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Faculty Advisor: Dr. Laura Crossey

Title: Environmental Fate of Sulfur in Sulphur Creek, Valles Caldera, NM: Implications for metal transport and water quality

Description of Problem and Objectives

The 1.13 Ma Valles Caldera (Smith and Bailey, 1968; Goff and Gardner, 1994) hosts a young igneous geothermal system consistent with the model presented by Goff and Janik (2000). The main vents of the acid-sulfate geothermal system occur at the Sulphur Springs area, recently acquired by Valles Caldera National Preserve. Waters discharging from Sulphur Springs are high in such geothermal components as aluminum, iron, sulfate, and acidity. These waters affect surface streams, such as Sulphur Creek. In-stream concentrations of these geothermal components reach their highest values just downstream of the Sulphur Springs area (Figure 1). These high concentrations are naturally attenuated further downstream by interactions with other surface streams, reaching their lowest values (and highest pH) just below the confluence with the snowmelt-fed Rio San Antonio. This research is investigating the specific

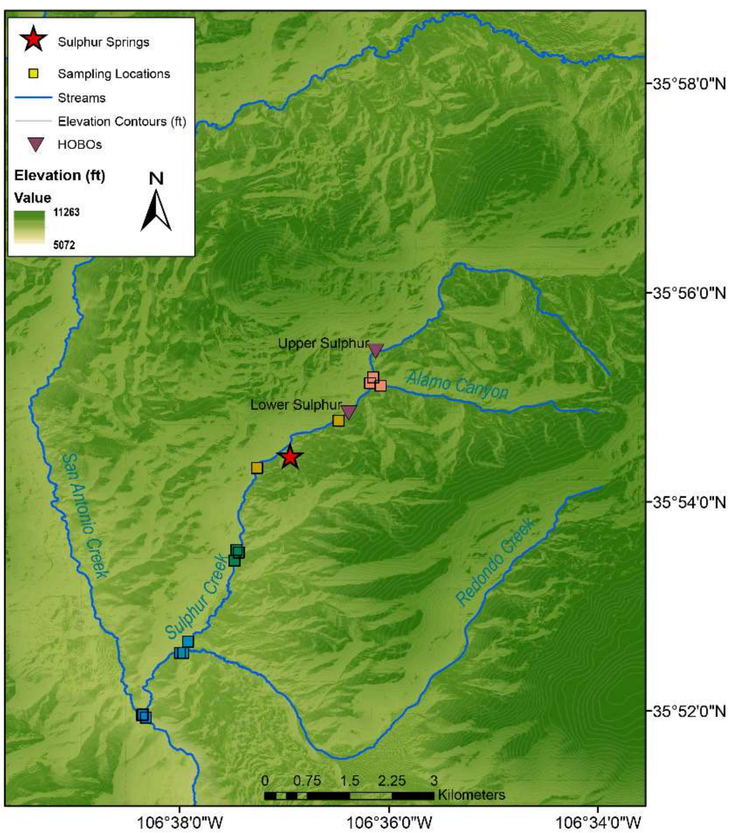

Figure 1 Digital Elevation Model of the field site for this study. Sulphur Springs lies on the flanks of the Valles resurgent dome. Sulphur Creek receives geothermal inputs from features along Alamo Canyon and Sulphur Springs.

processes and reactions that control this attenuation. Multiple geochemical tracers are used to investigate these processes, including field parameters, major ion compositions, and stable and radiogenic isotopes. Hypothesized attenuation processes include simple dilution by freshwater, removal of metals via hydrolysis, precipitation of acid-sulfate minerals, and sorption of components onto suspended sediment.

The objectives of this research project were to:

1. Frequently sample surface and springs waters from the Sulphur Creek drainage across seasons.
2. Assess the importance of geochemical processes/reactions to the natural attenuation of Sulphur Creek waters
3. Investigate the role of stream discharge in attenuating geothermal components. This objective has implications for the continued use of the geothermally-affected Jemez River under future precipitation regimes caused by climate change.
4. Expand on previous research on geothermal interactions with surface water (Golla, 2019; McCleskey et al., 2010a; McCleskey et al., 2010b; McGibbon et al., 2018; Nordstrom et al., 2009; Smith, 2016)

Methodology

- Field Parameters and Sampling

Field methods for this project involved frequent sample collection across different seasons to discern seasonal changes. Sampling sites were arranged in triads: at each important confluence in the field area, one sample was collected in each tributary upstream of the confluence and one sample was collected in the main branch of the stream downstream of the confluence. Sampling consisted of one sample bottle of filtered and acidified stream water and one sample bottle of raw stream water with no head space to prevent gas exchange after sample collection.

Additionally, field parameters were collected at each sample site with an Oakton pH/Con 300 meter. Temperature, electrical conductivity, total dissolved solids (TDS), and pH were collected at each site and recorded.

- Major Ion Compositions

Major ion compositions were analyzed in the UNM Earth and Planetary Science Analytical Chemistry Lab. Cation compositions were collected using inductively coupled plasma – optical emissions spectroscopy (ICP-OES). Anion compositions were collected using ion chromatography (IC). Bicarbonate alkalinity values were collected via a titration to pH 4.5 using H_2SO_4 in the UNM Earth and Planetary Science Diagenesis Lab.

- Stable Isotopes

Stable isotope compositions were analyzed in the UNM Center for Stable Isotopes using Picarro ring-down cavity spectroscopy. Stable isotopes analyzed for this research were ^{18}O and ^{2}H (D).

- Radiogenic Isotopes

Radiogenic isotope compositions were analyzed in the UNM Radiogenic Isotopes Lab using inductively coupled plasma – mass spectrometry (ICP-MS). $^{87}Sr/^{86}Sr$ collected for selected springs samples to determine subsurface flow path.

- Geochemical Modelling

Geochemical modelling was undertaken using The Geochemist's Workbench Student Edition and USGS PhreeqC software. Modelling results were used to infer concentrations of significant complexes and appropriate mineral saturation indices.

- Data Analysis

Charge balances were calculated for all collected samples as a quality assurance method. Balances were calculated using the following equation:

$$Charge\ Balance\ (\%) = \frac{\Sigma m_{cation} z_{cation} - \Sigma m_{anion} z_{anion}}{\Sigma m_{cation} z_{cation} + \Sigma m_{ani} \quad z_{anion}}$$

where m refers to the molar concentration (mg/kg) and z refers to the charge (as an integer) of each ion. Samples that exceeded ±10% charge balance were modelled in PhreeqC to achieve a satisfactory charge balance.

Results, Conclusions, Recommendations

Major ion results are summarized in Figure 2. All data are grouped by their sampling location (defined as the confluence at which the triad was collected) and group means are plotted alongside the data to parse out large-scale geochemical distinctions. Most solutes find their highest concentrations at or

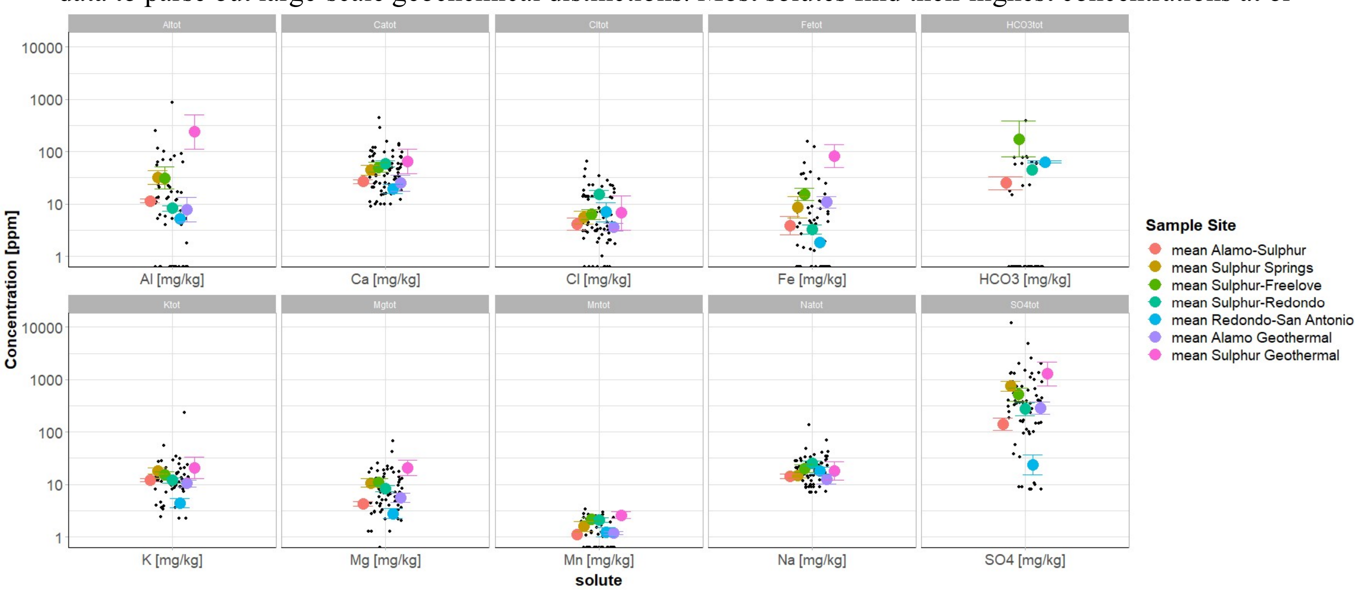

Figure 2 Summarized major ion results for Sulphur Creek waters. Group means are plotted alongside other data to display distinctions between all sampling sites.

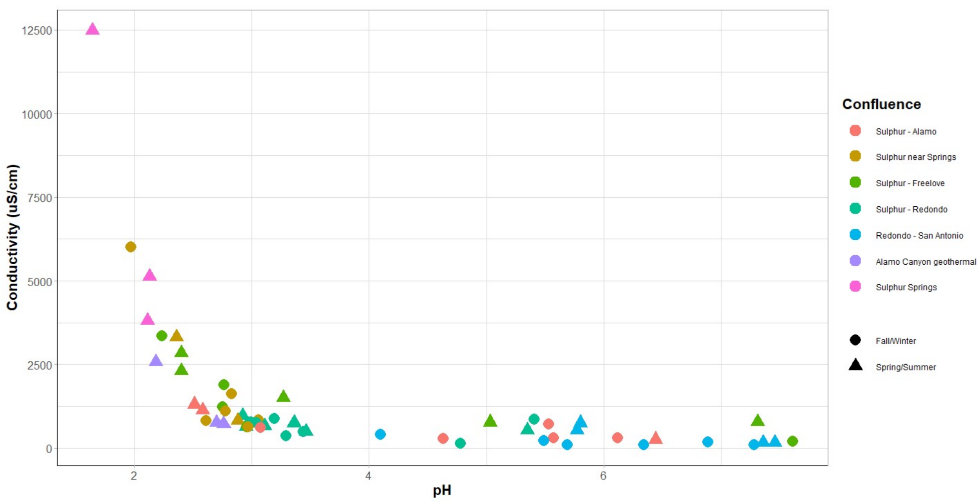

Figure 3 Conductivity vs pH. Note that conductivity decreases as pH increases, displaying the attenuation trend.

just below Sulphur Springs and their lowest concentrations at the confluence of Redondo Creek with the snowmelt-fed Rio San Antonio. Figure 3 compares electrical conductivity (in µS/cm) to pH and displays an integrative freshening trend. Specific attenuation processes cannot be distinguished with this method. This trend is not interpreted to be a true dilution trend as any processes that remove ions from solution would change the electrical conductivity, so we take this graph to only indicate the sum of the attenuation processes. However, the high-pH, low-conductivity waters sampled in Rio San Antonio are taken to be the fresh end-members in this field area. This does suggest a degree of dilution occurring at the downstream extent of the field area at the Redondo Creek – Rio San Antonio confluence.

One of the specific attenuation processes that is best represented in the data is that of metal hydrolysis. Aluminum hydrolysis proceeds according to the following reaction:

$$Al^{3+} + OH^{-} \rightarrow AlOH^{++} \quad pK_1 = 5$$

However, previous research (Nordstrom and Ball, 1986; McCleskey et al., 2010) has suggested that Al-hydroxide precipitation occurs at pK_1, which occurs at pH 5. Aluminum concentrations in Sulphur Creek waters show high concentrations at low pH, steeply decreasing with increasing pH (Figure 4). Most Al is attenuated by pH 5, however a few samples retain measurable Al concentrations at pH > 5. More investigation is required to investigate why Al remains in solution at these sites as it may refine our understanding of metal attenuation.

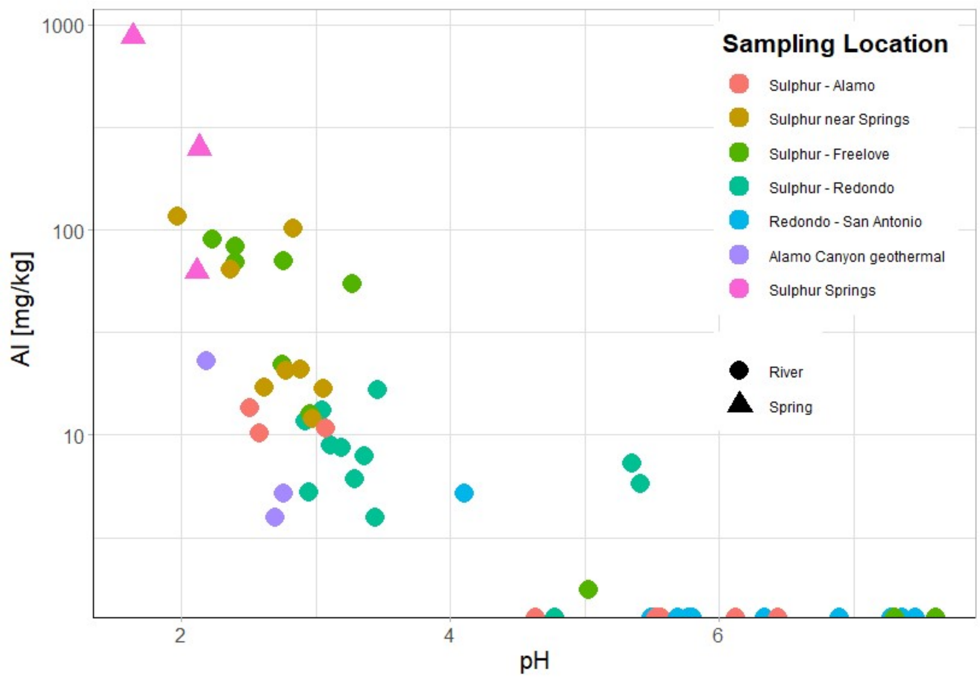

Figure 2 Al vs pH plot. Note that most Al is removed from solution at pH > 5 and tends to be below detection via ICP-OES. However, a few samples retain measurable concentrations and require further investigation

Current conclusions for this research emphasize the importance of in-stream pH changes in attenuating Al and dilution in attenuating SO_4. Al-mineralization is difficult to prove as the samples at pH's best suited to mineralization have concentrations low enough to fall outside the standard range of the ICP-OES used to assess the concentrations. However, geochemical modelling undertaken for this research has identified a small number of samples that are supersaturated with respect to Al-bearing minerals such as $Al(OH)_{3(am)}$, gibbsite ($Al(OH)_3$), and alunite ($KAl_3(SO_4)_2(OH)_6$). However, mineralization is not extensive enough to identify non-conservative trends (Figure 5).

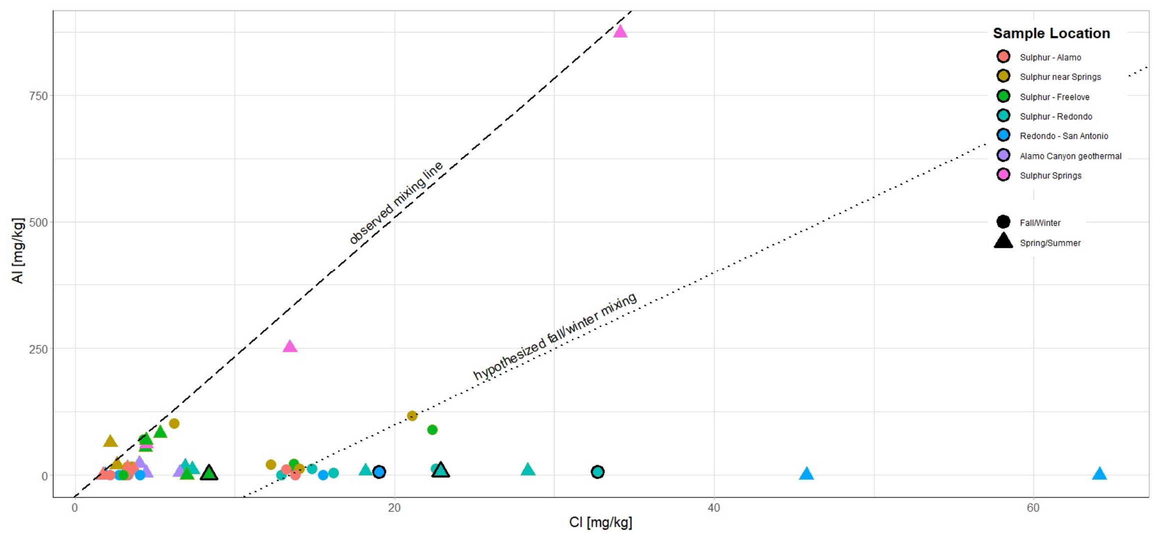

Figure 3 Al-Cl plot showing origin of Sulphur Creek waters downstream of Sulphur Springs area due to mixing between Sulphur Springs and Alamo Canyon waters. Note the bold-outlined data points are those supersaturated with respect to gibbsite, but do not define a non-conservative trend.

Other major ions show a similar relationship to Cl, however conclusions for these ions are not currently well-defined.

Discharge data for Sulphur Creek was obtained from the National Park Service Integrated Resource Management Applications portal. Discharge data for the Jemez River was obtained from the US Geological Survey National Water Dashboard. Two gauging stations were assessed for Sulphur Creek (Lower and Upper Sulphur Creek) and one gauging station for the Jemez River (Jemez Guad Gauge 08324000). Geochemical samples for this study were assigned the average daily discharge measured at the Lower Sulphur Creek gauging station for the collection date. Lower Sulphur Creek discharge was taken to be representative of the flow conditions of the field area. In this way, stream discharge was assessed as a categorical variable that could differentiate between high- and low-flow regimes. Figure 6 shows the relationship between discharge and in-stream Al concentrations.

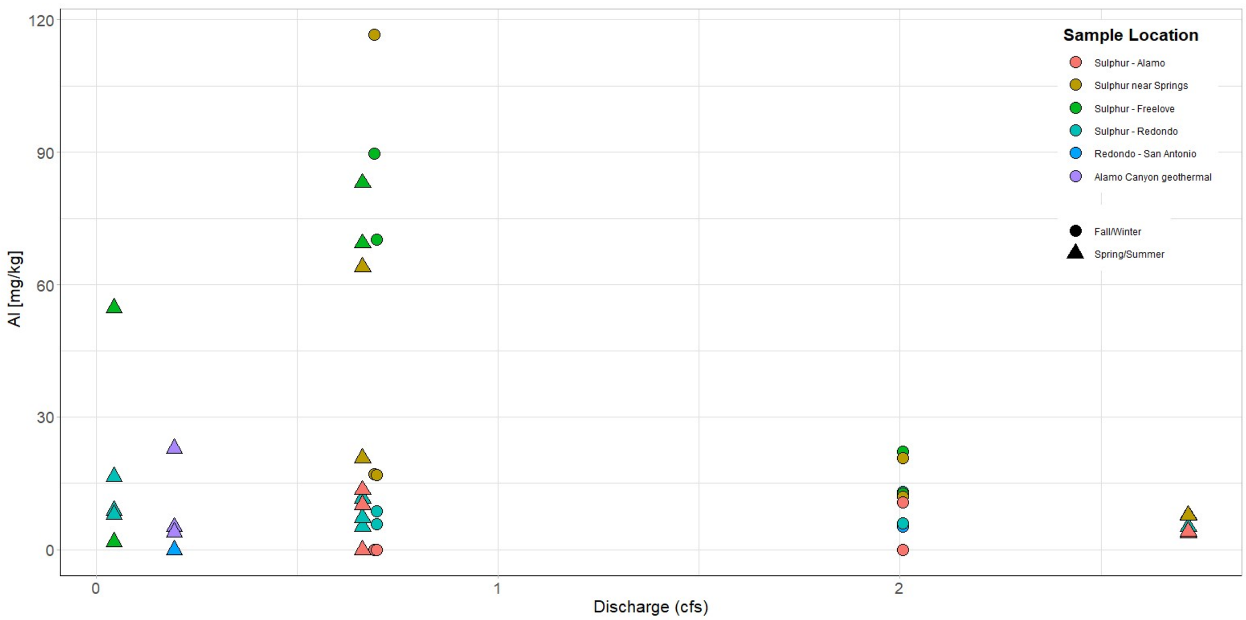

Figure 4 Al concentration vs mean daily discharge for sampling date. Note that high-discharge days show lower and less variable concentrations.

This relationship implies the importance of high-discharge conditions in attenuating the geothermal components that are loaded in-stream at the Sulphur Springs area.

Stakeholders and Beneficiaries of Work

This research can be provided to the NPS Valles Caldera National Preserve unit to aid in their interpretation of the recently-acquired Sulphur Springs area. Several housing subdivisions and agricultural enterprises are contained within the Sulphur Creek and Redondo Creek watersheds, which potentially impacts their water quality. Additionally, attenuation of geothermal components may change under future climate-change-induced precipitation regimes (Siirila-Woodburn et al., 2021), which suggests that this work is relevant for the whole Jemez River watershed and other geothermally-affected watersheds (i.e. watersheds of the Yellowstone Caldera).

Grant Spending

Item	Budget Spent to 05/30/2023
Lab Supplies	$700
Field Supplies	$0
In-State Travel	$866
Student Participation Costs	$0
Technical Services	$5212
Total Spent	**$6778**

Two budget revision requests have been accepted in the past year to move funds from one category to another. Specifically, money set aside for field supplies was transferred to in-state travel, lab supplies, and technical services categories in order to fund the last few sampling trips of this school year prior to my graduation.

Lab supplies were purchased from YSI in early 2023 to replenish pH buffer solutions and conductivity standards for field sampling in the spring/summer of 2023. In-state travel covered sampling trips to the Valles Caldera between the summer 2022 and spring 2023 as well as one trip to Las Cruces for the 2022 Water Conference. Technical services costs covered major ion and stable isotope lab analyses from summer 2022 to spring 2023.

Presentations

2022 New Mexico Water Conference
Lavery, D.J., Crossey, L.J., and Ali, A., 2022, *Environmental Fate of Sulfur and Metals in Sulphur Creek, Valles Caldera, NM: Implications for Metal Transport and Water Quality*: New Mexico Water Conference, Las Cruces, NM

2022 AGU Fall Meeting
Lavery, D.J., Crossey, L.J., and Ali, A., 2022, *Environmental Fate of Sulfur and Metals in Sulphur Creek,*

Valles Caldera, NM: Implications for Metal Transport and Water Quality: AGU Fall Meeting, Chicago, IL

2023 New Mexico Geological Society Spring Meeting
Lavery, D.J., Crossey, L.J., and Ali, A., 2023, *Environmental Fate of Sulfur and Metals in Sulphur Creek, Valles Caldera, NM: Implications for Metal Transport and Water Quality*: New Mexico Geological Society Spring Meeting, Socorro, NM

Publications and Reports- Master's thesis is in progress.

Project Assistance

- Kambray Townsend – field work and lab analyses
- Dr. Abdulmehdi Ali – lab analyses and interpretation
- Dr. Victor Polyak – lab analyses and interpretation
- Dr. Laura Burkemper – lab analyses
- Zach Strasberg – data analysis and interpretation

Special Recognition – None

Future Plans

Currently, M.S. thesis is on track to be completed by late June 2023. I have been hired for a hydrogeologist position in the NM Bureau of Geology Aquifer Mapping Program and will begin this job at the end of July of this year.

References

Bigham, J.M., and Nordstrom, D.K., 2000, Iron and Aluminum Hydroxysulfates from Acid Sulfate Waters: *Reviews in mineralogy and geochemistry*, v. 40, p. 351-403

Craig, H., 1961b, Isotopic Variations in Meteoric Waters: Science, v. 133, p. 1702-1703.

Gardner, J.N., Hulen, J.B., Lysne, P., Jacobson, R., Goff, F., Nielson, D.L., Pisto, L., Criswell, C.W., Gribble, R., Meeker, K., Musgrave, J.A., Smith, T., Wilson, D., 1989, Scientific Core Hole Valles Caldera #2b (VC-2B), New Mexico: Drilling and Some Initial Results: OSTI Report LA-UR-89-2025, 10 p.

Goff, F. and Gardner, J.N., 1994, Evolution of a Mineralized Geothermal System, Valles Caldera, New Mexico: Economic Geology, v. 89, p. 1803-1832.

Goff, F., Gardner, J., Vidale, R., and Charles, R., 1985, Geochemistry and Isotopes of Fluids from Sulphur Springs, Valles Caldera, New Mexico, v. 23, p. 273-297.

Goff, F. and Janik, C, 2000, Geothermal Systems: Encyclopedia of Volcanoes, p. 817-834.

Goff, F. and Janik, C.J., 2002, Gas geochemistry of the Valles caldera region, New Mexico and comparisons with gases at Yellowstone, Long Valley, and other geothermal system: Journal of Volcanology and Geothermal Research, v. 116, p. 299-323.

Golla, J.K., 2019, Natural Salinization of the Jemez River, New Mexico: An Insight from Trace Element Geochemistry [M.S. thesis]: University of New Mexico, 62 p.

Jones, A.M., Collins, R.N., and Waite, D.T., 2011, Mineral species control of aluminum solubility in sulfate-rich acidic waters: *Geochimica et Cosmochimica Acta*, v. 75, p. 965-977.

Karlstrom, K.E., Crossey, L.J., Hilton, D.R., Barry, P.H., 2013, Mantle ^{3}He and CO_2 degassing in carbonic and geothermal springs of Colorado and implications for neotectonics of the Rocky Mountains: Geology, v. 41, p. 495-498.

McCleskey, R.B., Nordstrom, D.K., Susong, D.D., Ball, J.W., Holloway, J.M., 2010a, Source and fate of inorganic solutes in the Gibbon River, Yellowstone National Park, Wyoming, USA: I. Low-flow discharge and major solute chemistry: Journal of Volcanology and Geothermal Research, v. 193, p. 189-202.

McCleskey, R.B., Nordstrom, D.K., Susong, D.D., Taylor, H.E., 2010b, Source and fate of inorganic solutes in the Gibbon River, Yellowstone National Park, Wyoming, USA. II. Trace element chemistry: Journal of Volcanology and Geothermal Research, v. 196, p. 139-155.

McGibbon, C., Crossey, L.J., Karlstrom, K.E., Grulke, T., 2018, Carbonic springs as distal manifestations of geothermal systems, highlighting the importance of fault pathways and hydrochemical mixing: Example from the Jemez Mountains, New Mexico: Applied Geochemistry, v. 98, p. 45-57, doi.org/10.1016/j.apgeochem.2018.08.015

Nordstrom, D.K., and Ball., J.W., 1986, The Geochemical Behavior of Aluminum in Acidified Surface Waters: *Science*, v. 232, p. 54-56

Nordstrom, D.K., Ball, J.W., and McCleskey, R.B., 2005, Ground Water to Surface Water: Chemistry of Thermal Outflows in Yellowstone National Park: *Geothermal biology and geochemistry in Yellowstone National Park*, p. 73-94

Nordstrom, D.K., McCleskey, R.B., and Ball, J.W., 2009 Sulfur geochemistry of hydrothermal waters in Yellowstone National Park: IV Acid-sulfate waters: Applied Geochemistry, v. 24, p. 191-207.

Sherson, L.R., 2012, Nutrient Dynamics in a Headwater Stream: Use of Continuous Water Quality Sensors to Examine Seasonal, Event, and Diurnal Processes in the East Fork Jemez River, NM [M.S. thesis]: University of New Mexico, 92 p.

Siirila-Woodburn, E.R., Rhoades, A.M., Hatchett, B.J., Huning, L.S., Szinai, J., Tague, C, Nico, P.S., Feldman, D.R., Jones, A.D., Collins, W.D., Kaatz, L., 2021, A low-to-no snow future and its impacts on water resources in the western United States: Nature Reviews Earth & Environment v. 2, p.800–819, https://doi.org/10.1038/s43017-021-00219-y

Smith, J., 2016, CO_2 Flux Along Faults of the Central Rio Grande Rift, New Mexico [M.S. thesis]: University of New Mexico, 115 p.

Smith, R.L., and Bailey, R.A., 1968, Resurgent Cauldrons: Memoir of the Geological Society of America, v. 116, p. 613-662.

Wilgus, J., Schmandt, B., Maguire, R., Jiang, C., and Chaput, J., 2023, Shear Velocity Evidence of Upper Crustal Magma Storage Beneath Valles Caldera: Geophysical Research Letters, v. 50.