



# The Yellowstone magmatic-hydrothermal system: using radiogenic and stable isotope geochemistry to constrain the processes of water-rock interaction

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**Abstract** The hot springs of Yellowstone National Park provide a broad range of isotopic data (e.g.  $^{238}\text{U}$ -,  $^{235}\text{U}$ -, and  $^{232}\text{Th}$ -series) that can be exploited to interpret the geochemical processes occurring at depth, including water-rock interaction, nuclide sourcing, and fluid residence times. Despite its worldwide notoriety, Yellowstone's hydrothermal system remains largely unconstrained. While major advances in the past century have helped us to understand the highly varied geochemical characteristics of Yellowstone's thermal features and their potential mechanisms of formation, many questions remain regarding where exactly the water resides before ascending to the surface, how long the water remains at depth, and what geochemical processes are occurring between these waters and the superheated aquifer rocks. One of the primary questions surrounding the Yellowstone hydrothermal system revolves around the concept of "phase separation", whereby ascending, pressurized hydrothermal fluids undergo decompressional boiling and separate into an acidic vapor phase and a neutral fluid phase. These diverging phases result in the two dominant spring chemistries viewed on the surface, acid-sulfate springs and neutral-chloride springs. Still, little is known about the timescales such a process operates on, and what geochemical parameters can be constrained to support the existence of this model. Herein we examine a handful of hydrothermal features throughout Yellowstone National Park in an effort to investigate the likelihood of phase separation's existence and whether or not the isotopic evidence supports the geochemical processes that we know to be occurring should this model persist within the plumbing of a continental hydrothermal system.

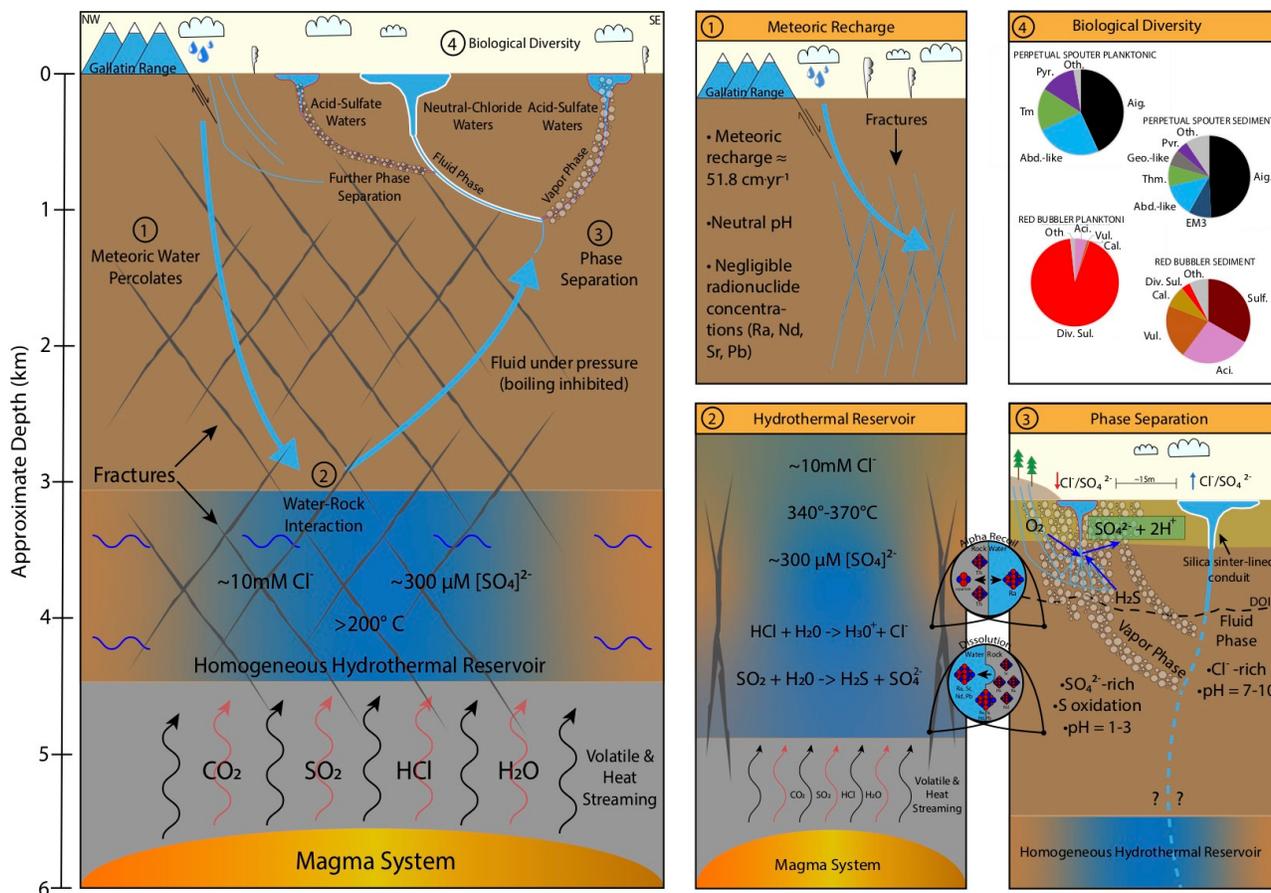
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## Introduction

Yellowstone National Park (WY, USA) is the focus of an intra-continental hydrothermal system that is fueled by meteoric water input and a near-surface mantle plume hotspot. The hydrothermal system remains unconstrained with regards to the processes of water-rock interaction, residence times, and the potentially multi-step model of phase separation. The primary questions we are currently investigating include 1) constraining the aquifer lithology or lithologies that the ascending hydrothermal water is dominantly interacting with (i.e. Quaternary volcanic deposits vs.

Mesozoic sedimentary units) and 2) approximating the timescales of water-rock interaction and fluid residence times at depth within a deep, homogeneous reservoir.

In this project, we are employing radiogenic isotope data in order to understand the model of phase separation (Figure 1). Using U- and Th-series isotopes and Nd, Sr, Pb, and Hf, our goal is to adequately answer the scientific questions posed above. During phase separation, an ascending hydrothermal fluid begins separating into a fluid phase and a gaseous phases following the crossing of a threshold that previously inhibited boiling. Upon phase separation, the



**Figure 1.** A conceptual diagram illustrating the geochemical process of phase separation that is believed to occur within the Yellowstone Hydrothermal System. (1) Meteoric water supplied by the Gallatin Range (northwest of Yellowstone N.P.) percolates to depth via fractures and is devoid of any significant radionuclide concentrations. (2) Percolating meteoric water recharges the homogeneous hydrothermal reservoir, is superheated, and becomes enriched in radionuclides supplied by the underlying magmatic system through mechanisms such as alpha-recoil and aquifer-rock dissolution. (3) Superheated water buoyantly ascends and, upon alleviation of pressure, phase separates into a neutral liquid phase and an acidic vapor phase, while alpha-recoil and aquifer-rock dissolution continuously occur. (4) The end-member hydrothermal fluids result in varying hot spring geochemistry and biological diversity [Data reproduced from National Park Service, Huang et al. (2015); Nordstrom et al. (2009); Lowenstern and Hurwitz (2008)]

fluid phase retains the conservative ion  $\text{Cl}^-$ , while the vapor phase concentrates sulfur-bearing species that contribute to the creation of acidity via  $\text{H}_2\text{SO}_4$  upon interacting with perched meteoric groundwater. This process is believed to be continuous during ascent (multi-step phase separation) and occurring on both large and small scales throughout Yellowstone National Park (park-wide vs. 15m apart). The acid-sulfate vapor phase will source from the aquifer lithology or lithologies to a different degree than will the neutral-chloride fluid phase. Therefore, we expect dif-

fering isotopic compositions and magnitudes depending on 1) the lithology being sourced from, 2) the degree of water-rock interaction and 3) the time spent interacting with a particular aquifer lithology upon departing from the deep, homogeneous reservoir.

Throughout this report we will detail how our continued research aims to answer the questions surrounding phase separation within the Yellowstone hydrothermal system. We note that the isotopic analysis is ongoing and that our preliminary data suggest we are headed in a direction of confirming the

existence of phase separation as the dominant process that controls thermal feature chemistry throughout this intra-continental hydrothermal system. This work will contribute to geologic regions beyond Yellowstone National Park alone, as these systems persist at depth in the oceans along mid-ocean ridges, near subduction zones at plate boundaries, and on moons of other planets throughout our solar system. Further, thermal features represent the nexus of biology and geology, as hot springs support what is believed to be some of the most ancient microbial life on Earth, and therefore our research has multi-disciplinary consequences that can help to understand the origins of life and intersection of geology with the biotic world.

## Methods

Hydrothermal fluid samples were collected in the field during three excursions from August to November of 2019. At each sampling site, geochemical parameters were recorded (3x) using a calibrated YSI multimeter. The average of the three measurements for each parameter are reported. The parameters recorded included pH, temperature, dissolved oxygen (%), total dissolved solids, and conductivity.

Fluid samples were collected from a variety of hydrothermal features in order to examine Pb, Nd, Sr, and Hf isotopes upon returning to the Wyoming High Precision Isotope Laboratory. All hosing and the filter housing were pre-contaminated with fluid prior to sample collection at each new hydrothermal feature site. Fluids were pumped from the thermal features using a peristaltic pump (GeoPump) equipped with a 0.1  $\mu\text{m}$  filter to ensure the removal of colloidal particles from the fluid. All sampling bottles (previously cleaned with 50% reagent grade HCl) were pre-contaminated with filtered hydrothermal fluid prior to sample collection. Fluids were pumped into the LDPE/HDPE/PP Nalgene sampling bottles. Following collection, all samples were acidified with 6N HCl (1 mL HCl per every 50 mL of fluid) in order to ensure all solutes remained in solution. The acidified samples were then returned to the Wyoming High Precision Isotope Laboratory where they were transferred to Savillex beakers and dried down on a hot plate

at ~90-100 °C in preparation for column chemistry and subsequent mass spectrometry. Following the dry down procedure, the remaining residue is brought back up to a certain concentration with HCl and fluxed overnight, then dried down again. The residue was the brought back up to a certain concentration of HNO<sub>3</sub> and fluxed overnight. This procedure aims to oxidize any remaining residue that could be attached to the walls of the beaker and ensure that all isotopes of interest (e.g. Pb, Nd, Sr, Hf) are completely in solution prior to conducting column chemistry.

Samples are currently being readied to undergo column chemistry, whereby U, Th, Fe, Pb, Sr, Nd, and Hf will be separated through anion exchange column chromatography. Following separation and the completion of column chromatography, samples will be analyzed for mass ratios using a Thermo Fisher Scientific Neptune Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS). Samples are introduced to the MC-ICP-MS in a solution of HNO<sub>3</sub> and ionized by an argon plasma torch. Isotopic ratios can then be measured through the interpretation of relative intensities. Sample analysis will be conducted using a standard bracketing procedure, whereby a standard is measured in between each sample run. The average of the two standard measurements that are carried out before and after a particular sample measurement are then averaged and used to calculate the delta values in the manner shown below, using Fe as an example:

$$\delta_{\frac{56}{54}} = \left( \frac{(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}}}{(^{56}\text{Fe}/^{54}\text{Fe})_{\text{standard}}} - 1 \right) * 1000$$

Hydrothermal fluids were also tested in-situ for radon activity using a Durrige Rad7 portable radon detector. The Rad7 is a solid state, silicon dome, scintillation chamber that records <sup>222</sup>Rn activity via its decay to its daughter product, polonium. 250 mL bottles were submerged to retrieve water samples for radon activity testing and capped immediately upon retrieval in order to minimize any subsequent degassing. The water samples were run through a 4-part cycle and the average <sup>222</sup>Rn activity was reported. The radon test typically takes ~25 min and provides us with an



**Figure 2.** A photograph of Cinder Pool in the Fall of 2018. Sulfur spheres are clearly coating the surface of the pool, a result of a molten sulfur layer present a depth.

activity immediately following the completion of the test.

Hydrothermal fluids were also collected for radium isotope activity measurements. In the field, a pony pump was used to collect 20-40 liter samples into pre-contaminated, plastic, collapsible carboy containers. If the fluid's pH was below 4 it was neutralized via the addition of NaOH pellets to attain a pH of 7. The collected waters were then attached to a series of 3 cartridges that were filled with pre-fluffed MnO<sub>2</sub>-coated acrylic fibers. These fibers have been proven to preferentially adsorb Ra with extremely high efficiency. The water is then allowed to flow via gravity through the cartridges at a flow rate of no more than 200 mL/min. The time at which the flow ceases is recorded as the time of sample collection for analytical calculations. These samples are then returned to the lab for isotope counting of <sup>223</sup>Ra and <sup>224</sup>Ra via a RaDeCC (Radium Delayed Coincidence Counter).

Using the RaDeCC, the MnO<sub>2</sub>-bearing cartridges are attached by tubing to a dual scintillation chamber. Helium is pumped through the system, acting as a carrier gas, to transport radon atoms to the counting chamber, whereby the activity of <sup>223</sup>Ra and <sup>224</sup>Ra is measured through the decay of its daughter isotope, radon, to polonium. Helium is also used to purge the system for 1 min prior to attaching the sample cartridges. The analyses are conducted for 90 min to at-



**Figure 3.** A photograph of Cinder Pool in the Fall of 2019. The pool has clearly undergone a transition relative to the Fall of 2018, whereby sulfur production has ceased, acidity increased, and the color has changed to a foggy turquoise.

tain an accurate reading.

## Preliminary results

### Cinder Pool

Our preliminary results are based upon both geochemical and observational measurements (Table 1). During the October, 2019 sampling campaign, we collected fluids from throughout the Norris Geyser Basin, a region abundant with both acidic and neutral pools just north of the caldera rim. Therefore, this region represents an ideal place to evaluate and develop the model of phase separation through an isotopic lens.

Of extreme interest in the Norris Geyser Basin is a feature known as Cinder Pool, a mildly acidic spring that exhibits a pH range 4.29 to 4.45, and is most well-known for its constant production of black, sulfuric spheres that emanate from what is believed to be a molten sulfur layer at depth (Figure 2). In October of 2019, our research team was fortunate enough to encounter Cinder Pool during a completely different state of geochemical conditions, whereby it had ceased its molten sulfur production, turned a turquoise blue color (Figure 3), and had become ~100x more acidic, reaching a pH of 2.32. This ex-

Norris Geyser Basin										
Geochemical Parameter	Red Bubbler (09/14/18)	1σ	Red Bubbler (10/11/19)	1σ	Perpetual Spouter (09/14/18)	1σ	Perpetual Spouter (10/11/19)	1σ	Cinder Pool (10/11/19)	1σ
Temperature (°C)	81.7	0.1	80.9	0.2	78.2	0.4	76.4	0.8	68.6	2.1
Pressure (atm)	0.7646	0.0	0.7677	0.0	0.7645	0.0	0.7671	0.0	0.7668	0.0
Dissolved Oxygen (%)	1	0.0	3	1.0	1	0.6	4	2.0	5	0.6
spc (µS/cm)	1963	0.0	2136	67.6	3171	33.5	3622	135.4	2142	450.7
Conductivity (µS/cm)	4086	1.7	4417	112.1	6396	92.7	7147	233.2	3621	222.0
Electrical Resistivity (Ω cm)	244.69	0.1	227.98	6.2	156.55	1.9	140.48	4.4	279.37	12.9
Total Dissolved Solids (tds)	1278.33	3.8	1378.00	23.4	2051.83	13.5	2328.30	82.9	1242.39	51.2
pH	3.10	0.0	2.80	0.0	7.13	0.0	6.88	0.3	2.32	0.0
Reduction Potential/ORP (mV)	25.97	16.4	241.10	1.2	-163.2	19.3	-30	18.7	263	0.5

Sentinel Meadows										
Geochemical Parameter	Steep Cone (09/13/18)	1σ	Steep Cone (10/10/19)	1σ	Ojo Caliente (11/07/19)	1σ	Narrow Gauge (09/15/18)	1σ	Narrow Gauge (10/12/19)	1σ
Temperature (°C)	81.4	0.6	79.6	1.17	80.70	1	45.2	1.5	53.1	1.5
Pressure (atm)	0.7695	0.0	0.7724	0.00	0.78	0	0.7853	0.0	0.7882	0.0
Dissolved Oxygen (%)	2	0.7	0.00	0.00	3.00	2	10	1.7	10	3.5
spc (µS/cm)	1806	36.8	1947	24.75	2409.33	257	3286	17.1	3516	76.2
Conductivity (µS/cm)	3720	130.1	4002	78.49	5016.33	563	4583	89.7	5438	208.0
Electrical Resistivity (Ω cm)	270.10	11.7	249.54	4.60	198.50	21	217.60	4.2	182.76	7.9
Total Dissolved Solids (tds)	1176	36.8	1266.15	20.72	1618.50	182	2136.33	16.4	2338.00	117.0
pH	7.72	0.0	7.99	0.12	7.70	0	7.58	0.1	6.14	0.2
Reduction Potential/ORP (mV)	-384.0	7.1	-102	7.78	-82.20	1	179.4	7.2	14.4	9.4

Upper Geyser Basin										
Geochemical Parameter	Old Faithful (11/07/19)	1σ	Acid Pool near Shipyards Pool (08/18/19)	1σ	Shipyards Pool (08/18/19)	1σ	Rabbit Creek	1σ	Beryl Spring Region	1σ
Temperature (°C)	60.63	1.5	36.4	0.4	24.7	29	36.4	0.4	78.3	1.0
Pressure (atm)	0.77	0.0	0.7651	0.0	0.3843	0	0.7651	0.0	0.8	0.0
Dissolved Oxygen (%)	19	6.0	39	10.3	18	15	3	1.5	3.7	1.5
spc (µS/cm)	3513	53.7	1213	105.2	1221	1619	1482	120.5	3029.3	128.9
Conductivity (µS/cm)	5724	345.4	1482	120.5	1918	2606	674.31	53.5	6153.7	277.2
Electrical Resistivity (Ω cm)	169.52	1.8	793.00	50.8	224.79	308	782.72	1059	162.3	7.3
Total Dissolved Solids (tds)	2277.17	9.9	210.7	3.3	14.1	151	2.72	0.1	1993.3	101.0
pH	8.97	0.0	2.10	0.0	2.94	4	2.72	0.1	7.0	0.3
Reduction Potential/ORP (mV)	-157.87	0.2	210.7	3.3	14.1	151	210.7	3.3	-36.6	16.5

Geyser Creek										
Geochemical Parameter	Enterprise Pool (08/19/19)	1σ	Jackhammer Pool (08/19/19)	1σ	"Intermediate" Pool (08/19/19)	1σ	Beryl Spring (11/08/19)	1σ	Beryl Spring Region	1σ
Temperature (°C)	79.2	0.17	77.2	0.3	78.5	0.3	78.3	1.0	78.3	1.0
Pressure (atm)	0.7138	0.07	0.7647	0.0	0.7651	0.0	0.8	0.0	0.8	0.0
Dissolved Oxygen (%)	3	0.00	3	0.0	5	0.0	3.7	1.5	3.7	1.5
spc (µS/cm)	3371	20.51	4069	84.9	10.44	0.0	3029.3	128.9	3029.3	128.9
Conductivity (µS/cm)	6855	25.46	8071	83.4	2086	0.0	6153.7	277.2	6153.7	277.2
Electrical Resistivity (Ω cm)	146.04	0.40	124.24	1.0	48.95	0.0	162.3	7.3	162.3	7.3
Total Dissolved Solids (tds)	2184.00	6.50	2610.67	18.5	663.00	0.0	1993.3	101.0	1993.3	101.0
pH	6.61	0.13	1.86	0.0	4.20	0.0	7.0	0.3	7.0	0.3
Reduction Potential/ORP (mV)	-3.0	0.00	293.8	6.1	146.4	1.4	-36.6	16.5	-36.6	16.5

**Table 1.** Geochemical parameters from thermal features sampled over the last year. Note the bimodal distribution of pH values and the low pH of Cinder Pool. Features such as Red Bubbler and Perpetual Spouter present contrasting spring chemistries yet are located within just meters of one another.

tre, and potentially transient, geochemical and hydrological transformation offered an ideal and unique scenario to further develop the temporal changes associated with phase separation and the subsurface processes that are likely at work. For this reason, we are focusing a large portion of our efforts on characterizing this feature's geochemical evolution.

We have a dataset of geochemical parameters and isotopic measurements from Cinder Pool prior to its transformation and have collected multiple fluid samples during the October, 2019 field campaign that are slated to undergo the same isotopic analyses in an effort to understand whether or not this major change in a pool's chemistry is indicative of perhaps mixing of fluid sources, closing of hydraulic pathways, hydrothermal interaction with different lithologic units, or of a larger-scale modification throughout Norris Geyser Basin. By comparing both isotopic data and geochemical data from before and after this transformation, we will be able to test and confirm an extremely important hypothesis. Acidic features often exhibit isotopic signals that indicate higher degrees of interaction with the Lava Creek Tuff, a volcanic unit that underlies much of the Yellowstone region, and therefore we hypothesize that Cinder Pool will exhibit signatures associated with lead and strontium isotopes that indicate such interaction. If the isotopic data does not exhibit enriched Pb and Sr signals, then we hypothesize that the hydrothermal fluids emanating from Cinder Pool are likely being transported from greater distances, perhaps along north-south trending faults that exist north of the Norris Geyser Basin and truncate against the caldera rim. To this end, we can exploit the unexpected isotopic results to produce a mixing theory that speaks to the multiple lithologic units that the water is interacting with, residence times beneath the subsurface, and distances of fluid travel. The unique opportunity presented by Cinder Pool will aid in constraining the model of phase separation greatly, and we plan to continue focusing our efforts on this feature.

### Beryl Spring

During the November, 2019 sampling trip, we collected fluids from the Beryl Spring region on two

successive days. Beryl Spring is an extremely hot, neutral-chloride pool that is surrounded by a highly active fumarole and accessory frying pan spring, representing another potential setting for near-surface phase separation. While the fumarole and frying pan are too dangerous to sample directly, fluids were collected from Beryl Spring itself for Ra isotope counting (Table 2) and long-lived radiogenic isotopic analysis. The Ra counts for Beryl Spring indicate that this neutral-chloride water is potentially younger and/or transported more quickly to the surface from the deep, homogenous reservoir. This is notable for a few reasons. First, neutral pools are believed to be the end-member candidate for the deep, homogeneous reservoir, representing the most chemically primitive and oldest waters emanating at the surface within Yellowstone National Park. For this reason, they are often “dead”, or below detection limit, when it comes to short-lived Ra isotopes  $^{224}\text{Ra}$  ( $t_{1/2} = 3.6$  d) and  $^{223}\text{Ra}$  ( $t_{1/2} = 11.4$  d). In other words, both  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  have completely decayed away within the transporting fluids prior to our sampling at the surface. Beryl Spring, on the other hand, exhibited notable Ra activity and therefore can be exploited to calculate timescales of water-rock interaction according to a model set forth by Clark and Turekian (1990). The second notable outcome of this analysis is that by greatly increasing the volume of water used for Ra counting ( $>2x$ , from  $\sim 20\text{L}$  to  $>50\text{L}$ ), we allowed for a higher likelihood of detecting often negligible Ra activity. This improvement in sampling methodology will prove useful at various thermal features in the future and is worthy of serious mention as this tactic for Ra isotope counting has been employed throughout various natural settings beyond hydrothermal systems alone.

Adjacent to Beryl Spring there were also a collection of two distinct, young features that were situated beneath a bridge. These features were not present in previous years and therefore represent an opportunity to sample fluid chemistry during the adolescent stages of hydrothermal spring formation. Further, these two young springs were exhibiting contrasting geochemical behavior, as one was neutral-chloride and the other acid-sulfate, just meters away from one another. Therefore, we opted to sample

<b>Beryl Spring</b> Collection Date: 11/8/2019 Collection Time: 9:45 PM Volume: 40L										
Cartridge Series	File Name	CPM219	Cnt219	CPM220	Cnt220	CPM Total	Cnt Total	Run Time (min)	Date of Completion	Time of Completion
Cartridge 1 (First)	Beryl_Spring_5C_11.8.19	0.328	59	7.172	1291	16.044	2888	180.00	11/10/19	7:21PM
Cartridge 2 (Second)	Beryl_Spring_5B_11.8.19	0	0	0.033	6	0.917	165	180.00	11/10/19	7:21PM
Cartridge 3 (Third)	Beryl_Spring_5B2_11.8.19	0.000	0	0.061	11	1.6	288	180.00	11/11/19	12:22PM
<b>Old Faithful Geyser, Upper Geyser Basin</b> Collection Date: 11/8/2019 Collection Time: 3:00 PM Volume: 53L										
Cartridge Series	File Name	CPM219	Cnt219	CPM220	Cnt220	CPM Total	Cnt Total	Run Time (min)	Date of Completion	Time of Completion
Cartridge 1 (First)	Old_Faithful_Geyser_SA_11.08.19	0.017	3	0.383	69	1.6	288	180.00	11/10/19	3:55PM
Cartridge 2 (Second)	Old_Faithful_Geyser_5B_11.08.19	0	0	0.022	4	0.717	129	180.00	11/10/19	3:55PM
Cartridge 3 (Third)	Old_Faithful_Geyser_SA2_11.08.19	0	0	0.106	19	2.689	484	180.00	11/11/19	12:22PM

**Table 2.** Ra counting data from Beryl Spring and Old Faithful Geyser. Cnt###: Detected number of decays of specific Rn isotope. CPM###: Calculated number of decays per minute.

these young features for long-lived radiogenic isotopes in an effort to understand whether or not these features are associated with nearby Beryl Spring or are genetically unrelated and represent a completely different migration of hydrothermal fluids to the surface. This investigation will help to answer questions regarding the connectivity of hydrothermal fluids in the subsurface and their cogenetic relation to a deep, homogenous reservoirs at depths of 3-4 km.

### Old Faithful

As a neutral-chloride thermal feature with predictable geysering events, Old Faithful presents an ideal opportunity to investigate radionuclide cycling and fluid residence time in a hydrothermal basin that has worldwide notoriety. We collected fluid samples from this high-profile and highly-valuable feature for both Ra counting, Rn counting, and measurement of long-lived radiogenic isotopes. When compared to the Ra isotope activity of Beryl Spring, Old Faithful remained just barely above or oftentimes below detection limit (Table 2), implying that this water is much older in age than that of the Beryl Spring region. This is an interesting observation because in a general sense it shows that intra-caldera springs, such as Old Faithful, are producing fluids that have resided at depth for greater periods of time than fluids emanating from north of the caldera rim, such as Beryl Spring. Many thermal features that spread north from the caldera rim are associated with a north-south trending, normal faulted zone called the Norris-Mammoth Corridor. This extensional faulting has allowed for the migration of fluids to the surface via fault-induced fractures and subsequently could be allowing for more rapid transport, and therefore more radionuclide-enriched waters, than compared to the fluids reaching the surface in regions such as the Upper Geyser Basin, the basin where Old Faithful is located. This is a working hypothesis regarding the differences in Ra isotope geochemistry between two regions of the park, and further analysis of long-lived radiogenic isotopes through mass spectrometry methods will aim to shed more light on this line of reasoning.

### Conclusions

We have gathered fluid samples from various regions throughout Yellowstone National Park in order to investigate processes and timescales associated with geochemical and hydrologic transitioning, near-surface phase separation, and water-rock interaction.

In Norris Geyser Basin, samples from Cinder Pool are being analyzed and compared with regards to their long-lived radiogenic isotopes (Nd, Sr, Hf, Pb) in an effort to understand the drastic geochemical and hydrologic transformation that took place there over the last year. This will help to answer questions regarding the transient nature of the Yellowstone hydrothermal system and its ability to mix and source from other fluid sources.

At Beryl Spring, research is beginning to point toward younger fluid ages, or shorter timescales of water-rock interaction/time spent in the deep, homogeneous reservoir. This is supported by the presence of short-lived Ra isotopes within the waters emanating at the surface of this neutral-chloride feature. Further, these younger ages help to place constraints of hydrologic timescales throughout the Yellowstone hydrothermal system, as it appears that intra-caldera springs represent older fluid timescales relative to springs reaching the surface outside of the caldera. Beryl Spring also presented two young features that have recently surfaced just a few meters away, one acid-sulfate and the other neutral-chloride. Samples have been collected from these features as well and will help to inform the process of phase separation at a near-surface level.

Finally, samples have been collected and analysis begun regarding Old Faithful fluids. These waters are essentially below detection limit when it comes to short-lived Ra isotopes, indicating old fluid ages and/or residence times. Analysis of long-lived radiogenic isotopes will help in understanding which aquifer rock these waters are interacting with. This intra-caldera feature will be vital in our comparison to the neutral-chloride Beryl Spring, which persists outside of the caldera rim.

In conclusion, our field observations, geochemical

measurements, and isotopic analyses has shed light on the timescales of fluid residence time and water-rock interaction. Continued analyses will help to constrain the length scales of phase separation in the near surface environment and also to understand transient changes in geochemical behavior within acidic features. This work is critical to understanding the geochemical and hydrologic evolution of the Yellowstone hydrothermal system and has already shown that this mid-continental system is far more dynamic, ever-changing, and unique than previously expected. In other words, no two thermal features are the same, and this offers a wonderful opportunity to diagnose sub-surface processes and changes throughout Yellowstone National Park, the supervolcano in our very own backyard.

### Future work

Future research is encouraged to implement many of the sampling methods that were improved upon in this study, including the sampling of over 2x greater volumes of water. This is to ensure that any significant radionuclides are detected and exploited for interpretation on timescales of water-rock interaction. In other words, higher volumes equate to a greater likelihood of radionuclide detection.

We also suggest that neutral-chloride geysers are sampled for “geyser eggs”. These eggs are well-rounded, cobble-sized rocks that tend to fill catch basins surrounding geysering thermal features. Their rounded shape comes from extensive time spent within the geyser conduit, where they are rounded continuously, like a rock tumbler would, before being ejected from the geyser during an eruption. Given the supersaturation of silica within neutral-chloride features, it should come as no surprise that these eggs are essentially silica concretions. This layering of amorphous silica sinter therefore can act as a

time record for fluid chemistry, as the oldest layers lie within the core of the eggs and become progressively younger moving outward toward the shell. Therefore, it is recommended that future research aim to quantify and characterize these concentric layers in an effort to constrain past fluid conditions within specific features or across entire hydrothermal basins.

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