

# Assessing Water Chemistry in Hot Springs, NC to Map the Shady Dolomite Formation

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## Abstract

Hot Springs, NC contains a hydrothermal system due to complex tectonic activity within the Appalachian Mountains. Previous studies have mapped several geologic units, which have been folded and faulted, at various outcrops in the area. This study analyzed private water well samples to map the location of the Shady Dolomite Formation northwest of downtown Hot Springs. Four samples were likely collected from within the Shady Dolomite, based on elevated concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$ , and the geologic contact was between the Shady Dolomite and the Rome Formation was approximated based on changes in groundwater chemistry. The results of this study suggest additional sampling could be conducted to further delineate the geologic contact between these two formations and learn more about the region's tectonic history.

## 1. Introduction

Hydrothermal systems typically occur in folded and faulted rocks located within mountainous regions.<sup>1</sup> These folds and faults can increase permeability and allow geothermally-heated water to discharge at the ground surface before it cools down. Hydrothermal systems can also have unique chemical compositions due to the dissolution of surrounding rock, allowing geologists to interpret the stratigraphy of the region.<sup>2</sup>

Numerous hydrothermal systems exist within the United States, including one in Hot Springs, North Carolina. Hot Springs is located in the Appalachian mountains, resulting from complex tectonic activity beginning over 300 Ma. The Silurian Taconic, Devonian Acadian, and Permian Alleghanian orogenies caused numerous folds and faults (Figures 1 and 2). The structural geology of the region impacts groundwater flow paths; previous studies noted geothermally-heated water as well as elevated  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  concentrations, which are associated with the Shady Dolomite Formation.<sup>3, 4</sup> One previous study constructed a geologic cross-section along Upper Shut-In Creek and its relation to the Shady Dolomite and Rome Formations (Figure 2). The Rome Formation is primarily composed of shale and abundant in feldspar; water having flowed through this formation would be expected to be abundant in  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ .<sup>5</sup>

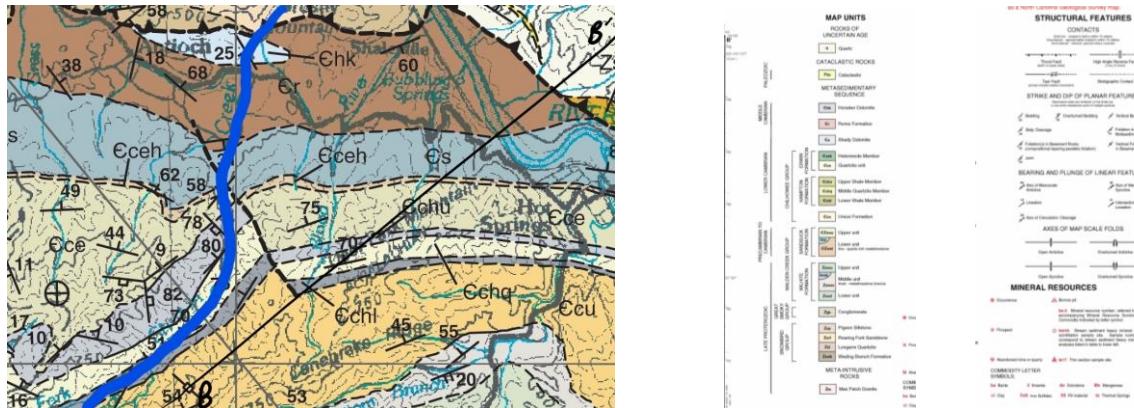


Figure 1. Geologic map of the Hot Springs Area. Upper Shut-In Creek flows N-S, crossing several units and an inferred fault line. B-B' is labeled with a black line. Cr is indicative of the Rome Formation and Cs is indicative of the Shady Dolomite Formation. Upper Shut-In Creek is indicated by a thick blue line.<sup>6</sup>

While some studies have been conducted on groundwater chemistry in the Hot Springs region, more research is needed to better understand groundwater flow paths and subsequent interpretation of underlying geology. This study was designed to investigate major-ion geochemistry to further investigate the hydrothermal flow system and determine the location of the Shady Dolomite Formation.

## 2. Materials and Methods

Seven samples were collected from private residential drinking-water wells along Upper Shut-In Road, adjacent to Upper Shut-In Creek (Figure 1). This road crosscuts an inferred fault line and several different vertical rock units (B-B' in Figure 2). A sample was also collected at Hot Springs Resort & Spa (HSR) because it is known to be located within the Shady Dolomite Formation. Specific sampling locations are noted in Figure 3. Conductivity, pH, and temperature were measured in the field using an Oakton pH/CON 10 meter. Samples were refrigerated in 25 mL polyethylene sample bottles using standard procedure. Samples were analyzed for major ions using a Dionex IC25 ion chromatograph (IC), after filtration through a 0.45  $\mu\text{m}$  nylon filter. Aliquots for cation analyses were acidified with 1 drop of conc.  $\text{HNO}_3$  (*aq*). Aliquots for anion analyses were not acidified. An alkalinity titration was performed to determine the concentration of  $\text{HCO}_3^-$ .

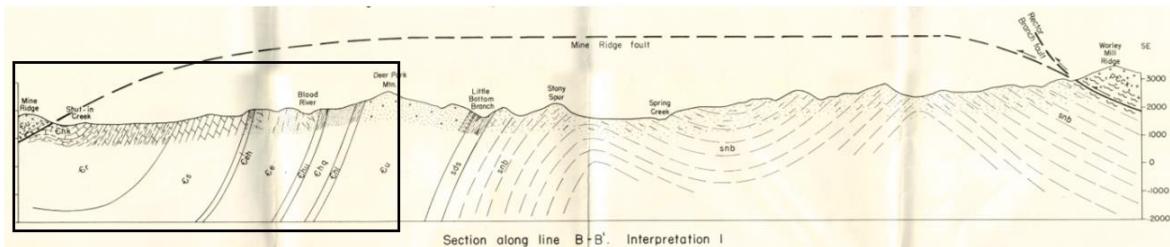


Figure 2. Previous geologic map of Hot Springs, NC along B-B', indicating that Cs and Cr are adjacent to Shut-In Creek. They concluded that Cr should be at a shallower depth than Cs.<sup>7</sup> Approximate area of Figure 1 is indicated with a black box.<sup>7</sup>



Figure 3. Locations of sample sites located on Upper Shut-In Rd. (A1-A7); HSR is located West of these locations. The map is oriented N-S.

### 3. Results

The locations with the largest conductivity values were from the Hot Springs Resort (HSR) and two samples about midway up Upper Shut-In Road (A1 and A2) (Table 1).

Table 1. Compilation of major ion concentrations, conductivity, temperature, pH, and charge balance error for all samples. Approximate well depths were located within the Madison County well logs from 2000 - 2017.

Ion Concentration (ppm)	A1	A2	A3	A4	A5	HSR	A6	A7
Ca <sup>2+</sup>	22.27	16.69	1.42	1.04	2.85	136.47	4.14	0.91
Mg <sup>2+</sup>	12.93	9.11	0.95	0.89	2.05	24.31	4.41	0.69
Na <sup>+</sup>	0.90	0.73	0.90	0.57	1.88	6.95	4.01	0.42
K <sup>+</sup>	1.04	1.02	2.75	1.75	4.75	8.29	2.09	4.04
NH <sub>4</sub> <sup>+</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl <sup>-</sup>	1.89	2.13	0.92	0.59	4.05	0.92	0.69	0.62
SO <sub>4</sub> <sup>2-</sup>	1.35	1.81	0.00	9.46	1.41	381.80	10.00	0.00
HCO <sub>3</sub> <sup>-</sup>	112.87	66.13	7.88	1.89	10.87	90.17	30.07	6.58
NO <sub>3</sub> <sup>-</sup>	6.45	6.09	4.31	0.00	11.71	0.00	0.00	3.14
Conductivity (uS/cm)	233.3	180.60	64.68	34.10	77.32	848	120.50	30.29
Temperature (C)	18.80	21.30	17.30	15.20	21.30	37.90	18.60	18.70
pH	7.74	7.68	6.84	7.18	-	7.39	7.13	-
Approximate Well Depth (ft)	445	-	-	0	-	5248	165	-
CBE (%)	4.80%	16.26%	6.86%	-11.18%	0.38%	-0.73%	5.02%	12.08%

The largest major anion concentrations were SO<sub>4</sub><sup>2-</sup>, and HCO<sub>3</sub><sup>-</sup>. A5 had the largest Cl<sup>-</sup> concentration, while A4, A7, and A6 had the lowest concentrations. HSR had the largest SO<sub>4</sub><sup>2-</sup> concentration, while SO<sub>4</sub><sup>2-</sup> was not quantified at A3 (Figure 5). A2 and A1 had the largest NO<sub>3</sub><sup>-</sup> concentrations, while no NO<sub>3</sub><sup>-</sup> was detected at A4, HSR, or A6.

A1, A2, and HSR had the largest conductivity values, as well as the largest concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and HCO<sub>3</sub><sup>-</sup> (Figure 4). Bicarbonate was the dominant anion for all samples except A4 and HSR, in which sulfate was by far the dominant anion (Figure 5). Cation abundance was more mixed; HSR was dominated by Ca<sup>2+</sup>, while all other samples have intermediate cation concentrations. HSR, A1, and A2 had the largest relative abundances of Ca<sup>2+</sup> when compared to Na<sup>+</sup> and K<sup>+</sup>; contrastingly, A3, A5, and A7 had exceedingly more K<sup>+</sup>, when compared to Ca<sup>2+</sup> and Na<sup>+</sup> (Figure 4).



Figure 4. Relative concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{CO}_3^-$ , the primary ions observed within the Shady Dolomite Formation ( $\text{Cs}$ ), compared with  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ , the dominant cations expected in the Rome Formation ( $\text{Cr}$ ).

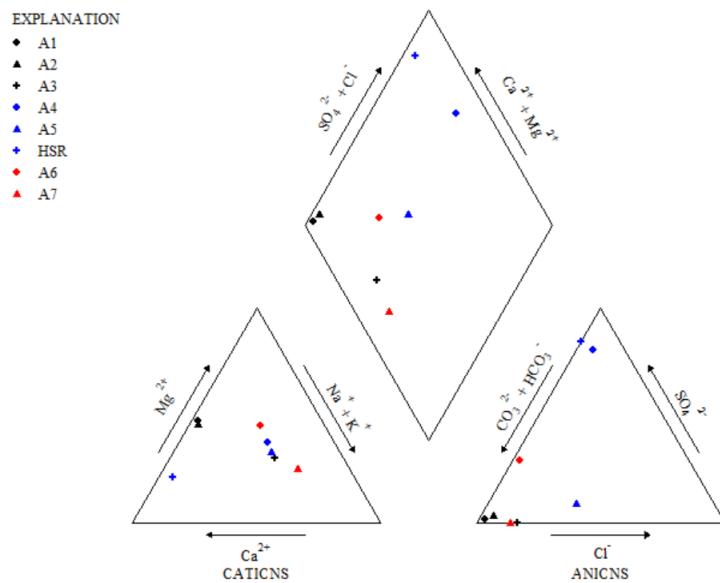


Figure 5. Piper diagram of all major ion concentrations for eight sample sites.

#### 4. Discussion

Samples from A3 and A1 were determined to have intermediate ion concentrations, suggesting the presence of a geologic contact (Figure 4). It can be inferred that A3 is located on the edge of the Rome Formation, and A1 is located on the edge of the Shady Dolomite Formation. This conclusion is consistent with the location of the inferred contact in previous studies within the Hot Springs area.

The Rome Formation ( $\text{Cr}$ ) is abundant in  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ , while the Shady Dolomite Formation ( $\text{Cs}$ ) is abundant in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$ . HSR, A4, and A6 are adjacent samples all abundant in sulfate, suggesting that these chemical similarities are due to water traveling through the same underlying stratum, potentially  $\text{Cs}$  (Figure 5). The Rome Formation ( $\text{Cr}$ ) is abundant in  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ , while the Shady Dolomite Formation ( $\text{Cs}$ ) is abundant in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$ . Based on the relative abundances of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  when compared to their conductivity values ( $\mu\text{S}/\text{cm}$ ), A3, A5, and A7 are presumed to be located within  $\text{Cr}$ , while A1, A2, A6, and HSR are believed to be located within  $\text{Cs}$ , as noted in Figures 4 and 6.<sup>7,8</sup> The contact between  $\text{Cs}$  and  $\text{Cr}$  is known to be gradational, with its approximated contact located between A4 and A6.<sup>7,8</sup> A4 has an intermediate chemical composition when compared to HSR and A6, suggesting that this sample traveled through both  $\text{Cs}$  and  $\text{Cr}$ .



Figure 6. Approximate boundaries between the Rome ( $\epsilon_r$ ), Shady Dolomite ( $\epsilon_s$ ), and Erwin ( $\epsilon_e$ ) Formations. The contact between  $\epsilon_e$  and  $\epsilon_s$  is gradational, while the contact between  $\epsilon_r$  and  $\epsilon_s$  is sharp.

There is a correlation between samples with known well depths and their temperature. It can be concluded that samples with deeper wells, such as HSR, traveled deeper within the strata, causing geothermal heating. On the other hand, sample A4 is sourced from an exposed spring so it is at a lower temperature than other samples.

A2 is abundant in  $\text{NO}_3^-$ , which is still well below the drinking water standard of 45 mg/L, or 10 mg/L as N. There is no significant correlation between concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  across samples, indicating that additional sampling is necessary to better understand these chemical differences. The well depth of A2 is unknown, so no definitive conclusions can be drawn regarding the flow paths of A2 and HSR. Charge balance error (CBE (%)) values are typically positively correlated with larger conductivity values, suggesting minimal errors with quality control (Table 1). The only sample that may have skewed the results of this study was located at A2.

## 5. Conclusion

HSR, A2, A1, and A6 were concluded to be located within the Shady Dolomite Formation, while A3, A4, and A5 were located within the Rome Formation. The contact between the Rome Formation and the Shady Dolomite is therefore located between A3 and A1. Samples consistent with the Shady Dolomite Formation were typically found to have higher field temperature measurements, indicating that this formation is at a greater depth than the Rome Formation. These findings are consistent with previous studies conducted within the Hot Springs Area.<sup>3, 4</sup> The uncertainties regarding geologic contacts are due to the lack of known well depths, as well as an insufficient number of samples. Directions of future research include additional sampling in order to form a more definitive conclusion about the location of the geologic contact between these two formations.

## 6. Acknowledgements

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