1. Introduction

Several methods have been proposed for estimating subsurface temperatures based on chemical analyses of natural springs and well discharges. In addition, indices based on trace constituents of subsurface fluids and deposits have been advocated as aids to geothermal exploration and in proposing chemical models of interaction of fluids with host rocks. In non-volcanic systems the origin of thermal springs is often attributed to normal or elevated regional heat flow. However, care is necessary in analysis of silica from dissolution of silica in geothermal fluids and on the relative reluctance of quartz to precipitate from supersaturated solutions. (Fournier, 1981; Fournier and Potter, 1982) have discussed equations for quartz saturation with conductive cooling. However, care is necessary in analysis of silica from re-equilibration during upward flow.

Though considerable amount of progress has been made concerning the use of geochemical thermometry of thermal springs very little work has been carried out on chemical analyses of non-thermal fluids extracted from groundwater wells. The focus of the present work is on application of chemical thermometry to non-thermal waters extracted from groundwater wells in Brazil.

2. Methodology

Data on groundwater systems in Brazil is available through a computerized system known as SIAGAS (Freitas et al, 2007) maintained by the State geological survey – CPRM
3. Temperatures from Silica Concentrations

Earlier studies on solubility of silica in thermal waters were carried out, among others by (Kennedy, 1950; White et al, 1956; Morey et al, 1961; Morey et al, 1962; Noguchi and Nix, 1963). The fundamental relations of for the use of silica geothermometer were developed by (Fournier and Rowe, 1966). It is based on the assumption that quantity of dissolved silica in spring waters is dependent on the in-situ temperatures of geothermal reservoirs. Further studies on the use of silica geothermometers were carried out by (Truesdell, 1976; Rimstidt, 1977; Fournier, 1977; Santoyo and Verma, 1993; López, 1994).

In these earlier studies, the method employed for calculation of reservoir temperatures make use of empirical approximations, the characteristic constants of which are based on generalized numerical fits to experimental solubility data (see for example, Fournier and Potter, 1982; Alexandrino, 2018). Examination of such relations revealed that the quality of statistical fits can be improved by considering a segmented approach. In this case, the solubility data is subdivided into separate sections and specific empirical relations developed for each individual section. In the present work, the lowermost limit for silica concentrations was set at 6.1 ppm. The upper limits considered for the four classes of silica concentrations are 47.4, 199.8, 595.3 and 763.6 ppm. The overall relation for these intervals may be written as:

\[ T_{SiO_2}(SiO_2) = A + B(SiO_2) + C(SiO_2)^2 + D\ln(SiO_2) \]  

where \(SiO_2\) is the concentration of silica in ppm and \(T_{SiO_2}\) the reservoir temperature in °C. The values of the constants \(A\), \(B\), \(C\) and \(D\) are provided in Table 1.

4. Silica Concentrations and Temperatures

The histograms of silica concentrations and corresponding temperatures for the different regions considered are given the set of Figures 2-7. The provinces considered include intracratonic basins of Parana, Parnaiba and basins of the Amazon region and the Proterozoic basin of Sao Francisco.

The upper panel in figure 2 illustrates the relative frequency distribution of silica concentrations for 537 wells located in the Parana basin.

In this figure, the silica concentrations vary between 17 and 147 ppm. However, 88% of the wells have silica concentrations between 17 and 68 ppm, and the mean value is 44±17 ppm. The lower panel of this figure illustrates temperatures derived from these concentrations. It varies between 56 e 109°C and has a mean value of 93±18 °C.

The upper panel in figure 3 illustrates the relative frequency distribution of silica concentrations for 56 well in the Parnaiba basin. The concentrations vary between 13 and 106 ppm. However, 75% of the wells have concentrations between 13 and 44 ppm, and the mean value 36±16 ppm. The lower panel of this figure illustrates temperature values derived from these concentrations. It varies between 47 to 134°C and has a mean value of 83±19 °C
A similar procedure was adopted for data collected for wells in the Amazon basins. Thus, upper panel in figure 4 illustrates the relative frequency distribution of silica concentrations for 39 wells located in basins of the Amazon region. The concentrations vary between 14 and 120 ppm. However, 80% of the wells have concentrations lower than 32 ppm, and the mean value 28±10 ppm. The lower panel of this figure illustrates temperature values derived from these concentrations. It points to values of temperature 51 to 83ºC and has a mean value of 78±18 ºC.

The upper panel in figure 5 illustrates the relative frequency distribution of silica concentrations for 712 wells located in basins of the Sao Francisco basin. The concentrations vary between 9 and 67 ppm. However, 80% of the wells have concentrations lower than 38 ppm, and the mean value 28±12 ppm. The lower panel of this figure illustrates temperature values derived from these concentrations. It points to a mean value of temperature of 75±18ºC.

The above procedures were also adopted for data from wells in the coastal basins. Thus, upper panel in figure (6) illustrates the relative frequency distribution of silica concentrations for 38 wells in basins of Sergipe-Alagoas, located along the continental margin of Northeast Brazil. The mean concentration of SiO2 is 41±25 ppm. However, 68% of the wells have concentrations lower than 49 ppm. The lower panel of this figure illustrates mean temperature value of 86±24ºC. In 13% of wells the temperatures are higher than 100ºC.
The upper panel in figure 7 illustrates the relative frequency distribution of silica concentrations for 615 wells in the Proterozoic province of Borborema in Northeast Brazil. The concentration of SiO2 is between 16 and 170 ppm. However, 90% of the wells have concentrations between 16 and 68 ppm, with a mean value 38±17 ppm. The lower panel in figure 7b illustrates that temperature values are between 56 and 168ºC, with a mean value of 85±18ºC.

A summary of silica temperatures derived from equation 1 are given in Table 2. The standard deviation for silica temperature values is better than 25ºC. Note that highest values of silica temperatures were for wells in the Paraná basin which has been affected by magmatic activities of Cretaceous times. Relatively lower values were found for wells in other Paleozoic basins such as Parnaiba and Amazon. The wells in late Proterozoic basin of São Francisco is found to have the lowest value of silica. The basins along the continental margin have relatively high value of 41ppm, but the adjacent Proterozoic fold belts have lower value of 38ppm.

Table 2 - Dissolved SiO2 and corresponding temperatures derived using equation (1) for selected regions.

<table>
<thead>
<tr>
<th>Region</th>
<th>Region</th>
<th>N</th>
<th>SiO2 (ppm)</th>
<th>TSiO2 (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paleozoic Basin</td>
<td>Paraná</td>
<td>540</td>
<td>44±17</td>
<td>93±18</td>
</tr>
<tr>
<td></td>
<td>Parnaiba</td>
<td>56</td>
<td>36±16</td>
<td>83±19</td>
</tr>
<tr>
<td></td>
<td>Amazon</td>
<td>39</td>
<td>28±10</td>
<td>75±18</td>
</tr>
<tr>
<td>Late Proterozoic</td>
<td>São Francisco</td>
<td>722</td>
<td>28±12</td>
<td>75±18</td>
</tr>
<tr>
<td>Continental Margin</td>
<td>Sergipe</td>
<td>38</td>
<td>41±25</td>
<td>86±24</td>
</tr>
<tr>
<td></td>
<td>Alagoas</td>
<td>615</td>
<td>38±17</td>
<td>85±18</td>
</tr>
</tbody>
</table>

5. Silica Temperature – Heat Flow Relation

Results of chemical geothermometry may be employed in obtaining first-order estimates of conductive heat flow in stable tectonic provinces. This approach is based on the use of an empirical relation between content of dissolved silica in thermal waters and regional heat flow values. Foremost among such attempts are the empirical relations reported by Swanberg and Morgan (1978, 1980 and 1985) for western USA, the Colorado Plateau and adjacent areas. Such relations have been widely employed as convenient means in obtaining estimates of heat flow for several regions worldwide. In the present case we assume that similar empirical relations may also be developed for silica concentrations in non-thermal waters extracted from groundwater wells.

The empirical relation proposed by Swanberg and Morgan (1978) for estimating heat flow from silica content of thermal waters in USA may be written as:

$$T_{SiO2} = mq + b$$

where $T_{SiO2}$ is the reservoir temperature deuced from the silica content, $q$ the surface heat flux and $m$ $b$ are constants. The constant $m$ is related to the depth of circulation while $b$ indicates the mean annual surface temperature. The values
established for m and b by Swanberg and Morgan (1978) are $680 \pm 67 \text{ Cm}^2\text{W}^{-1}$ and $12.4 \pm 5.1 \text{C}$. It is clear that modifications are necessary in the use of value for the second constant (b) in relation 2 for regions with different climate conditions.

In the present work, values of constants m and b that are specific to the tectonic provinces of Brazil have been adopted in calculating heat flow values. The tectonic units considered include the Precambrian province of Borborema, Paleozoic sedimentary basins of Parnaiba and Paraná as well as basins of the Amazon region and the coastal basins of Sergipe-Alagoas. For this purpose, use was made of temperatures derived from the silica concentrations illustrated in Figure 2 along with mean heat flow values reported by Vieira (2015). The results obtained, illustrated in Figure 8.

![Figure 8 - Relation between silica temperatures and heat flow values for the main geological provinces in Brazil.](image)

In this case the values obtained for m and b are respectively $1071 \pm 125 \text{ Cm}^2\text{W}^{-1}$ and $25.5 \pm 6.7 \text{C}$. The reason for the higher value of b for Brazil is obvious, in view of the distinctly different climate conditions. However, it is interesting to speculate on the higher value of the second parameter (m). As per conventional interpretation, it implies greater depths of circulation of ground waters in stable tectonic regions of Brazil. A possible mechanism could be the differences in the history of tectonic evolution. Note that basement rocks of western USA have been affected by relatively recent tectonic episodes and associated crustal thinning processes. Such processes may have induced shallower depths of circulation of groundwaters. On the other hand, the platform areas in Brazil have undergone thinning as a result of relatively recent magmatic interaction processes, when compared with those of the Brazilian Platform areas.

6. Conclusions

A major conclusion of the present work is that silica content of non-thermal ground waters may be employed in obtaining estimates of deep temperatures in stable tectonic settings. The procedure adopted is based on the use of an improved geo-thermometry relation for solubility of silica in ground waters. Such results open up the possibility of establishing improved and regionally relevant empirical relations between silica content and heat flow. Consequently, silica content of non-thermal ground waters may be used for obtaining reliable estimates of conductive heat flow in areas where practical limitations impede use of conventional methods.

Another result of considerable interest concerns the depths of circulation of ground waters. In platform areas of Brazil, the depths of circulation of ground waters are found to be higher than those reported for similar regions in western North America. We advocate the hypothesis that such differences in circulation depths may be related to the fact that crustal segments in the western part of North American lithosphere have undergone thinning as a result of relatively recent magmatic interaction processes, when compared with those of the Brazilian Platform areas.

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