Geothermometry of Warm Springs in the Rico Area, Colorado

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Rico, Colorado, geothermometry, silica, cation, isotopic, hydrology

ABSTRACT

Mapping of statewide heat flow and geothermal gradients indicates an area of both high heat flow and increased geothermal gradient in southwest Colorado centered on the Town of Rico. Seven flowing thermal springs were sampled in this area: four springs near Rico in the Dolores River valley; and Dunton Spring, Paradise Spring, and Geyser Warm Spring in the West Fork Dolores River valley. All of these springs have surface temperatures in a narrow range between 40 and 44°C, excepting Geyser Warm Spring at 28.5°C. The springs were analyzed for a suite of 44 constituents including major ions, silica, CO$_2$, deuterium, and $^{18}$O.

Geothermometer calculations applied to these data, and to previous 1970’s water chemistry data, variously estimate subsurface reservoir temperatures ranging from 60°C to 150°C. Water samples from the Rico area springs exhibit less agreement, with silica, Na-Ca and isotopic geothermometers giving subsurface temperature estimates of ~120-140°C, whereas K-Mg and Na-K-Ca geothermometers estimate ~60°C. Springs in the West Fork Dolores River valley have relative agreement between silica and K-Mg geothermometers, with subsurface temperatures at Dunton and Geyser Warm Springs of ~60-70°C, and at Paradise Spring of ~150°C. All of the springs in this area are strongly effervescent with CO$_2$, some of which obtain a minor geyser action as a result of CO$_2$ out gassing.

Isotopic analyses indicate that all the samples are very similar to meteoric waters. Temperature data from mineral exploration drill holes within a 0.75 km radius of Rico yield geothermal gradients of 91 and 92 °C km$^{-1}$. Therefore, meteoric water circulation depths ranging from about 0.6 to 1.9 km are necessary to meet the range of subsurface reservoir temperatures predicted by the geothermometers.

Introduction

Recent work by the Colorado Geological Survey to assess the statewide heat flow (Berkman and Carroll, 2007) and geothermal gradient (Berkman and Watterson, 2010) present in Colorado indicates that there is an area of high heat flow and high geothermal gradient centered around the Town of Rico in southwest Colorado (Figure 1). In this area there are several hot springs and wells that are surface expressions of geothermal heat at some depth.
These recent heat flow and gradient data indicate a geothermal resource with potential for direct use in recreational spas and pools, agriculture, greenhouses, light industrial processes, and space heating situations. In addition, potential may exist for producing electricity. On the other hand, data from previous studies (Barrett and Pearl, 1978) indicate, through geothermometry, that the temperature at depth is not much more than that expressed at the surface. The purpose of this study is to investigate improvements in geothermometry methods to determine if better control and confidence could be attained regarding the temperature of the geothermal resource at depth.

Immediately north of the Town of Rico is a group of three springs and up to four flowing drill holes that together comprise the Rico Group (Figure 2). The group of drill holes is referred to as the Rico Drill Hole Group and are referred to by individual numbers. Water samples from these drill holes were taken and analyzed in 1976 (Barrett and Pearl, 1976). As of 2010, two of these drill holes were locatable but are not able to be sampled. The Rico Springs Group is comprised of three surface springs sampled in July 2008, and a simple numbering system is employed to designate these springs. Along the West Fork of the Dolores River, one valley to the northwest, are Dunton and Paradise Springs. Geyser Warm Spring is located along Geyser Creek, which is a tributary to the West Fork of the Dolores River. These three springs comprise the West Fork of the Dolores Group. All of the springs and drill holes in this investigation are strongly effervescent with CO2 and some obtain a minor geyser action as a result of CO2 out gassing. Some of the springs and drill holes were sampled in 1975 and 1976, and again in July of 2008. These various data sets are combined, analyzed and discussed in this paper.

Methods of Investigation

During the course of this investigation, six thermal springs were visited in July 2008 and field measurements of temperature, pH, conductivity, dissolved oxygen and alkalinity were made. Water samples were collected for chemical and isotopic analysis and were sampled in a two step process: two liters of spring water were collected and then brought to a suitable sub-sampling location where the bulkier sampling equipment was located. All samples collected during the course of this investigation were handled according to standard methods for dissolved and total recoverable fractions for cations, anions, and chemical constituents, with the addition of a cooling coil designed to enhance preservation of dissolved CO2 in the sample water. Field measurements of surface temperature, pH, specific conductance, alkalinity and dissolved oxygen were made. Laboratory analyses of water samples were conducted for a suite of metals and ions (Cl-, F-, NO3-, PO43-, SO42-, HCO3-, CO32-, OH-), as well as silica (SiO2) and carbon dioxide (CO2). Laboratory isotopic analyses for 2H (deuterium) and 18O (oxygen) were also conducted. Hydrologic and geochemical data from Barrett and Pearl (1976) for the Rico Drill Hole Group and the West Fork Dolores Group are also used in this study.

The USGS water speciation modeling code PHREEQC (Parkhurst and Appelo, 1999) was used to determine the saturation state of silica in the water and the degree to which the water was in equilibrium with the silica phases quartz and chalcedony. Various silica-based quartz and chalcedony geothermometers were applied to the silica concentration data to estimate subsurface reservoir temperatures (Fournier, 1977; Fournier and Potter, 1982; Arnorsson et al, 1983; Arnorsson et al, 1998). The cation-based K-Mg, Na-Ca and Na-K-Ca geothermometers were applied to the concentration data for those elements and were chosen because these geothermometers are applicable to the lower temperature systems indicated by the surface temperature of the spring and drill holes in this study (Fournier and Truesdell, 1973; Tonani, 1980; Giggenbach, 1988). The methane-hydrogen gas and water-hydrogen gas isotope geothermometers were applied to the deuterium and 18O isotope data because they are also applicable to these lower temperature systems (Bottinga, 1969; Richet et al, 1977).

Geothermometry Results

Geothermometer estimates of subsurface temperatures for the water samples collected in July 2008 as well as data from Barrett and Pearl, 1976, are shown in Table 1. No isotope geothermometer results are available for the 1970’s samples because no isotope data was collected for them. The Na-Ca geothermometer results for Geyser Warm Spring and Paradise Spring and the Na-K-Ca results for Paradise Spring are considered not applicable as they gave unrealistically high temperature estimates and are marked as “N/A”.

The Rico Group samples all have very similar water chemistry and yield similar geothermometry estimates of subsurface temperatures. Generally, the subsurface temperature estimates yielded by the various geothermometers are either ~60°C (Na-K-Ca and K-Mg) or ~120°C to ~140°C (silica, Na-Ca, isotopes). The Rico Group is relatively close to equilibrium with both the quartz and chalcedony geothermometers with silica Saturation Indices of ±1. In contrast, the Rico Group samples are not in equilibrium with the Na-K-Mg system, as evaluated by the Giggenbach approach (Figure 2) (Giggenbach, 1988). The most likely subsurface temperature estimate for the Rico Group samples is 120°C to 140°C.
The Dunton Spring samples have similar major ion chemistry to the Rico Group samples, but have lower concentrations of silica which yields lower silica geothermometer estimates of ~50°C to ~90°C, although they are close to equilibrium with silica saturation. The Na-K-Ca and K-Mg geothermometers yield estimates of ~50°C to ~65°C and the Na-Ca and isotope geothermometers yield ~115°C. The Dunton samples are not in equilibrium with the Giggenbach Na-K-Mg system (Figure 3). Dunton Spring subsurface temperature estimates are somewhat ambiguous, but the most likely subsurface temperature estimate is ~70°C.

Geyser Warm Spring’s silica content is near equilibrium and yields subsurface temperature estimates of ~60°C to ~90°C. The cation geothermometers are not in agreement with Na-K-Ca (~100°C) and K-Mg (~73°C). Isotopic geothermometers yield ~120°C. A reliable subsurface temperature estimate based on Geyser Warm Springs water chemistry is not apparent.

Paradise Spring yields the most consistent and reliable subsurface temperature estimates in this study. In terms of chemical equilibrium, Paradise water is the closest to equilibrium with silica content as well as with the Giggenbach Na-K-Mg system (Figure 3). All of the geothermometer estimates of subsurface temperature show good agreement and indicate 120°C to 180°C.

Table 1. Geothermometer results summary for samples in this study (all temperatures are in °C; NA = not applicable, NM = not measured).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured Temperature</th>
<th>Silica Geothermometers</th>
<th>Cation Geothermometers</th>
<th>Isotope Geothermometers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Quartz</td>
<td>Chaledony</td>
<td>Na-K-Ca</td>
</tr>
<tr>
<td>Rico Little Spring 9/75</td>
<td>38.0</td>
<td>131.6 - 147.8</td>
<td>119.7 - 122.1</td>
<td>N/A</td>
</tr>
<tr>
<td>Rico Little Spring 1/76</td>
<td>39.0</td>
<td>131.6 - 147.8</td>
<td>119.7 - 122.1</td>
<td>57.8</td>
</tr>
<tr>
<td>Rico Big Geyser 9/75</td>
<td>34.0</td>
<td>127.0 - 142.8</td>
<td>114.5 - 116.5</td>
<td>115.2</td>
</tr>
<tr>
<td>Rico Big Geyser 4/76</td>
<td>36.0</td>
<td>140.0 - 157.2</td>
<td>129.2 - 132.5</td>
<td>55.6</td>
</tr>
<tr>
<td>Rico Geyser Warm Spring 9/75</td>
<td>38.0</td>
<td>127.0 - 142.8</td>
<td>114.5 - 116.5</td>
<td>58.5</td>
</tr>
<tr>
<td>Rico DDH 1/76</td>
<td>44.0</td>
<td>131.6 - 147.8</td>
<td>119.7 - 122.1</td>
<td>55.5</td>
</tr>
<tr>
<td>Rico #1 7/2008</td>
<td>40.8</td>
<td>137.0 - 153.8</td>
<td>125.8 - 128.8</td>
<td>48.3</td>
</tr>
<tr>
<td>Rico #2 7/2008</td>
<td>42.8</td>
<td>135.3 - 151.9</td>
<td>123.8 - 126.6</td>
<td>49.6</td>
</tr>
<tr>
<td>Rico #3 7/2008</td>
<td>41.1</td>
<td>137.9 - 154.8</td>
<td>126.8 - 129.9</td>
<td>55.1</td>
</tr>
<tr>
<td>Dunton Spring 9/75</td>
<td>44.0</td>
<td>70.4 - 87.6</td>
<td>53.6 - 56.0</td>
<td>49.6</td>
</tr>
<tr>
<td>Dunton Spring 1/76</td>
<td>42.0</td>
<td>67.8 - 85.4</td>
<td>50.9 - 53.4</td>
<td>50.5</td>
</tr>
<tr>
<td>Dunton Spring 4/76</td>
<td>42.0</td>
<td>71.0 - 86.5</td>
<td>52.3 - 54.7</td>
<td>51.6</td>
</tr>
<tr>
<td>Dunton Spring 7/2008</td>
<td>41.4</td>
<td>75.9 - 92.3</td>
<td>59.3 - 61.3</td>
<td>47.7</td>
</tr>
<tr>
<td>Geyser Warm Spring 9/75</td>
<td>28.0</td>
<td>74.1 - 90.8</td>
<td>57.4 - 59.6</td>
<td>103.3</td>
</tr>
<tr>
<td>Geyser Warm Spring 2008</td>
<td>28.5</td>
<td>80.7 - 96.4</td>
<td>64.3 - 66.0</td>
<td>99.7</td>
</tr>
<tr>
<td>Paradise Spring 9/75</td>
<td>46.0</td>
<td>143.9 - 161.5</td>
<td>133.6 - 137.4</td>
<td>154.2</td>
</tr>
<tr>
<td>Paradise Spring 4/76</td>
<td>40.0</td>
<td>161.0 - 180.6</td>
<td>153.1 - 158.8</td>
<td>N/A</td>
</tr>
<tr>
<td>Paradise Spring 4/76</td>
<td>42.0</td>
<td>143.9 - 161.5</td>
<td>133.6 - 137.4</td>
<td>154.6</td>
</tr>
<tr>
<td>Paradise Spring 7/2008</td>
<td>43.4</td>
<td>150.8 - 169.2</td>
<td>141.5 - 146.0</td>
<td>154.0</td>
</tr>
</tbody>
</table>

Figure 3. Giggenbach geoinicator diagram with samples plotted. The Rico and Dunton position are very similar and are plotted with one symbol for clarity.

Inclusion of the CO2 correction to the Na-K-Ca geothermometer (Paces, 1975) does not yield reasonable estimates of subsurface temperatures for the water samples in this study and these results are not included in this discussion. The magnesium correction to the Na-K-Ca geothermometer is not applicable to waters in the Rico area as its authors recommend that it not be applied to waters whose calculated Na-K-Ca temperature is less than 70°C of the correction (as in the case of the Rico Group and Dunton Spring) and whose resulting magnesium-correction temperature value is negative (as in the case of Paradise and Geyser Warm Springs) (for further details see Fournier and Potter, 1979).

Water and Heat Source Discussion

Geothermometry calculations can yield possible subsurface reservoir temperatures based on the chemistry of a water sample. In order to make more meaningful interpretations of these subsurface reservoir temperature estimates, it is necessary to evaluate the hydrologic and hydrochemical setting of the thermal springs.

By comparing the overall hydrochemistry of the water samples in this study, useful observations can be made. Within each spring group there is considerable spatial and temporal chemical similarity between water samples, but each group has a unique chemical composition as compared to the others. By classifying the spring waters by the dominant ionic species and plotting them into a Piper Diagram, these relationships are apparent (Figure 4). Included in this comparison figure is a Dolores River water sample that was collected by the USGS in November 1978 from the Dolores River at the nearest stream gaging station to the Rico Group, which is located just downstream of the Town of Rico. This sample’s chemical composition in terms of major ions is as follows: calcium 96 mg/L, magnesium 12 mg/L, sodium 5.6 mg/L, potassium 1.4 mg/L, bicarbonate 190 mg/L, sulfate 130 mg/L, chloride 0.9 mg/L.
The composition of the West Fork Dolores River is assumed to be similar to the Dolores River sample.

The Rico group and the Dunton Spring samples are the most chemically similar and appear to be very similar to Dolores River water, all three being termed calcium sulfate-type waters. Geyser Warm Spring water is sodium bicarbonate-type, while Paradise Spring water is sodium chloride-type. These relationships among the major-ion content of the groups is interesting because it suggests a similar source for the Rico and Dunton thermal waters, or that these springs may be composed of a large component of water contributed by the Dolores River and its associated alluvial aquifer (Figure 4). It also suggests that Paradise and Geyser Warm Spring waters are significantly different than the other waters in the study.

Similar groupings are found in the isotopic composition of the waters as shown in Figure 5. The Rico Group and Dunton Spring samples plot close together and right on or above the Local Meteoric Water Line (LMWL) which represents the ratio of deuterium to $^{18}$O atoms present in meteoric waters found in this part of the world (Figure 5). This indicates that the Rico Group and the Dunton Spring waters are very similar isotopically. Geyser Warm Spring’s isotopic ratio plots lower down along the LMWL and slightly below it. Paradise Spring’s isotopic composition plots higher along the LMWL than the Rico and Dunton samples and slightly below the LMWL. The small magnitude of all of the samples’ shift to above or below the LMWL suggests that all of these waters are strongly dominated by meteoric water and that there may be a minor component of water that is either not meteoric in origin, or that is meteoric in origin but has undergone geochemical changes that have altered its isotopic ratio.

When considering the degree to which the surface water expression of the Rico Group and Dunton Spring is representative of deeper thermal waters it is important to conceptually consider the similar hydrologic setting of both the Rico Group and Dunton Spring. Situated within 200 feet of the Dolores and West Fork Dolores Rivers, and emanating from or through the alluvium in the valley bottom, it is very likely that the spring waters have mixed with shallower alluvial water as they ascended from depth. The effects of extensive faulting present throughout the area and the possible flow paths that the water has encountered are not possible to assess. Because of the chemical and isotopic similarity of the Rico and Dunton water samples to each other and to that of Dolores River and meteoric waters (Figures 4 and 5), it is probable that the ascending thermal waters have mixed with shallow groundwaters, both diluting them chemically and cooling them down.

Paradise Spring has a similar hydrologic setting to that of the Rico Group and Dunton Spring, however the water is sodium chloride-type and is unique among water samples in this study with very high specific conductance (~10 mS/cm) and elevated concentrations of lithium (~9 mg/L), potassium (~370 mg/L), sodium (~1900 mg/L) and chloride (~3100 mg/L) (Figure 4). Paradise Spring water is also distinct isotopically, plotting higher along the LMWL than other samples in this study, although it is still very close to the LMWL (Figure 5). The extent to which Paradise Spring water is mixed with shallow groundwater or alluvial water is uncertain given its distinct chemical composition juxtaposed with is location directly adjacent to the West Fork Dolores River in the valley bottom alluvium.

Geyser Warm Spring is unique in this study, as it is not situated in a river valley bottom and the surface temperature of its water is lower than the other springs (~28°C vs. ~40°C). Chemically and isotopically, the water is distinct as well (Figures 4 and 5). Geyser Warm Spring is situated in a steep-sided, rocky canyon approximately 30 feet above a small stream that flows in a bedrock channel, and is ~600 feet in elevation above the West Fork Dolores river valley. Geyser Warm Spring waters are likely mixed with shallow groundwater that exists in fractures in the bedrock. The low surface temperature of Geyser Warm Spring may be explained by a high degree of mixing with shallow groundwater coupled with increased residence time in lower temperature bedrock fractures as the waters migrate to the surface. This assumption is not testable within the context of this study as nearby non-thermal groundwater was not sampled and analyzed.

While the individual springs each have a specific chemical signature indicating a unique geochemical evolution, it is likely...
that all of the springs’ waters are meteoric in origin, given their similar isotopic composition to local meteoric waters (Figure 5). It is also likely because of the springs close geographic proximity to each other, that the meteoric waters that are circulating in both the alluvial and deeper aquifers in the area are heated by the same subsurface heat source.

Temperature data from mineral exploration drill holes within a 3.5 km radius of the Town of Rico yield geothermal gradients ranging from 24 to 114°C km⁻¹ (Medlin, 1983; Decker et al., 1988; unpublished mining data, compiled 2009, personal communication M. Nakagawa, 2010). Therefore, meteoric water circulation depths ranging from about 0.5 to >2.5 km are necessary to meet the range of subsurface reservoir temperatures predicted by the geothermometers. Temperature data from two drill holes within a 0.75 km radius of the geochemical sampling points north of Rico yield geothermal gradients of 91 and 92°C km⁻¹, narrowing down the probable range of meteoric water circulation depths to 0.6 to 1.9 km. This analysis assumes a linear extrapolation of the geothermal gradient to depth, and does not consider deviations from linearity in the geothermal gradient.

Conclusions

This study was undertaken to determine whether advances in the science and practice of geothermometry could allow for better control and confidence in the estimation of the temperature of the geothermal resource at depth in the Rico, Dunton and West Fork Dolores River areas. In broad terms, the warm spring waters examined in this study remain ambiguous with respect to a definitive subsurface temperature estimate. The geological systems represented by the water samples examined in this study are extremely complex. The factors affecting the chemistry of these waters include complex regional geologic structure and mineralization, difficult to assess hydrogeology, and the anthropogenic effects of mining and mineral exploration overprinting the natural system.

All geothermometry models are based on various assumptions, that when satisfied, allow for some level of confidence in the subsurface temperature estimates generated. In the case of the waters examined in this study, nearly all of these assumptions have the potential to be unsatisfied. Nevertheless, geothermometer estimates of subsurface temperature can be combined with chemical, isotopic and hydrologic analyses and can give insight into the qualities of the subsurface heat source in the area.

Geothermometer calculations applied to these data, and to previous 1970’s water chemistry data, variously estimate subsurface reservoir temperatures ranging from 60°C to 150°C. Springs in the West Fork Dolores River valley have relative agreement between silica and K-Mg geothermometers, with subsurface temperatures at Dunton and Geyser Warm Springs of ~60-70°C, and at Paradise Spring of ~150°C. Samples from the Rico area springs exhibit less agreement, with silica geothermometers giving subsurface temperature estimates of ~120-150°C, whereas K-Mg and Na-K-Ca geothermometers estimate ~60°C.

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References