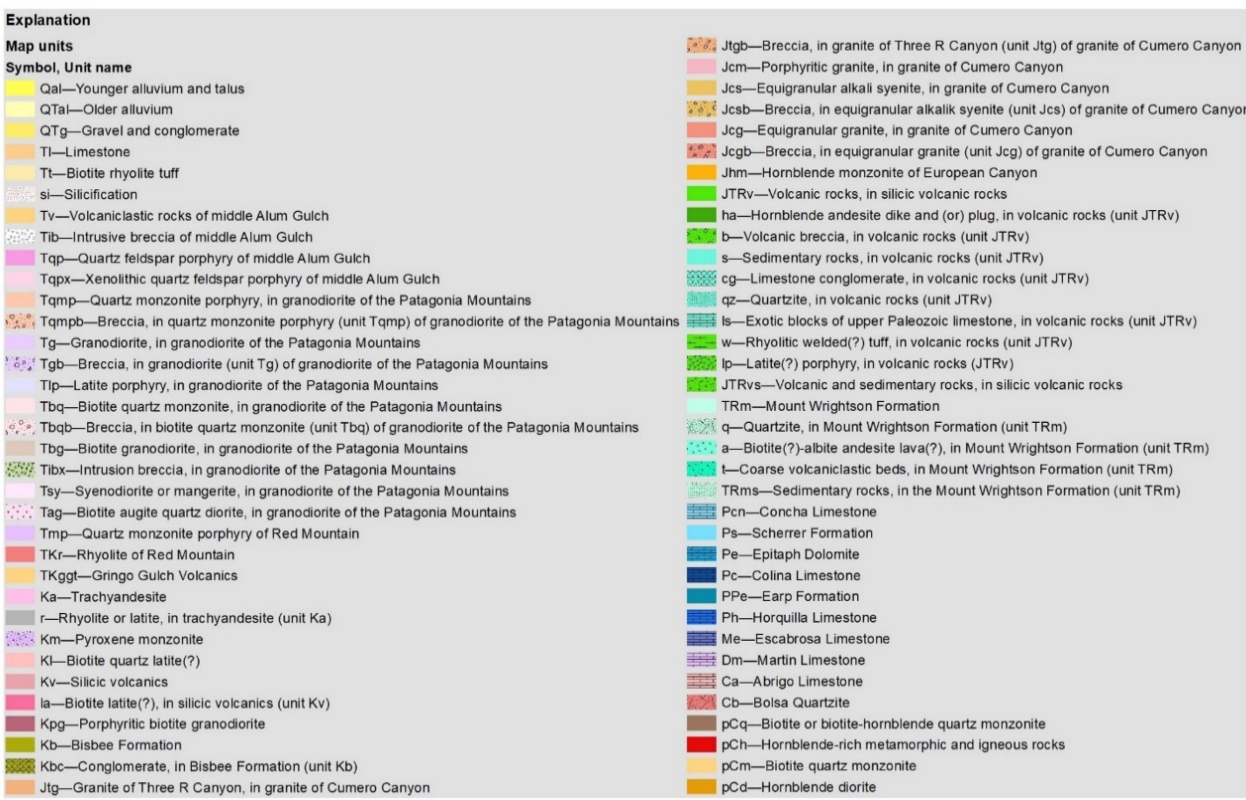

FIGURE 3C: EXPLANATION OF UNITS IN THE DETAILED GEOLOGIC MAP AND CROSS SECTION [2]

[1] Cross Section from Graybeal et al. (2015).

[2] Explanation of units from Graybeal et al. (2015).

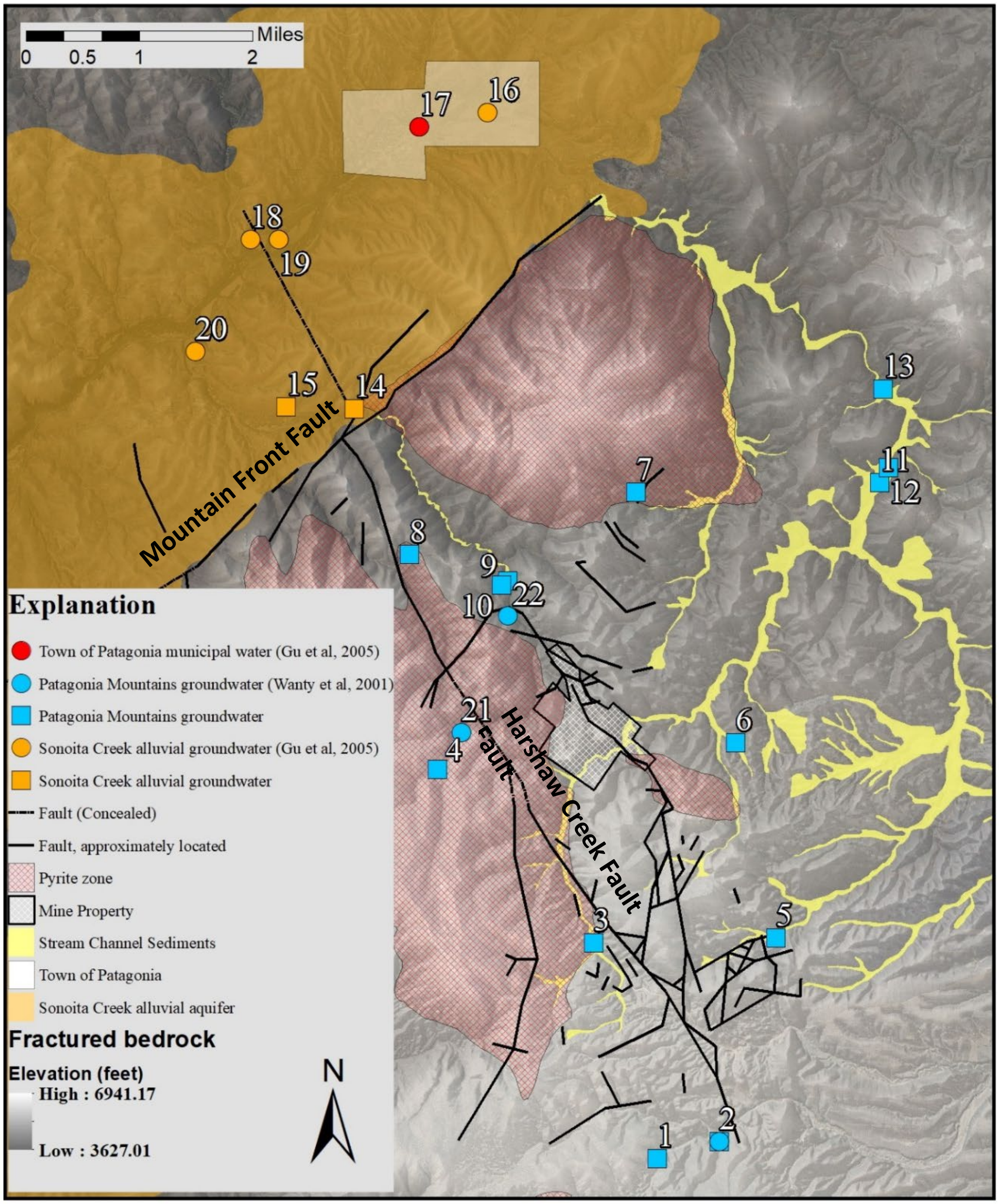

FIGURE 4: HYDROGEOLOGIC MAP OF THE STUDY SITE [1]

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[1] Pyrite zones from Graybeal et al. (2015), faults and the boundary of Sonoita Creek alluvial aquifer are from Montgomery & Associates (1999). Stream channel sediments boundaries were estimated using Geographic Information Software (GIS). Boundaries of Town of Patagonia and Mine Property are not representative of the full extent of either the Town or the mine.

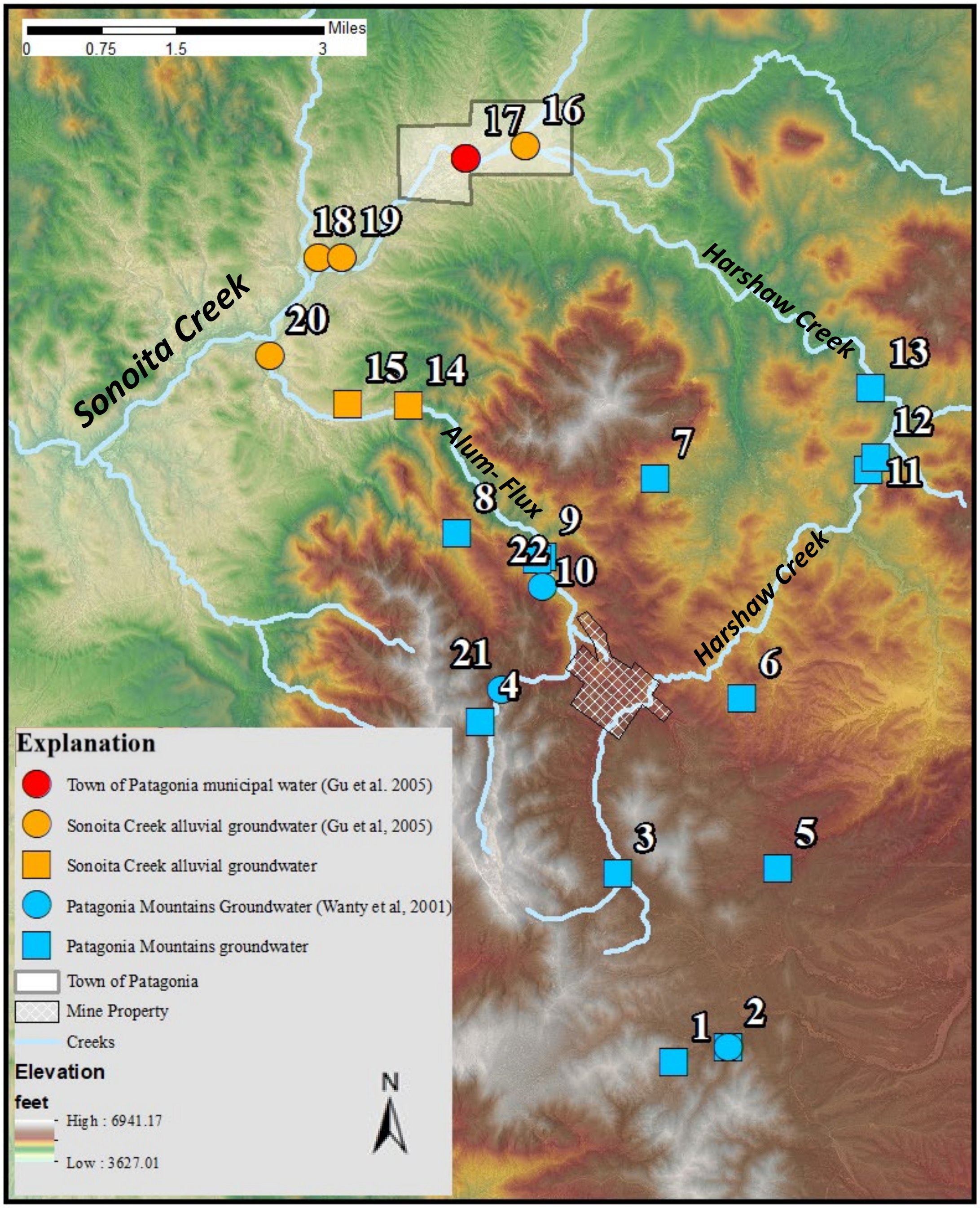

FIGURE 5: MAP OF SAMPLE SITES AND SOURCES OF DATA [1]

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[1] Data from Paymaster Spring (site # 2) was reported by Wanty et al. (2001) and was also sampled by the author. Boundaries of Town of Patagonia and Mine Property are not representative of the full extent of either the Town or the mine.

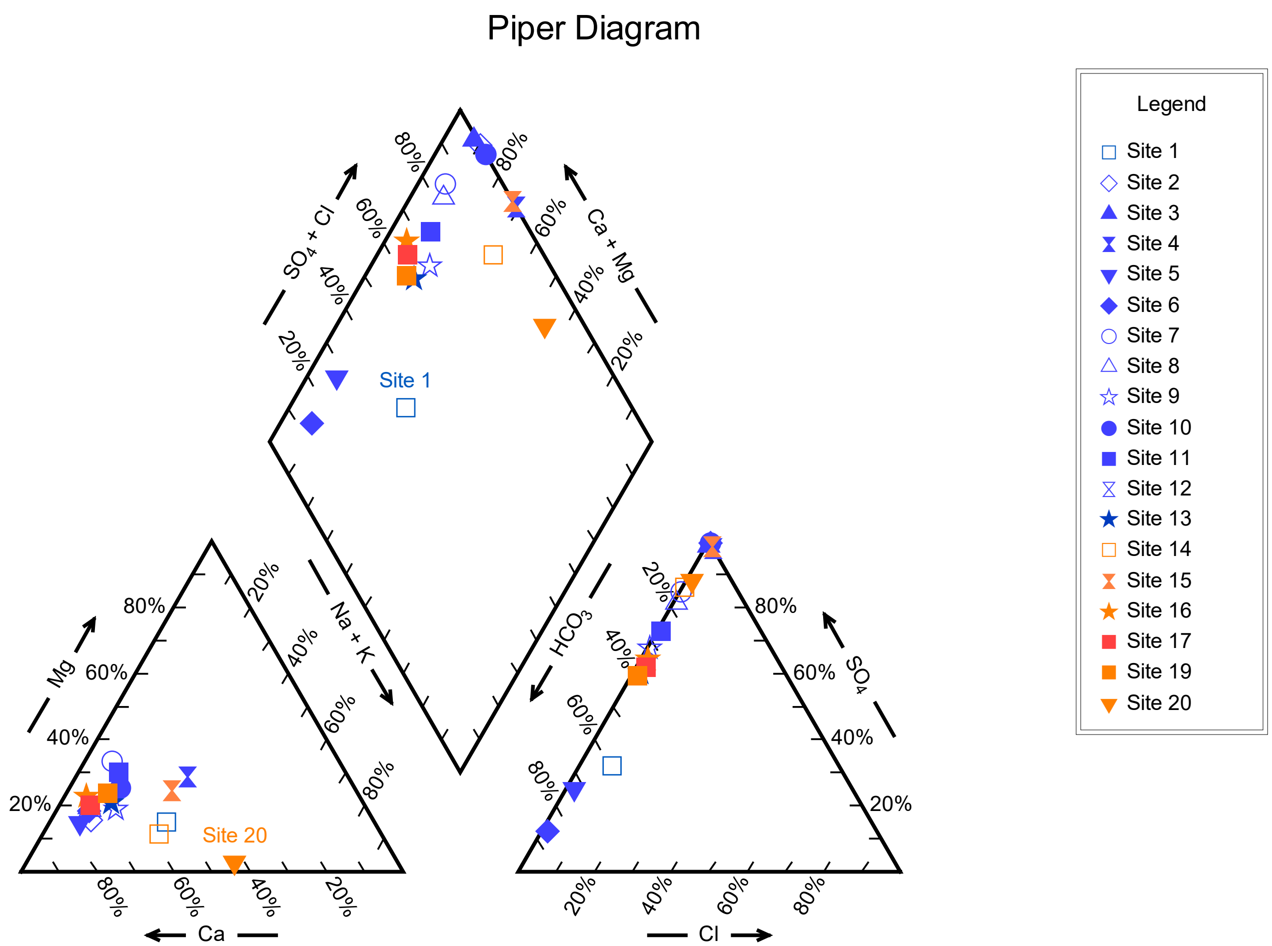

FIGURE 6: PIPER DIAGRAM[1]

[1] Includes data sampled by the author and data reported by Gu et al. (2005)

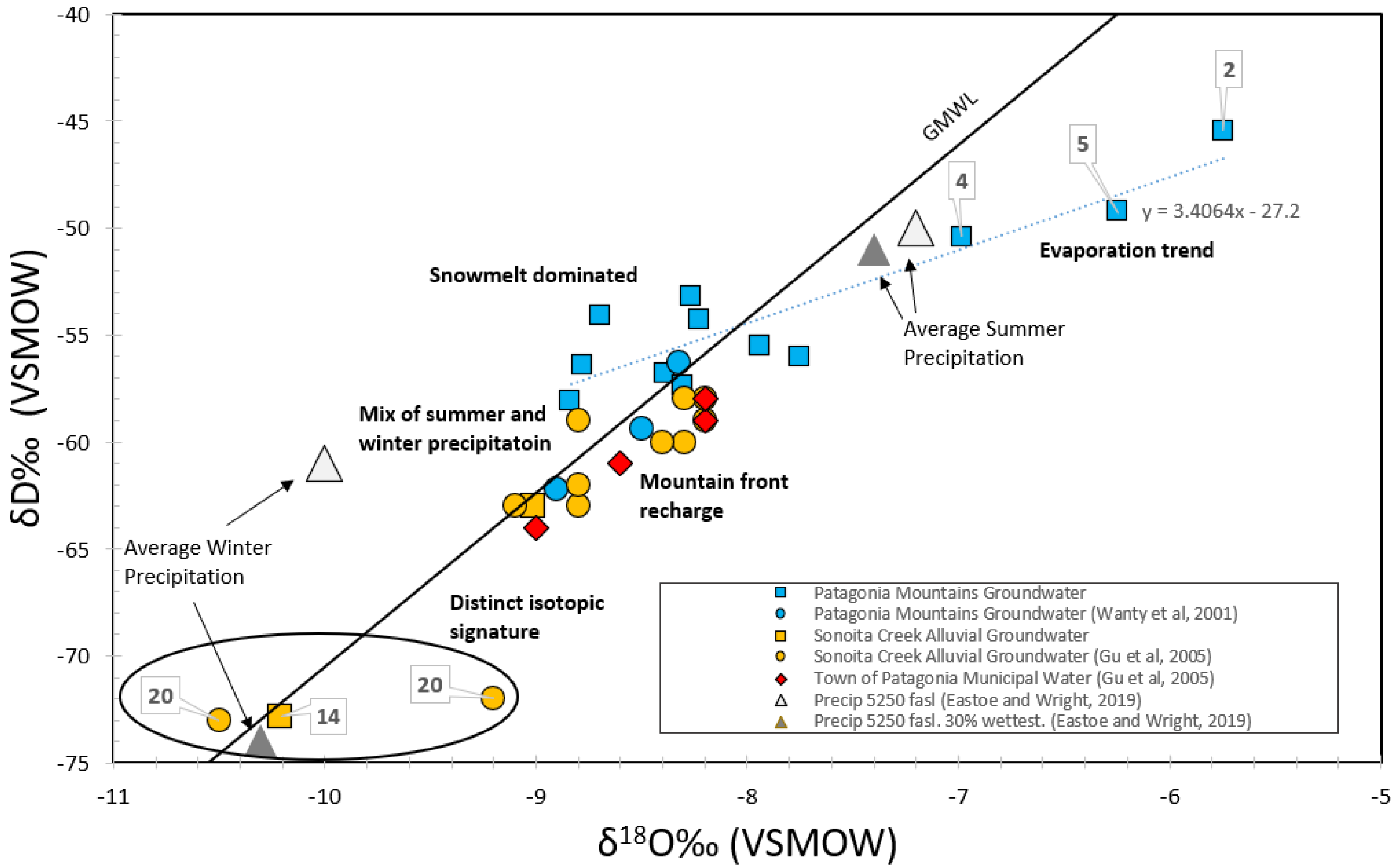

FIGURE 7: STABLE WATER ISOTOPES [1]

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[1] GMWL = Global Meteoric Water Line. Values used for the Global Meteoric Water Line are from Craig (1961). Square icons are representative of samples collected by the author. All other icons are from values that were reported by others and are included for comparison. The trendline includes all Patagonia Mountains Groundwater samples. Precipitation values are long-term amount-weighted mean data, adjusted for altitude, from the Tucson basin.

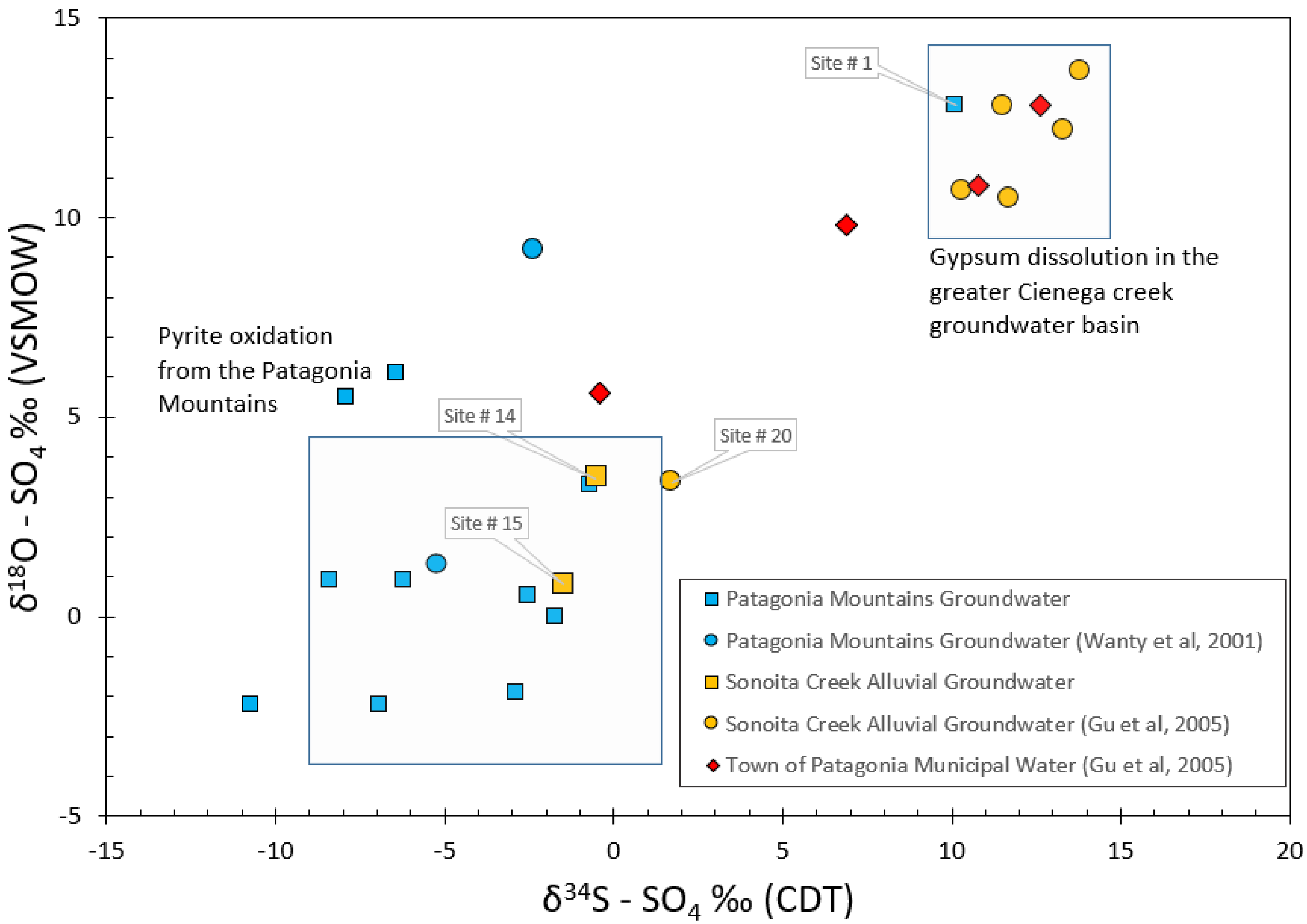

FIGURE 8A: STABLE ISOTOPES OF SO_4 [1]

[1] Square icons are representative of samples collected by the author. All other icons are from values that were reported by others and are included for comparison. Values for pyrite oxidation and gypsum dissolution are approximated from Gu et al. (2005). The four Town of Patagonia Municipal Water samples were taken from the same location at different times by others.

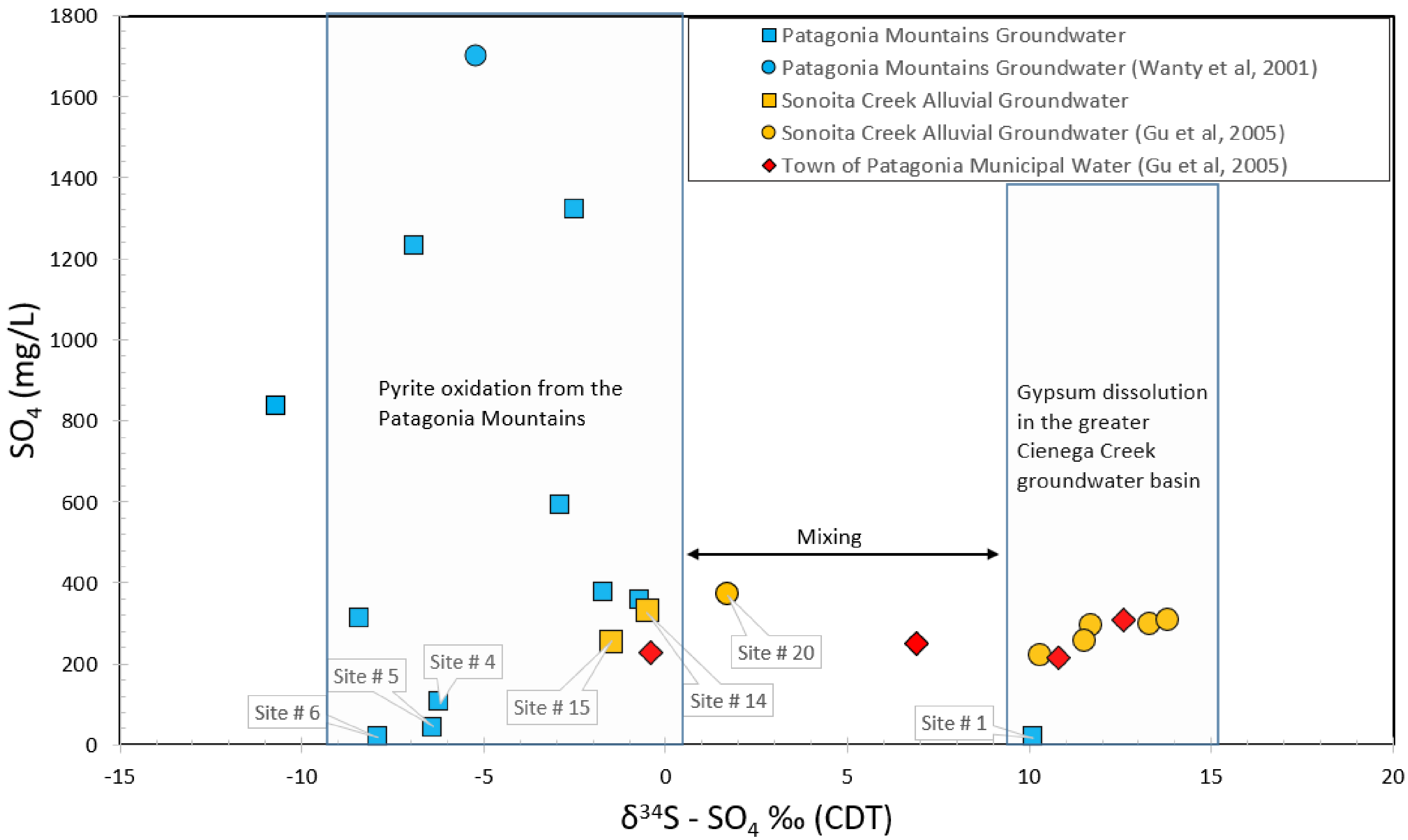

FIGURE 8B: COMPARISON OF ^{34}S - SO_4 VS[1]

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[1] Square icons are representative of samples collected by the author. All other icons are from values that were reported by others and are included for comparison. Values for pyrite oxidation and gypsum dissolution are approximated from Gu et al. (2005). The four Town of Patagonia Municipal Water samples were taken from the same location at different times by others.

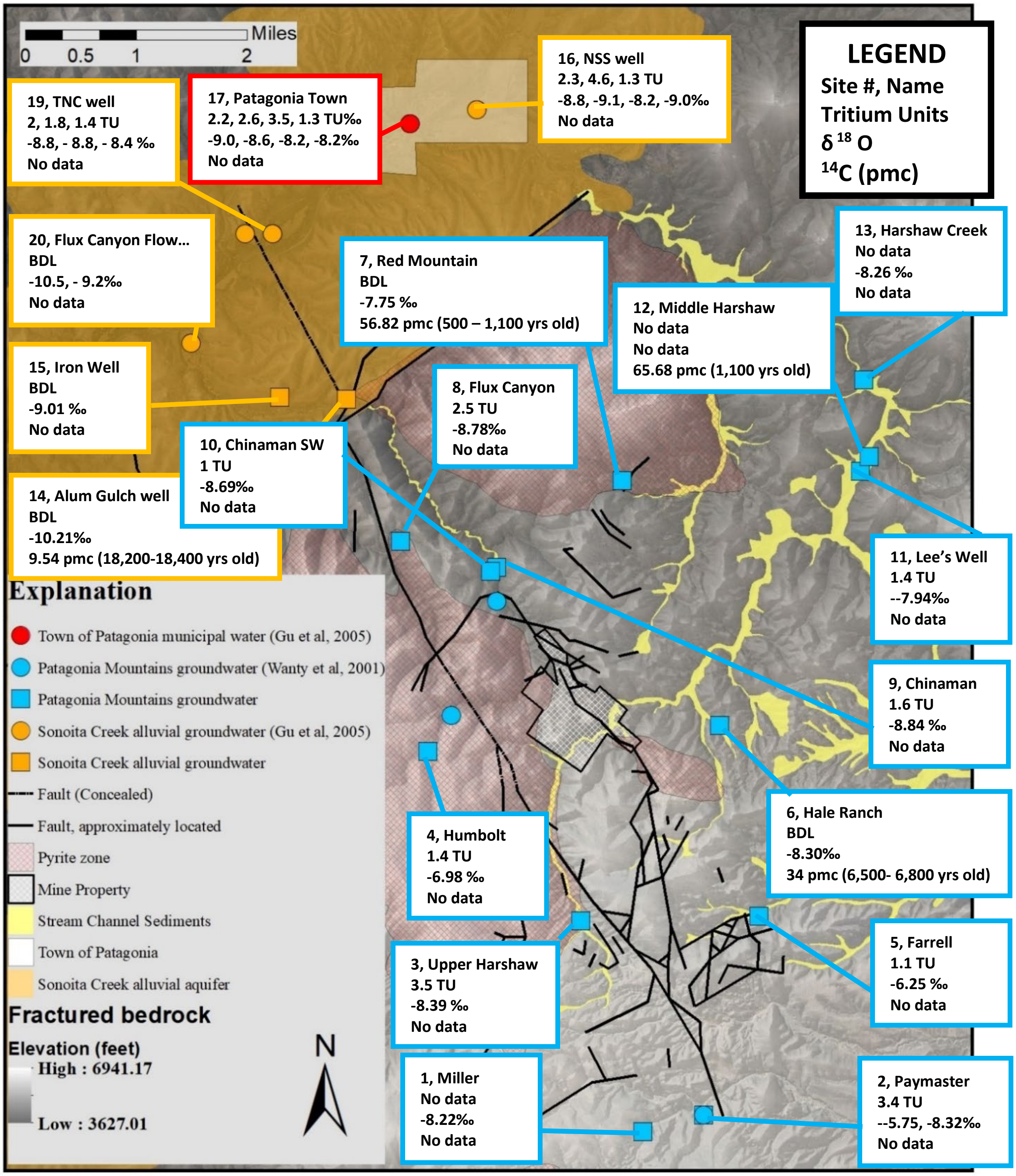

FIGURE 9: MAPPED TRITIUM, ^{18}O, AND ^{14}C [1]

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[1] For sites that included more than one sampling event, all recorded values are included. Pyrite zones from Graybeal et al. (2015), faults and the boundary of Sonoita Creek alluvial aquifer are from Montgomery & Associates (1999), stream channel sediments boundaries were estimated using GIS. Boundaries of Town of Patagonia and Mine Property are not representative of the full extent of either the Town or the mine.

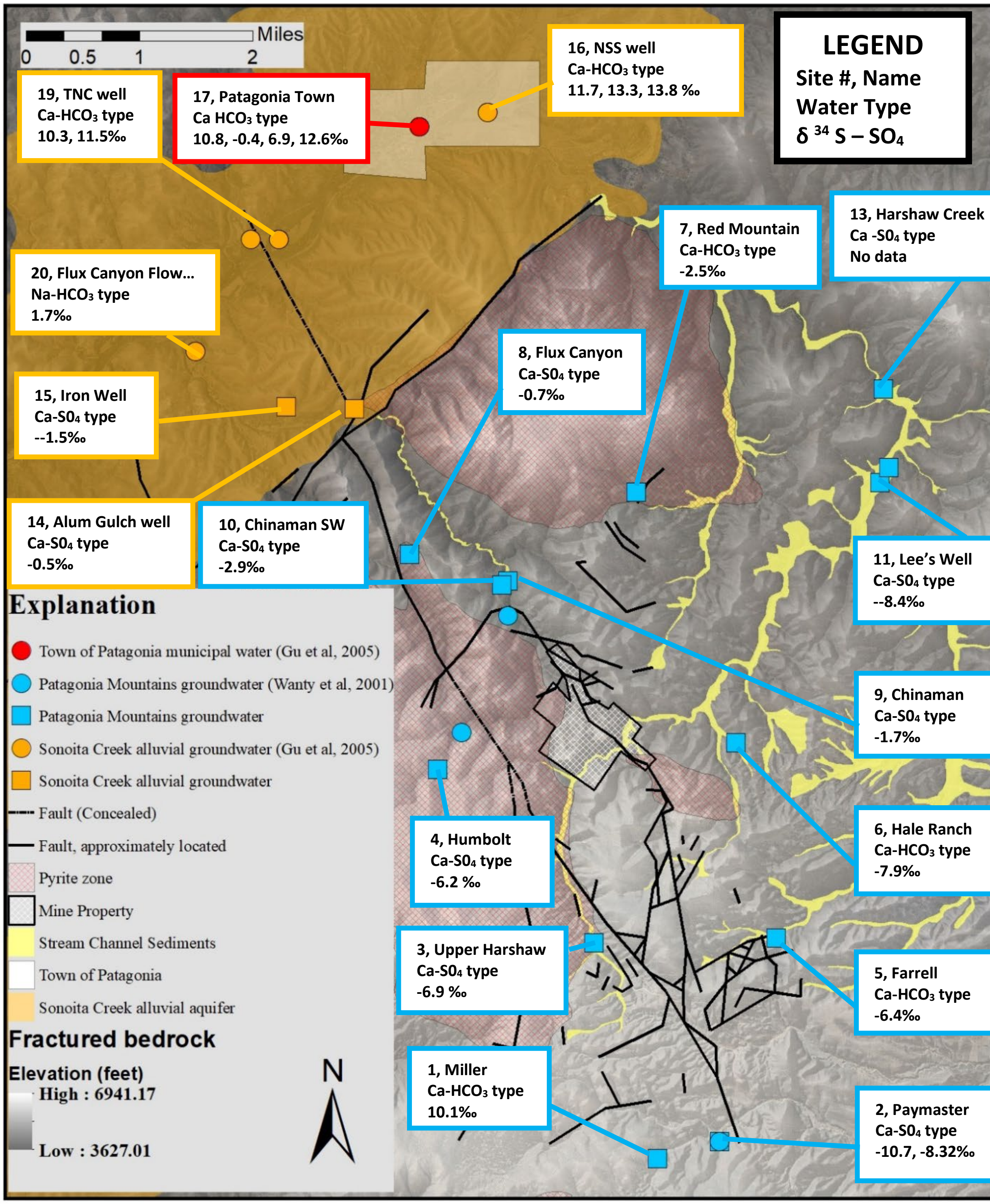

FIGURE 10: MAPPED WATER TYPE, ^{34}S [1]

[1] Pyrite zones from Graybeal et al. (2015), faults and the boundary of Sonoita Creek alluvial aquifer are from Montgomery & Associates (1999), stream channel sediments boundaries were estimated using GIS. Boundaries of Town of Patagonia and Mine Property are not representative of the full extent of either the Town or the mine.

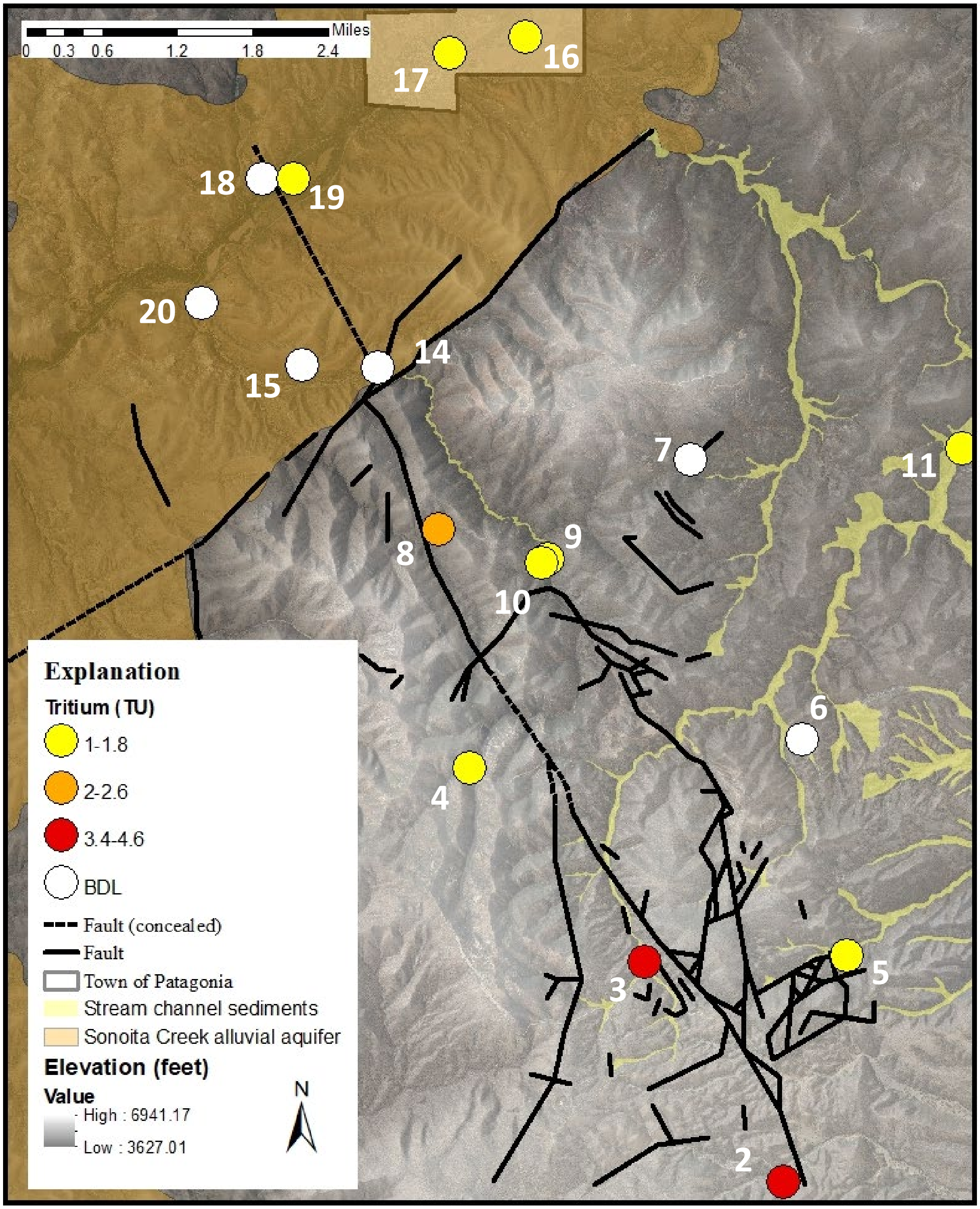

FIGURE 11: MAPPED TRITIUM VALUES [1]

[1] Only sample sites with available tritium data were mapped. For sites with more than one tritium measurement (sites 16, 17, 19), the mean value was used for the figure. Faults and the boundary of Sonoita Creek alluvial aquifer are from Montgomery & Associates (1999), stream channel sediments boundaries were estimated using GIS. Boundaries of Town of Patagonia and Mine Property are not representative of the full extent of either the Town or the mine.

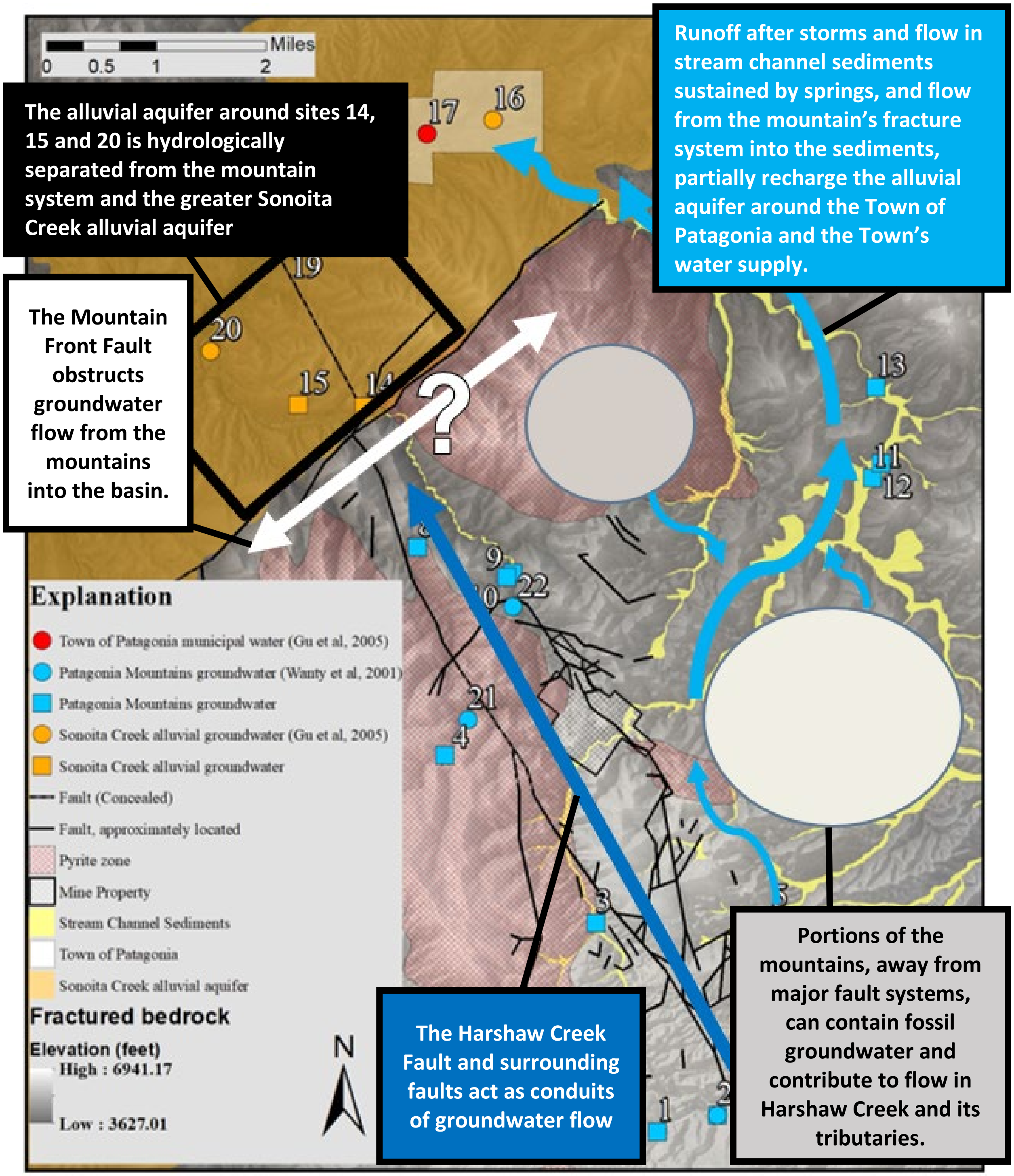

FIGURE 12: CONCEPTUAL MODEL OF GROUNDWATER FLOW IN THE NORTHERN PATAGONIA MOUNTAINS [1]

[1] Faults and the boundary of Sonoita Creek alluvial aquifer are from Montgomery & Associates (1999), stream channel sediments boundaries were estimated using GIS. Boundaries of Town of Patagonia and Mine Property are not representative of the full extent of either the Town or the mine.

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