



# Water Quality in the Homestake Mine Near the Sanford Underground Research Facility

Caitlyn Larson, Augustana University, Sioux Falls, SD | Micheal Zehfus, Black Hills State University, Spearfish, SD michael.zehfus@bhsu.edu



## Introduction

The Homestake Mine was one of the most successful gold mines in the US and was operational from the mid 1870's until December of 2001. It has since been converted into a high-quality science facility, housing experiments from many disciplines. Some of the well-known experiments from the lab are in area physics; these include the Davis experiments, which discovered neutrinos back in 1965, and more recently the LUX detector, which searched for dark matter.

The mine is the largest in the western hemisphere with miles of underground tunnels. In this project water was collected from four different levels of the mine ranging from 300 feet to 4850 feet underground and analyzed at Black Hills State University. While the project was originally conceived as a way to document the water used in biological experiments, last year it was discovered that there were substantial differences between water collected at the 4100 and 4850 levels. This year the search has been expanded to include the 300 and 1700 levels in addition to more sampling on the 4100 and 4850.



## Materials and Methods

- Underground collection
  - Samples were collected in a 500 mL plastic bottle when necessary, a 50 mL plastic syringe was used to extract water from shallow pools
  - Air pressure- Vernier Lab Quest with appropriate probe
  - Air temperature- Vernier Lab Quest with appropriate probe
  - Water temperature- Vernier Lab Quest with appropriate probe
  - Conductivity- Vernier Lab Quest with appropriate probe
  - Ammonia- Vernier Lab Quest with appropriate probe
    - The ammonia probe was calibrated using 1 ppm and 100 ppm standard solutions.
  - Dissolved Oxygen- Vernier Lab Quest with appropriate probe, except sites L, M, and N
    - The dissolved oxygen probe was calibrated using magnesium sulfate
  - Dissolved Oxygen- HACH kit with dissolved oxygen accuvac ampuls
  - pH meter with temperature compensation- Oakton Acorn meter kit
    - pH meter calibrated using pH 7 and 10 solutions
- At BHSU lab
  - Atomic Absorption in acetylene flame- Perkin Elmer Analyst 300



Element	Wavelength (nm)	Standard Solutions (ppm)
Na <sup>+</sup>	589.0	50,37.5,25,12.5,5
K <sup>+</sup>	766.5	20,15,10,5,2
Ca <sup>2+</sup>	422.7	10,7.5,5,2.5
Mg <sup>2+</sup>	285.2	3,2,1
Total Fe	248.3	6,4,2

- Sulfate (SO<sub>4</sub><sup>2-</sup>)- BaCl<sub>2</sub> added to sample and the resulting BaSO<sub>4</sub> precipitate was measured using nephelometry at 419.8 nm
  - $Ba_{(aq)}^{+2} + SO_{4(aq)}^{-2} \rightarrow BaSO_{4(s)}$
- Nitrate (NO<sub>3</sub><sup>-</sup>)- photometrically using a HACH kit using NitraVer 5 Nitrate Reagent pouch
- Chloride (Cl<sup>-</sup>)- titration for the precipitation of AgCl connected to an electrochemical cell
  - $Ag_{(aq)}^{+} + Cl_{(aq)}^{-} \rightarrow AgCl_{(s)}$
  - $Cu_{(s)}|Cu_{(aq)}^{+2}||Ag_{(aq)}^{+2}|Ag_{(s)}$
- Alkalinity, Carbonate, and Bicarbonate- titration with drop counter
  - $H_{(aq)}^{+} + CO_{3(aq)}^{-2} \rightarrow HCO_{3(aq)}^{-}$  &  $H_{(aq)}^{+} + HCO_{3(aq)}^{-} \rightarrow H_2CO_{3(aq)}$
- Hardness- EDTA titration until a raspberry to blue color change occurred
  - $[EDTA - H_2]^{-2} + M^{+2} \rightarrow [EDTA - M]^{-2} + 2H^{+}$
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS)- Agilent Technologies 7900 ICP-MS
  - 1:100 dilution on all samples
  - 50 ppb spike added to sample with most Cl<sup>-</sup> to ensure the machine is working



## Results

Test	300 ft Level		1700 ft Level				4100 ft level			4850 ft level			
	300-1 (B)	300-2 (C)	1700-1 (D)	1700-2 (E)	1700-3 (F)	1700-4 (G)	4100-1 (I)	4100-2 (J)	4100-3 (K)	4850-1 (A)	4850-2 (L)	4850-3 (M)	4850-4 (N)
Air Temperature (°C)	-	-	17.3	14.7	16.2	15.8	23.3	23.5	22.6	31.2	32.5	32.7	32.6
Water Temperature (°C)	-	-	16.6	12.5	16	15.4	24	23.7	22.9	32.7	33.7	33.6	32.6
pH	7.43	7.68	7.74	8.07	7.14	7.43	6.73	7.93	8.00	8.49	8.10	8.15	8.34
Conductivity (ppm)	-	-	526	159.2	732	1053	70.33	151	150.6	740	940	900	570
Air Pressure (torr)	-	-	680.1	696	702.5	708.1	1235?	857.6	792.2	743	818.9	844.4	810.7
Dissolved Oxygen (mg/L)	-	-	8.5	17.6?	6.8	8.8	-	-	-	7.0	4.4	4.6	1.2
Ammonia (mg/L)	0.4	0.3	0.6	0.7	0.7	2.5	-	-	-	0.3	1.4	0.9	0.5
Na <sup>+</sup> (mg/L)	7.255 (0.047)	11.66 (0.102)	42.80 (0.32)	27.89 (0.10)	32.8 (0.15)	95.5 (0.60)	266 (1.6)	247 (2.52)	643 (2.2)	287.2 (1.87)	425 (2.6)	445 (4.6)	266 (2.72)
K <sup>+</sup> (mg/L)	8.393 (0.025)	4.938 (0.016)	5.65 (0.04)	3.89 (0.02)	3.77 (0.03)	11.96 (0.03)	203 (1.55)	124 (1.03)	47.21 (0.06)	10.89 (0.034)	37.2 (0.18)	30.4 (0.11)	9.42 (0.09)
Mg <sup>2+</sup> (mg/L)	36.0 (0.2)	132.1 (0.7)	145.2 (3.4)	84.2 (2.8)	80.6 (4.9)	252.8 (0.3)	4990 (80)	1503 (7)	10.1 (1.3)	1.142 (0.010)	11.02 (0.16)	4.28 (0.03)	1.055 (0.004)
Ca <sup>2+</sup> (mg/L)	66.56 (0.37)	97.25 (0.81)	105.9 (1.33)	90.3 (0.4)	101.9 (0.5)	298.6 (3.6)	477.8 (3.2)	5.71 (0.787)	3.849 (0.072)	1.675 (0.035)	4.852 (0.040)	3.359 (0.047)	1.240 (0.023)
Fe (total) (mg/L)	0.191 (0.032)	<LOD	0.068 (0.003)	<LOD	<LOD	<LOD	0.557 (0.003)	<LOD	<LOD	0.03 (0.01)	<LOD	<LOD	<LOD
Sulfate (mg/L)	317	360	1426	4926	1779	2015	10441	12500	683.8	73.75	613.2	595.6	127.9
Carbonate (mg/L)	8.44	14.6	18.2	36.5	0	0	0	22.1	22.8	51.5	47.3	57.8	45.6
Bicarbonate (mg/L)	152	176	275	191	460	452	512	138	721	461	676	665	503
Chloride (mg/L)	10.86	84.23	34.46	60.97	28.98	78.33	21.27	10.32	20.48	17.73	1.19	20.73	9.36
Nitrate (mg/L)	1.1	0.1	0.5	0	0.4	0	N/A	0	0.8	0.8	1.0	1.0	1.0
Total Alkalinity (mg/L CaCO <sub>3</sub> )	139	169	256	191	377	371	420	150	630	464	633	642	489
Total Hardness (mg/L CaCO <sub>3</sub> )	255	373	578	454	450	1134	11241	3396	47.1	6.82	51.6	23.1	8.32
Date Collected	6/22/2017	6/22/2017	6/29/2017	6/29/2017	6/29/2017	6/29/2017	6/29/2017	6/29/2017	6/29/2017	6/14/2017	7/6/2017	7/6/2017	7/6/2017

Table 1: This table demonstrates all of the on site, and lab tests done to the water samples. Air and water temperature, air pressure, pH, conductivity, dissolved oxygen and ammonia were taken on site. The remaining tests were performed at BHSU. Standard deviation is presented within the parenthesis. Question marks denote possible instrument failure. LOD stands for below limit of detection.

Level	Sample ID	Element			
		Ba	As	Mn	Sb
300	300-1 (B)	<LOQ	<LOD	322 (39)	<LOQ
	300-2 (C)	<LOQ	<LOD	72 (2)	<LOQ
1700	1700-1 (D)	38 (2)	<LOQ	124 (8)	<LOQ
	1700-2 (E)	<LOQ	<LOD	16 (1)	<LOQ
	1700-3 (F)	<LOQ	24 (2)	31 (1)	2.8 (0.4)
	1700-4 (G)	<LOQ	150 (11)	221 (8)	38 (1.6)
4100	4100-1 (I)	26 (2)	528 (18)	2590 (61)	<LOQ
	4100-2 (J)	<LOQ	5 (2)	928 (50)	<LOQ
	4100-3 (K)	42 (3)	<LOD	13 (1)	<LOQ
4850	4850-1 (A)	92 (9)	<LOD	<LOQ	<LOQ
	4850-2 (L)	42 (3)	12 (2)	<LOD	<LOD
	4850-3 (M)	50 (3)	5 (1)	<LOD	<LOD
	4850-4 (N)	119 (5)	5.9 (0.9)	<LOD	<LOD

Table 2: The values received from the ICP-MS are displayed here. LOD means that the value was below the limit of detection. LOQ means the value was below the limit of quantification, which is three times the LOD.

Below Limit of Detection (LOD)	Cu	Ag	Tl	Pb	Zn	Hg	V	Cr	Se	Cd	Ni*
LOD (ppb)	0.52	5.5	3.6	2.8	3.5	170	0.99	35	0.61	0.52	0.26

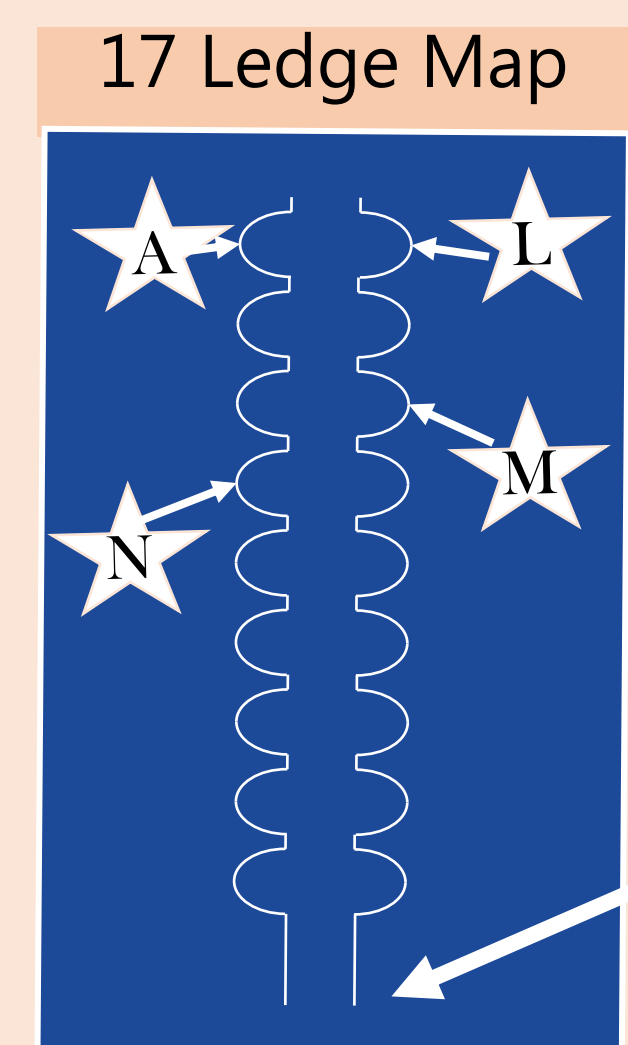
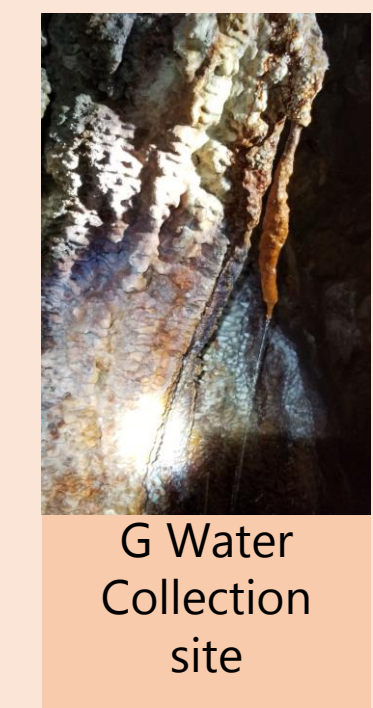
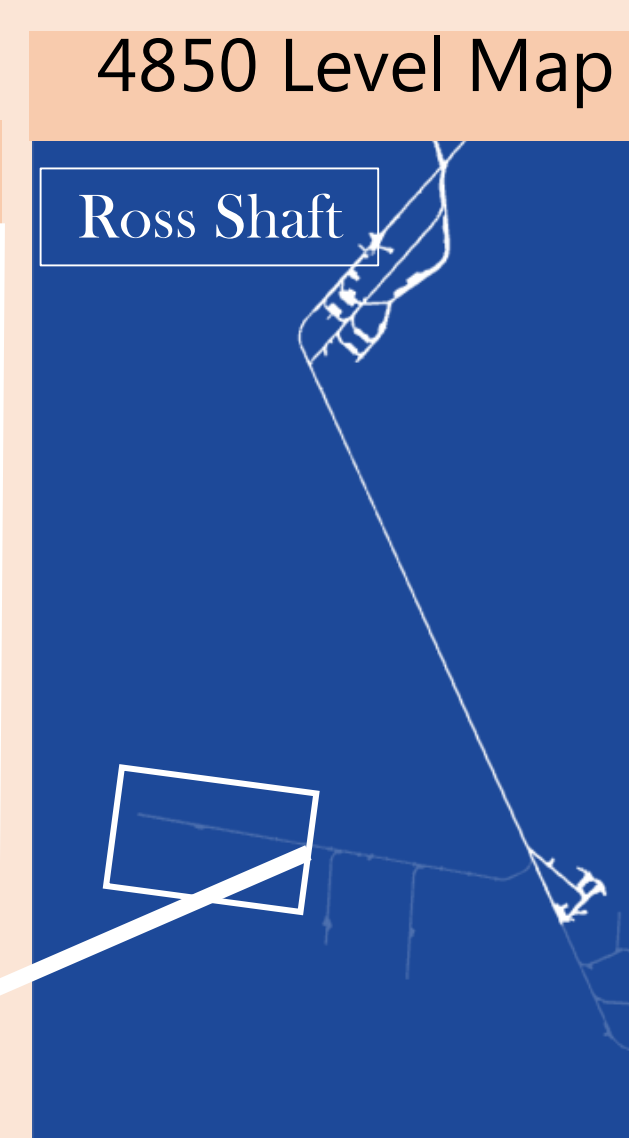
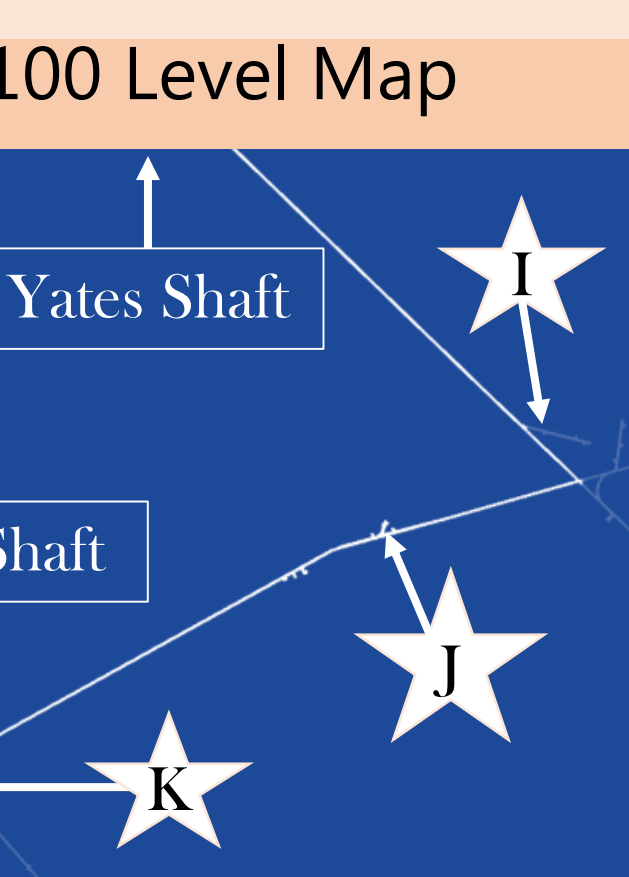
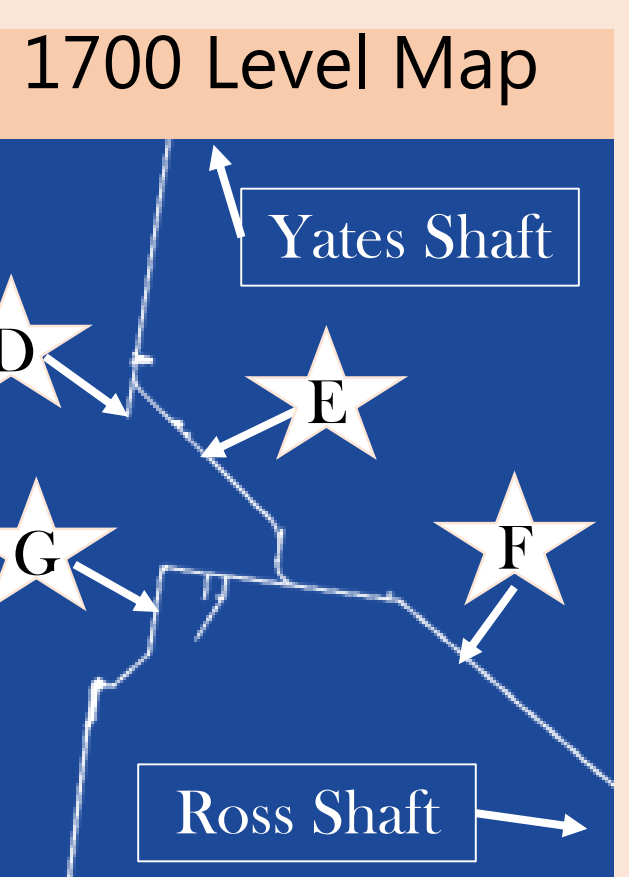
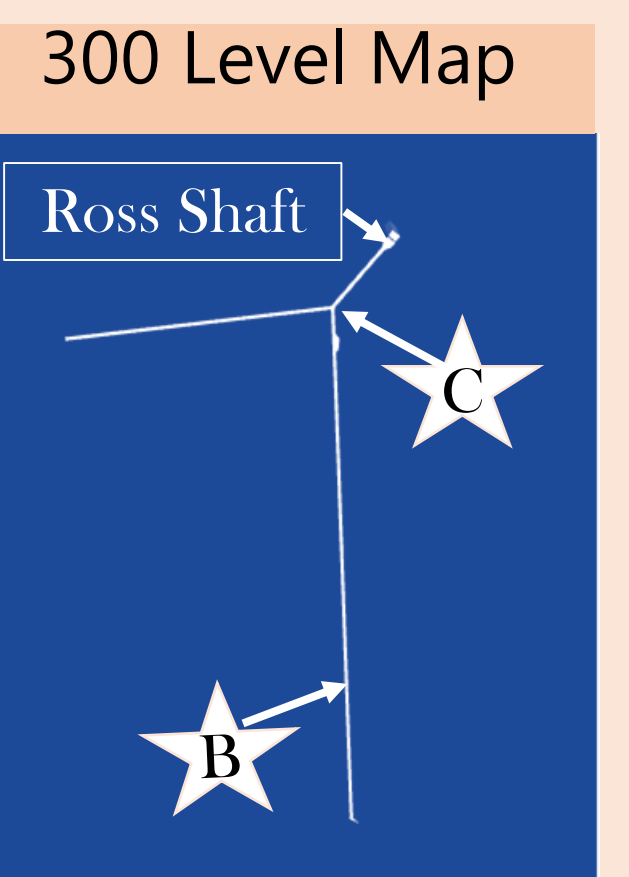
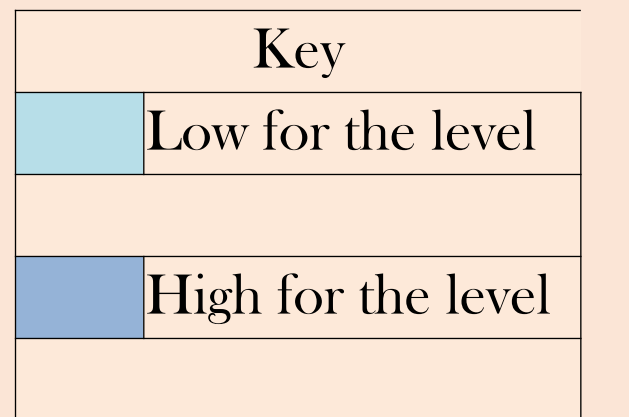
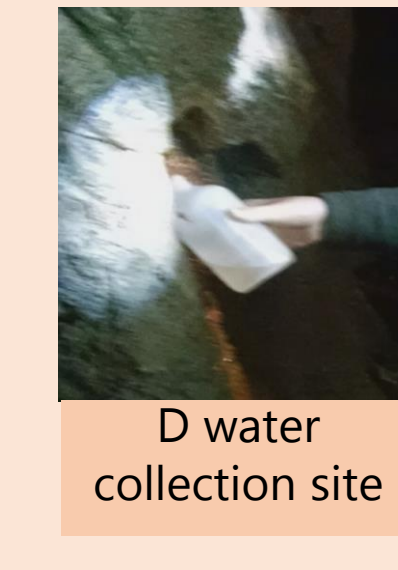
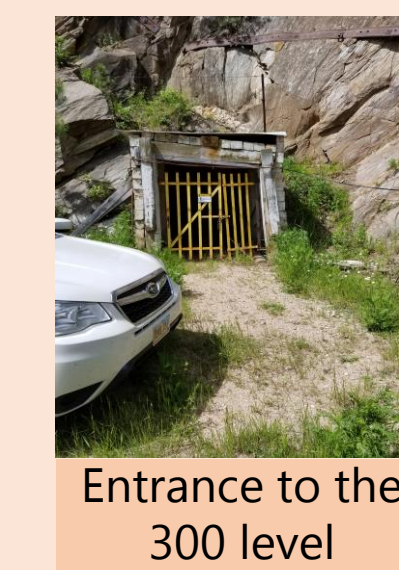
Table 3: The values demonstrate the other elements tested which were below the limit of detection in all cases. The \* on Ni means that it was below the LOD.

Element	V	Cr	Mn	Ni	Cu	Zn	As	Se	Ag	Cd	Sb	Ba	Hg
LOD (ppb)	0.52	5.5	3.6	2.8	3.5	170	0.99	35	0.61	0.52	0.26	7.2	1.5

Table 4: For all elements tested using ICP-MS the limits of detection are shown in ppb.

Test	300 Level	1700 Level	4100 Level	4850 Level	2016	
					4100	4850
Air Temperature (°C)	-	16 (1)	23.1 (0.5)	32.3 (0.7)	23.6 (0.3)	26.3 (3.8)
Water Temperature (°C)	-	15 (2)	23.5 (0.6)	33.2 (0.6)	23.0 (0.5)	26.5 (4.6)
pH	7.555 (0.2)	7.6 (0.4)	7.6 (0.7)	8.3 (0.2)	7.5 (0.6)	8.4 (0.1)
Conductivity (ppm)	-	618 (37.5)	124 (46)	788 (169)		
Air Pressure (torr)	-	697 (12)	825 (46)	804 (43)	721.9 (1.3)	742.4 (3.7)
Dissolved Oxygen (mg/L)	-	8 (1)	-	4.3 (2.4)	3.0 (1.3)	6.4 (1.2)
Ammonia (mg/L)	0.35 (0.07)	1.1 (0.9)	-	0.78 (0.49)	14.5 (3.6)	1.6 (1.1)
Na <sup>+</sup> (mg/L)	9.5 (3.1)	50. (31)	385 (223)	356 (92)	356.9 (16.4)	347.3 (117.9)
K <sup>+</sup> (mg/L)	6.7 (2.4)	6.3 (3.9)	125 (78)	22 (14)	166.2 (47.7)	19.2 (7.4)
Mg <sup>2+</sup> (mg/L)	84 (68)	141 (80)	2168 (2556)	4.4 (4.7)	2013.7 (1050.7)	21.3 (29.7)
Ca <sup>2+</sup> (mg/L)	82 (22)	150 (100)	162 (273)	2.8 (1.7)	401.9 (85.9)	4.3 (3.0)
Fe (total) (mg/L)	0.10 (0.14)	0.017 (0.034)	0.19 (0.32)	0.01 (0.02)	6.8 (4.8)	0.1
Sulfate (mg/L)	339 (30)	2537 (1611)	7875 (6312)	353 (292)	7033.3 (3550.1)	259.3 (236.1)
Carbonate (mg/L)	11.5 (4.4)	14 (17)	15 (13)	51 (5)	0 (0)	113.7 (100.6)
Bicarbonate (mg/L)	164 (17)	345 (133)	457 (295)	576 (110)	244.0 (102.2)	512.5 (176.7)
Chloride (mg/L)	48 (52)	51 (23)	17 (6)	12 (9)	52.2 (27.6)	47.6 (13.7)
Nitrate (mg/L)	0.6 (0.7)	0.23 (0.26)	0.4 (0.6)	0.95 (0.1)	0.8 (0.2)	0.9 (0.4)
Total Alkalinity (mg/L CaCO <sub>3</sub> )	154 (21)	299 (91)	400. (240)	557 (94)	200.0 (84.1)	610.3 (120.7)
Total Hardness (mg/L CaCO <sub>3</sub> )	314 (83)	654 (325)	4895 (5745)	22 (21)	9286.7 (4959.3)	111.9 (144.7)

Table 5: The average values for each level are shown with their standard deviations in the parenthesis. Last year's averages for the 4100 and 4850 levels are also shown under the 2016.



## Conclusion

Last year several statistically significant differences were found between the water on the 4100 and 4850 levels of the Homestake Mine, thus the first task was to see if this could be confirmed. As seen in Table 5, the general differences between the 4100 and 4850 levels remained the approximately the same. However, differences between the other levels could not be established because there was high variability between each site, as seen by the large standard deviation for many of the averages. The only test that seemed to differentiate between levels was air and water temperature.

Samples from the 300-level differed in Mg<sup>2+</sup>, Ca<sup>2+</sup>, Fe<sub>total</sub>, and Cl<sup>-</sup>. Sample C, from further down the tunnel, had more Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Cl<sup>-</sup>; and sample B, from near the tunnel entrance, had more Fe<sub>total</sub>. Samples from the 1700-level were more variable than any other level; here even temperature and pH changed from site to site. This variability could be explained by either the great distance between collection sites, or the unique character of each collection site. Sample G, which was collected from water dripping off a stalactite, had higher concentrations of nearly all dissolved ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Cl<sup>-</sup>) than any other sample on the same level. Sample D, from an old 300 ft. drill hole, contained Ba and relatively high Mg<sup>2+</sup>. Sample E, from a fast-flowing pipe carrying water from the #2 air rise, had low conductivity, but high CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>. Only samples from the 1700 and 4100 levels had As, and those on the 1700 that had As also had Sb present. Arsenopyrite (FeAsS) is known to be in the mine, and is common near gold formations. It is likely that these formations occur on both the 1700 and 4100 levels, where the FeAsS could have been oxidized (possibly by bacteria), releasing the As. On the 1700, stibnite (Sb<sub>2</sub>S<sub>3</sub>) could also be present to provide the Sb. Sb<sub>2</sub>S<sub>3</sub> is common near FeAsS formations, as well as Au and calcite formations. One of the most surprising discoveries was on the 4850-level; samples A and L, which were less than 25 ft. apart, were extremely dissimilar. Sample L was higher in dissolved ions (As, Mn, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>), and far lower in Cl<sup>-</sup> than any other site at this level. Sample A had the highest dissolved oxygen of any sample on the 4850-level, which is explained by the large surface area of the pool.

In summary, last year we observed several differences between levels that could have been caused by the limited diversity of sampling sites. This year a deliberate effort was made to sample more sites at each level to get a more representative data set for that level. It was found site-to-site variability makes it difficult to find overarching trends for an entire level.

## Acknowledgments

A big thank you to Tom Regan and all of the SURF staff for showing us around the mine and keeping us safe as we ventured on various levels. A thank you to the NSF REU Grant Award No. 1560474 for making this possible. Finally, a shout out to Dr. Marcelo Guerra for his ICP-MS assistance and expertise.

## References

Baird, C.; Cunn, M. The Chemistry of Natural Waters. In *Environmental chemistry*; Freeman: New York, NY, 2012.

Barthelmy, D. Mineral Species containing Arsenic (As) <http://webmineral.com/chem/Chem-As.shtml#WXilW4jtPb> (accessed Jul 26, 2017).

Boehnke, D. N.; Delmonya, R. D. *Laboratory Experiments in Environmental Chemistry*; Prentice Hall: Upper Saddle River, NJ, 2000.

HAACH DR820 Colorimeter Procedure Manual, 2nd ed.; Hach Company: Loveland, CO, 1999.

Kegley, S. E.; Andrews, J. *The Chemistry of Water*; University Science Books: Sausalito, CA, 1997.

Science | Sanford Lab Homestake Visitor Center, Lead SD <http://sanfordlabhomestake.com/science> (accessed Jul 19, 2017).