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New Data from an Old Well: Changes in the Chemistry of Runoff Geothermal Well Water

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ABSTRACT

Water samples from geothermal wells are challenging to collect. Sample collection from a well is easiest when the water is near ambient pressure and temperature, but the water at a geothermal well's wellhead is often above its boiling point and pressurized. Because these traits make water sampling difficult, even low-temperature geothermal wells often are sampled after the water has cooled, decompressed, and interacted with the atmosphere. Study of natural geothermal features has shown that waters rapidly re-equilibrate after reaching the surface (Lewicki, 2013). When geothermal well waters must be sampled far from a wellhead, are reliable data irretrievable? The Center for Economic Geology Research at the University of Wyoming recently sampled from a recharge-pressurized low-temperature geothermal well in Wyoming's Great Divide Basin. The well has likely been flowing ever since it was abandoned shortly after completion in 1925. The age and disrepair of this well have resulted in a significant amount of bore scale in the well bore and near-bore temperature equilibration. A series of samples were taken starting inside the bore then at several points along the run-off stream until it terminates in an evaporate lake. These samples showed that some species equilibrate rapidly and as predicted, but that many other species remained consistent until the run-off stream terminated in an evaporate lake, at which point significant changes in almost every analyte occurred. This study shows that most analytes of interest to geothermal operations can be sampled further from the wellhead than previously thought, but only if evaporation is minimized.

1. INTRODUCTION

Many wells drilled in the course of oil and gas exploration are dry holes, which do not bring any significant hydrocarbons to the surface. In the days before regulation specified that a company must have the funds to properly plug and abandon any well it drilled, exploration companies often left these dry holes open. Most unplugged dry holes don't connect a confined aquifer of high hydrostatic head to the surface, but when they do they present an opportunity to study a steady-state system.

Wyoming's Great Divide Basin is an endorheic basin where all water enters as rain and leaves by evaporation. At Separation Rim, rain that infiltrates the Dakota sandstone in its recharge area, travels down the hydrologic gradient within the Dakota confined aquifer until it reaches one of several artesian springs or a human-made conduit to the surface (Gregory and Bagdonas 2012). To ensure a stable and well-constrained system this work considered a well at the south end of Bull Spring Lake (Figure 1).

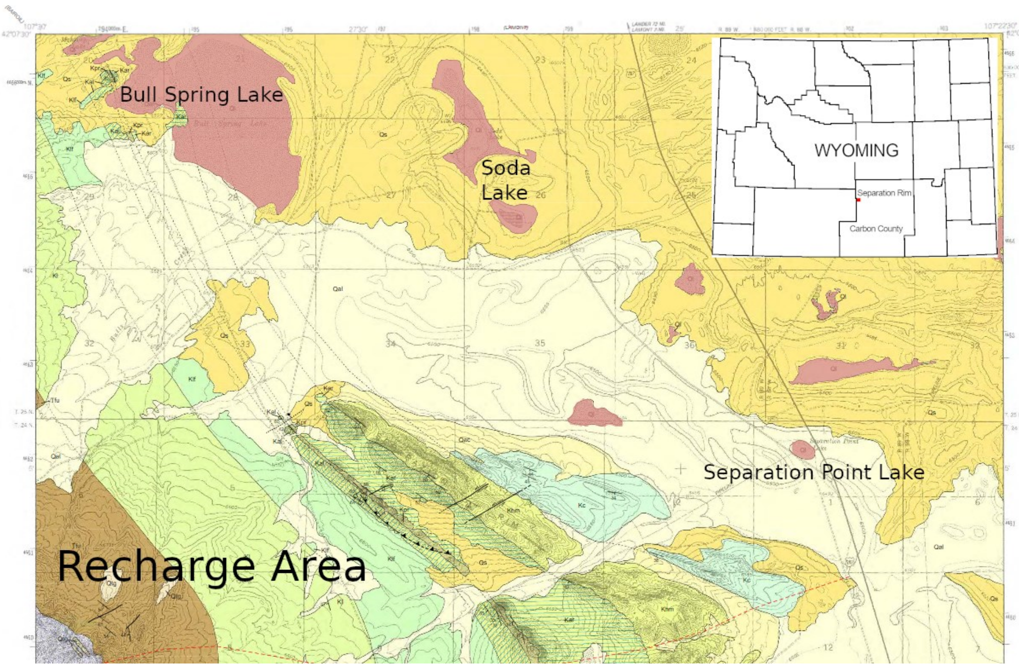

Figure 1: Detail of Gregory and Bagdonas' 2012 map, with evaporative lakes emphasized in red. Also indicated are the exposed strata in the southwest where significant recharge occurs, and the location of this area within Wyoming.

An unknown exploration company drilled this well to 3,439 feet below land surface, in 1925 as a wildcat well. When the well proved to be a dry hole, the company abandoned the open well. It has been open and flowing ever since. Due to the well's long and stable history the water and well components are assumedly in steady state equilibrium. This eliminates confounding variables of well treatment, chemical reactions within the well, and changes in recharge volumes and flow path.

Section 2 discusses sample methodology for four samples from 1) the well, 2) the pool of water around the well's base, 3) the runoff stream, and 4) the terminal evaporate lake. Section 3 identifies basic geochemical parameters and geochemical analytes in these samples as stable or unstable over a given interval of the water's flow path.

2. COLLECTION AND ANALYSIS

All four samples were collected in brown glass bottles because the elevated temperature of the water coming out of the well might have been too hot for LDPE bottles. The 500ml bottles had been HCl acid-washed and rinsed with ultra-pure water (>18 MΩ-cm). The bottles were rinsed again in the field with the sample before final collection. Field measurements were taken with a hand-held Myron Ultrameter II and included pH, temperature, conductivity, and Oxidation-Reduction Potential (ORP). The samples were stored and transported at less than 3°C until analysis. This included overnight freezing to arrest biological activity. The following morning, they were thawed, filtered, split, and acidified. Filtering used 0.45 micron MCE filter papers to remove particulate and microbes. The split allowed analysis for anions that require an unacidified sample, and also cations that can be better preserved in an acidified sample. The acid used for this acidification was trace metal grade 69% Optima nitric acid. Less than 2ml were needed to lower the pH of the 500ml samples to ~2 as measured with pH test strips. Monoatomic and polyatomic anions were analyzed by ion chromatography at Energy Laboratories, and cations were analyzed as elements by ICP-OES, also at Energy Laboratories. Stable isotopes ratios were measured at the University of Wyoming's Stable Isotope Facility. All QA/QC tests met the requirements of A2320 B, E300.0, E200.7, E200.8, E350.1. The standard deviation of the percent recovery on all QA samples was ±9.89%.

The wellhead sample was collected by fully inserting the brown glass bottle into the wellhead. Combined with the steady flow out of the well, this minimized the introduction of atmospheric air. Due to constant subsurface temperatures and passivation of the well bore over the last 90 years, this sample may be representative of the water chemistry at 3,439 feet depth in the Dakota formation.

The well pool sample was collected by tipping the brown glass bottle on its side in the pool around the wellhead, before it started flowing down the run-off stream. This minimized introduction of pool sediment to the sample, but reflected the atmospheric interaction that occurred within a few seconds of the water reaching the surface.

The runoff stream sample was collected by tipping, as before, and was taken in a laminar section of the stream about half way between Bull Spring Lake and the well.

The Bull Spring Lake sample was collected by attaching the bottle to a long pole, and reaching about 20 feet out into the lake before tipping the bottle to minimize sediment introduction. Because the lake shore and near shore are very shallow and muddy this sample was physically challenging to collect, and is the most likely to include sediment.

3. DATA AND RESULTS

The following tables present and discuss the interpretation of the stable isotope ratios (Table 1), field parameters (Table 2), and geochemistry (Table 3). The stability of those data along the flow path is discussed in the following section.

3.1 Data tables and interpretation

Most data shows consistent variation along the water's flow path, decreasing or increasing as the water moves from the wellhead to the lake.

	$\delta^{13}C$	**δD**	**$\delta^{18}O$**
Wellhead	18.677	-123.47	-16.598
Well Pool	18.653	-122.35	-16.304
Run off Stream	18.662	-121.47	-15.918
Bull Spring Lake	17.625	-73.32	-5.149

Table 2: Stable isotope compositions for the four samples. Most stable isotopes do not change very much until reaching the evaporate lake. Hydrogen and oxygen isotopes show some signs of evaporation even in the pool around the wellhead, with the water losing light isotopes at each sampling point. Carbon isotopes are almost identical within the range of instrument error until the water reaches the lake.

The extremely negative ratios of hydrogen and oxygen are consistent with most Wyoming waters, and typical for an arid environment far from the ocean. They are near, but right of and below, the global meteoric waterline, as expected for geothermal waters without sulfide contribution (Carter, 2008; Coplen and Kendall, 2000). The extremely positive carbon isotopes suggest vibrant microbial activity at depth or contribution from coalbed methane (Mook and Tan, 1991; Sharma and Frost, 2008).

	pH (units)	Conductivity (mS/cm)	Temperature (°C)	ORP (mV)
Wellhead	7.40	4.70	31.1	-36
Well Pool	8.15	4.18	29.4	8
Run off Stream	8.30	11.3	27.2	22
Bull Spring Lake	8.81	80.0	17.7	13

Table 2: Field measurements collected at the time of sampling. Most show a steady change as the water travels to the lake. The measurements that do not follow a pattern of steady change along the water's flow path are the conductivity in the well pool, and the ORP in the lake.

As the water travels from the well to the lake it cools, becomes more basic, more oxidized, and more concentrated. The two exceptions to this are the small decrease in conductivity between the wellhead and well pool and ORP between the stream and the lake. The decrease in conductivity in the pool could be a result of metals oxidizing to oxides and hydroxides or precipitating from solution as conditions become more alkaline. In either case, the effect would be minor as those ions make up a very small part of the total dissolved load (see Table 3). The decrease in the ORP measurement from the lake could be a result of disturbing the fine sediment inches from the surface of the lake during collection, possibly introducing comparatively anoxic water from within the ooze bed. Alternatively, it could be that agitation and turbulent flow in the run-off stream charges the water with more oxygen than the calm lake.

	Alkalinity, Total as CaCO3	Bromide	Calcium	Chloride	Fluoride	Magnesium	Nitrogen, Ammonia as N	Potassium	Sodium	Sulfate
Wellhead	2080	1	3	107	3.6	ND	0.78	3	887	2
Well Pool	1840	0.9	4	103	3.4	ND	0.71	4	1020	ND
Bull Spring Lake	4390	32	18	11000	0	1000	0.09	247	27900	38000

Table 3a: Major element chemistry in three samples. All values are in mg/L (ppm). ND indicates non-detects below the detection limit of the instrument. In addition to these analytes, nitrate and nitrite were below detection limits in all samples.

	Arsenic	Barium	Boron	Iron	Manganese	Molybdenum	Silicon	Strontium
Wellhead	ND	1.53	ND	ND	0.003	0.001	9	0.52
Well Pool	ND	1.85	ND	ND	0.003	ND	10	0.6
Bull Spring Lake	0.036	0.09	9.8	0.1	0.005	0.028	2	5.44

Table 3b: Minor element chemistry in three samples. All values are in mg/L (ppm). ND indicates non-detects below the detection limit of the instrument. In addition to these analytes, aluminum was below detection limits in all samples.

Trends in major and minor geochemistry are not as straightforward as the field measurements. Some analytes are methodical, such as sodium's steady increase, and ammonia's steady decrease as the water nears and enters the lake. Many elements show conservation in the lake water as expected, such as bromine, and strontium. However, the vast majority experience a small counterintuitive perturbation in the well pool sample. This deviation might be possible to dismiss as instrument or field error, but more likely represents a slight and real change. The container of runoff stream water, which had been intended for geochemical analysis, shattered during handling and the sample was lost. That sample could have resolved some of the above ambiguity. Future collections should not only be able to avoid similar loss, but also be able to sample more than one point on the runoff stream.

3.2 Stability of the data with progression along the flow path.

To assess the amount of exposure to surface conditions that would minimally alter the sample, the data presented above were divided by the wellhead values and multiplied by 100 to give the percent change from the original wellhead value. In this methodology, an analyte which remains consistently at 100 may be measured far down the water's flow path with high confidence that it continues to represent the original wellhead sample. While any deviation from the original wellhead value is undesirable, Figures 2 and 3 show the plus and minus 10% range highlighted in grey to indicate acceptable drift if a sample must be measured away from the wellhead.

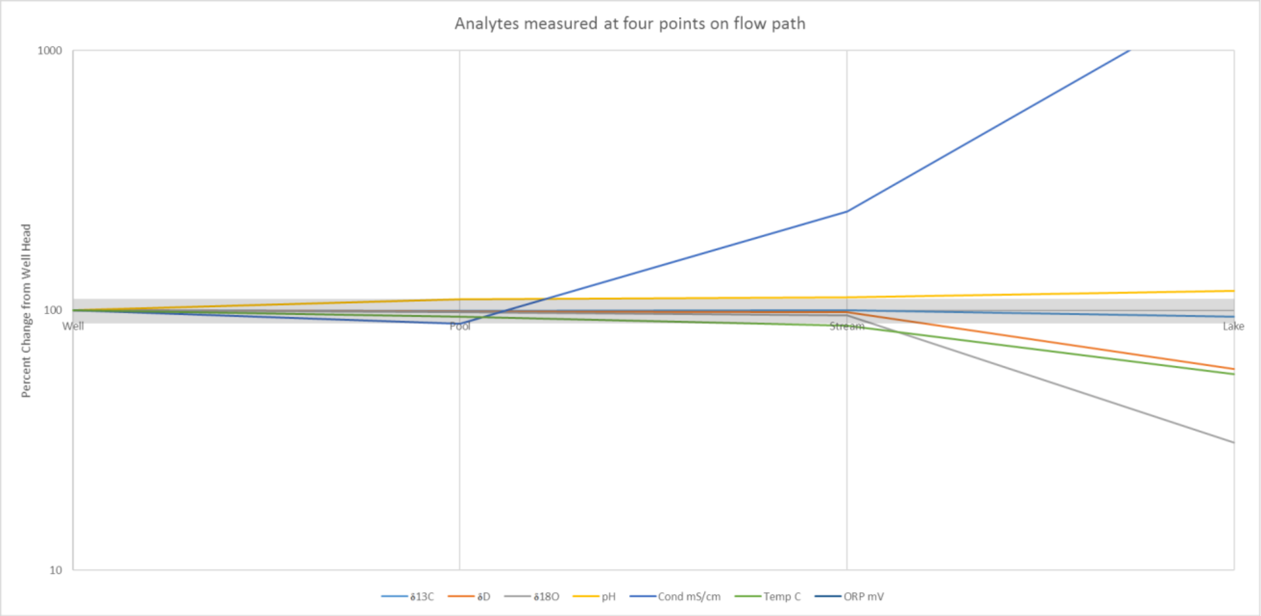

Figure 2: Field and isotope measurement stability at four points along the geothermal water's surface flow path.

The analytes shown in Figure 2 are generally stable over the ~3feet distance of water splashing out of the wellhead and into the well pool. The two exceptions to this are ORP (which alters sign and moves so radically it is not visible on this plot), which can *only* be accurately measured at the wellhead, and pH, which is marginal. After ~50feet of travel to the mid-point of the runoff stream, conductivity can no longer be measured, and temperature is marginal. In the lake, almost all analytes have deviated very far from the well head values, but surprisingly stable isotopes of carbon remain within the aforementioned 10% window and could still provide support for almost exactly the same interpretation as they would provide at the well head.

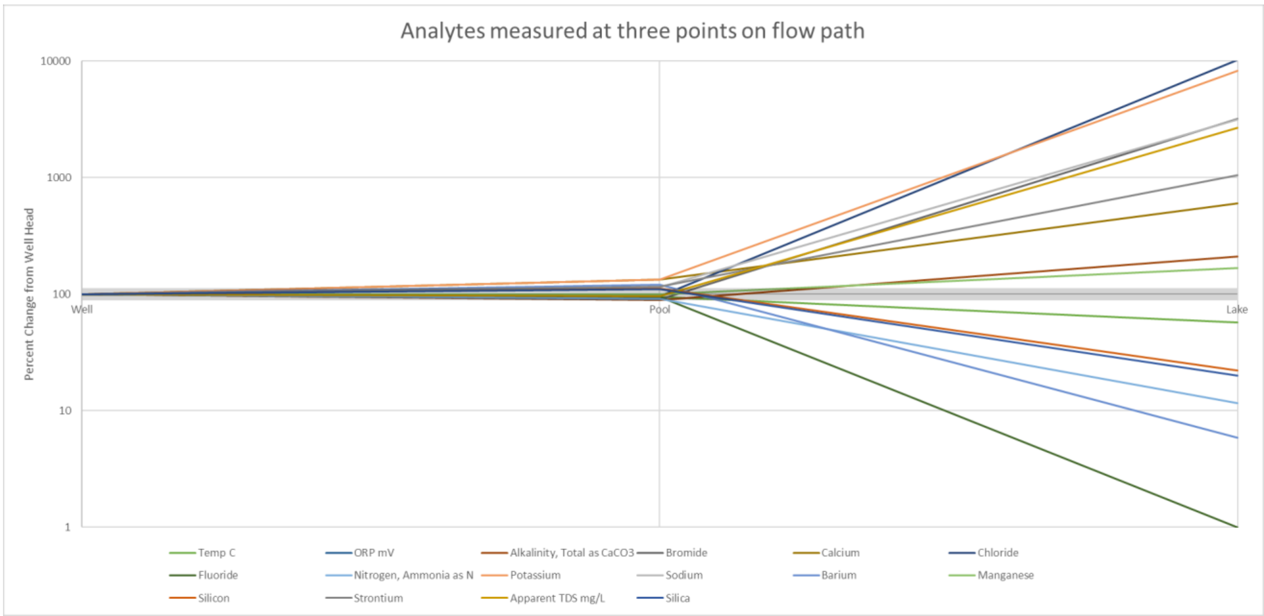

Figure 3: Geochemistry changes between the well, the pool, and the lake.

Like the field measurements in Figure 2 the geochemical analytes shown in Figure 3 are generally stable after falling ~3feet from the top of the well head to the pool around its casing. The exceptions include potassium, calcium, barium, sodium, strontium, and silicon, all of which are present in the pool at greater concentrations than in the wellhead. Bromine and (bi)carbonate – are marginal and lower than in the well head sample. However, by the time water reaches the lake, no analyte is within 10% of the wellhead value.

4. CONCLUSION

While it is never desirable to collect a geothermal sample far from the point of interest, it is sometimes expedient and/or necessary. In such cases, ORP and pH should be expected to be entirely unreliable. However, a short transport, even with turbulent freefall through atmospheric air, will allow many geochemical and isotopic analytes to be treated as though they were the true value at the point of interest. Transport of more than a few feet, especially in contact with stream sediment, will render temperature and conductivity too altered from their values to be reliable, with most geochemical analytes failing soon after those. If significant evaporation has occurred, as in the lake, then the sample may only be useable for stable isotopes of carbon. It is possible some future development, technique, or exceptional modeling advancements will be able to recover such abused samples, but unless they are accompanied by ample supporting evidence such work to reverse the complex processes associated with surficial transport of geothermal waters should be viewed with extreme skepticism.

This work points to minimizing evaporation as the most significant means to improve sample quality if a proxy sample must be taken far from the point of interest.

5. CONTRIBUTIONS AND ACKNOWLEDGEMENTS

Charles Nye conceived of the work, wrote this manuscript, collected and processed all samples except the lake sample. Contributors include Davin Badgonas who fabricated the collection pole and collected the lake sample. The author would also like to thank the landowners who allowed access to their properties.

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