

Application of a Magnesium Correction to the Sodium-Potassium-Calcium Geothermometer For Selected Thermal Waters in Southeastern Idaho

H. W. Young and R. E. Lewis

U.S. Geological Survey
550 West Fort Street
Boise, Idaho 83724

ABSTRACT

Initial reservoir temperatures estimated by use of chemical geothermometers for thermal waters in southeastern Idaho generally resulted in poor agreement between the sodium-potassium-calcium and silica geothermometers. Concentrations of magnesium in these thermal waters ranged from 7.1 to 260 milligrams per liter. By applying a magnesium correction to the sodium-potassium-calcium geothermometer, estimated reservoir temperatures previously reported are reduced between 39 degrees and 268 degrees Celsius and result in much closer agreement between the sodium-potassium-calcium- and silica-estimated reservoir temperatures. Reservoir temperatures in southeastern Idaho probably do not exceed 128 degrees Celsius.

Fournier and Potter (1979) observed that in many low-temperature, magnesium-rich waters, reservoir temperatures estimated using the Na-K-Ca geothermometer were well above 150°C. This disparity between the measured and Na-K-Ca-estimated reservoir temperatures casts considerable doubt on the usefulness of the geothermometer for magnesium-rich waters. On the basis of cation ratios involving magnesium, Fournier and Potter (1979) devised equations and graphs to apply an empirical correction to attenuate the adverse effect of magnesium on the Na-K-Ca geothermometer.

The purpose of this study is to apply the magnesium correction of Fournier and Potter (1979) to reservoir temperatures estimated by Young and Mitchell (1973) using the Na-K-Ca geothermometer and thereby obtain more reasonable agreement with the silica geothermometer.

CHEMICAL CHARACTER

Thermal waters for which the magnesium correction was applied were sampled over a wide area, geographically, and ranged in temperature from 25.0° to 82.0°C. Chemical analyses of these waters are given in Table 1, and their locations are shown in Figure 1.

Waters from sampled springs and wells varied widely in chemical composition. Concentrations of magnesium ranged from 7.1 to 260 mg/L, and pH (6.3-7.8) was near neutrality. Waters were either a sodium or calcium mixed anion type. Dissolved-solids concentrations ranged from 706 to 13,700 mg/L. Concentrations of chloride and sulfate were highly variable and ranged from 40 to 7,700 mg/L and from 15 to 980 mg/L, respectively.

MAGNESIUM CORRECTION TO THE SODIUM-POTASSIUM-CALCIUM GEOTHERMOMETER

Using equations and graphs, Fournier and Potter (1979) devised an empirical technique to correct for the adverse effects of magnesium on the Na-K-Ca geothermometer. By plotting the Mg⁺² concentration relative to the sum of dissolved Mg⁺², K⁺², and Ca⁺² (R value), versus the Na-K-Ca-estimated temperature for well waters that issue from a single aquifer at known tem-

INTRODUCTION

As part of their assessment of Idaho's geothermal potential, Young and Mitchell (1973) analyzed water from 19 thermal springs and 4 thermal wells in southeastern Idaho and estimated geothermal reservoir temperatures by use of silica and Na-K-Ca (sodium-potassium-calcium) geothermometers. For the southeastern Idaho waters, reservoir temperatures estimated using the Na-K-Ca geothermometer ranged from 170° to 368°C and exceeded temperatures estimated using the silica geothermometer by more than 100°C. On the basis of reservoir temperatures estimated using the silica geothermometer, Muffler (1979) suggested that reservoir temperatures in southeastern Idaho probably do not exceed 125°C. The wide discrepancy between the more reasonable silica-estimated reservoir temperatures and the inordinately high temperatures estimated by use of the Na-K-Ca geothermometer casts some doubt on the applicability of the latter for the magnesium-rich thermal waters in southeastern Idaho.

| Spring or well No. | Flow rate (gal/min) | Specific conductance (µmho/cm) | pH | Water temperature (°C) | Calcium (Ca) | Magnesium (Mg) | Sodium (Na) | Potassium (K) | Bicarbonate (HCO ₃) | Sulfate (SO ₄) | Chloride (Cl) | Silica (SiO ₂) | Dissolved solids (calculated) |
|--------------------|---------------------|--------------------------------|-----|------------------------|--------------|----------------|-------------|---------------|---------------------------------|----------------------------|---------------|----------------------------|-------------------------------|
| 4N-40E-25DCB1S | ¹ 60 | 8,840 | 6.7 | ² 49.0 | 450 | 82 | 1,500 | 190 | 1,100 | 740 | 2,400 | 30 | 5,940 |
| 1N-43E- 9CBB1S | ¹ 70 | 7,950 | 6.3 | 25.0 | 440 | 96 | 1,110 | 120 | 1,200 | 390 | 1,900 | 11 | 4,650 |
| 5S-34E-26DAB1 | 15 | 1,170 | 7.7 | 40.5 | 70 | 25 | 150 | 21 | 478 | 95 | 87 | 20 | 706 |
| 6S-41E-19BAA1S | ¹ 1,300 | 4,590 | 6.8 | 42.0 | 660 | 260 | 94 | 240 | 2,500 | 980 | 40 | 24 | 3,530 |
| 9S-38E-21DDA1S | -- | 1,580 | 6.6 | 44.5 | 120 | 32 | 170 | 39 | 542 | 110 | 190 | 32 | 962 |
| 13S-41E- 7ACA1S | 350 | 3,160 | 7.3 | 76.0 | 89 | 24 | 490 | 110 | 491 | 260 | 630 | 55 | 1,900 |
| 14S-36E-27CDA1S | 44 | 7,590 | 6.5 | 25.0 | 240 | 79 | 1,200 | 210 | 958 | 25 | 2,100 | 19 | 4,350 |
| 14S-39E-36ADA1 | -- | 1,890 | 7.3 | 44.5 | 25 | 7.1 | 360 | 24 | 524 | 15 | 320 | 80 | 1,110 |
| 15S-35E- 3AAB1S | 3,810 | 2,190 | 6.8 | 25.0 | 110 | 33 | 280 | 29 | 331 | 110 | 470 | 21 | 1,220 |
| 15S-39E- 8BDC1S | ¹ 900 | 16,400 | 7.0 | 77.0 | 160 | 16 | 3,100 | 660 | 699 | 50 | 5,400 | 80 | 9,830 |
| 17BCD1 | 25 | 22,200 | 7.8 | 82.0 | 250 | 23 | 4,300 | 880 | 733 | 54 | 7,700 | 130 | 13,700 |
| 15S-44E-13CCA1S | -- | 2,040 | 6.6 | 47.5 | 210 | 55 | 180 | 61 | 256 | 800 | 79 | 35 | 1,560 |
| 16S-36E-10BBC1S | -- | 5,370 | 7.3 | 27.0 | 130 | 45 | 910 | 87 | 454 | 58 | 1,600 | 29 | 3,090 |

¹Flow rate estimated.

²Measured temperature is probably lower than at point of discharge.

Table 1. Chemical analyses of water from selected springs and wells. Chemical constituents in mg/L unless otherwise noted. Analyses from Young and Mitchell, 1973.

perature, Δt temperature-contour lines that can be used to obtain a temperature correction were interpolated. The temperature correction obtained was then subtracted from the Na-K-Ca-estimated temperature to arrive at the magnesium-corrected reservoir temperature.

Using the procedure suggested by Fournier and Potter (1979), R values were computed for thermal waters from 10 springs and 3 wells in southeastern Idaho, where

$$R = \left[\frac{\text{Mg}}{\text{Mg} + \text{Ca} + \text{K}} \right] \times 100.$$

Cation concentrations are expressed in equivalents. Values for R ranged between about 5 and 35 for Idaho waters. Then, using the equation for 5 > R < 50, the magnesium correction, Δt_{Mg}, was calculated, where

$$\Delta t_{Mg} = 10.66 - 4.741 R + 325.87 (\log R)^2 - 1.032 \times 10^5 (\log R)^2 / T - 1.968 \times 10^7 (\log R)^2 / T^2 + 1.605 \times 10^7 (\log R)^3 / T^2,$$

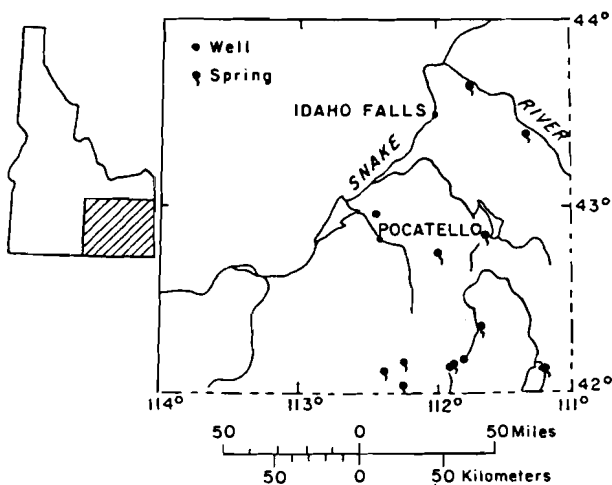


Figure 1. Locations of selected thermal springs and wells, southeastern Idaho.

and was subtracted from the Na-K-Ca-estimated reservoir temperature, T . Values for Δt_{Mg} computed using the above equation ranged from 39° to 268°C. The magnesium corrections, when applied to reservoir temperatures estimated previously using the Na-K-Ca geothermometer, reduced the estimates to between 45° and 230°C (Table 2). The reservoir temperatures estimated by use of the magnesium-corrected Na-K-Ca geothermometer are in better agreement with temperatures estimated by use of the silica geothermometer, although some degree of variance is still apparent. The largest variations occur in estimated reservoir temperatures for spring

15S-39E-8BDC1S and well 15S-39E-17BCD1. However, as shown in Table 2, waters from this spring and well are supersaturated with respect to aragonite and calcite and may be precipitating calcium without an adjustment of the sodium and potassium concentrations. For these and other waters listed in Table 2 where supersaturation is indicated, the silica geothermometer probably gives the better estimate of reservoir temperature. On the basis of the magnesium-corrected Na-K-Ca and the silica geothermometers (assuming chalcedony is controlling the silica concentrations for the majority of the wells and springs), reservoir temperatures for southeastern Idaho probably do not exceed 128°C.

| Well or spring No. | Water temperature at the surface (°C) | Estimated reservoir temperatures based on geothermometers (°C) | | | | Magnesium correction | | Free energy of formation ¹ | |
|--------------------|---------------------------------------|----------------------------------------------------------------|----------------------------------------------|--------------------------|-------------------|----------------------|-----------------------------|---------------------------------------|---------|
| | | Sodium-potassium-calcium | Magnesium-corrected sodium-potassium-calcium | Silica quartz-conductive | Silica chalcedony | R value | Temperature correction (°C) | Aragonite | Calcite |
| 4N-40E-25DCB1S | 249.0 | 206 | 95 | 80 | (³) | 19.8 | 111 | 0.9 | 1.0 |
| 1N-43E-9CBB1S | 25.0 | 191 | 75 | 42 | (³) | 24.0 | 116 | 0 | 0 |
| 5S-34E-26DAB1 | 40.5 | 185 | 45 | 64 | (³) | 33.8 | 140 | 1.0 | 1.0 |
| 6S-41E-19BAA1S | 42.0 | 368 | 100 | 70 | (³) | 35.4 | 268 | 1.5 | 1.5 |
| 9S-38E-21DDA1S | 44.5 | 211 | 68 | 82 | 51 | 27.4 | 143 | -0.2 | -0.1 |
| 13S-41E-7ACA1S | 76.0 | 236 | 98 | 106 | 77 | 21.4 | 138 | 1.1 | 1.2 |
| 14S-36E-27CDA1S | 25.0 | 228 | 72 | 62 | 30 | 27.2 | 156 | -0.1 | -0.1 |
| 14S-39E-36ADAL | 44.5 | 170 | 73 | 125 | 97 | 23.9 | 97 | -0.1 | 0 |
| 15S-35E-3AAB1S | 25.0 | 176 | 54 | 65 | 33 | 30.3 | 122 | -0.6 | -0.5 |
| 15S-39E-8BDC1S | 77.0 | 269 | 230 | 125 | 97 | 5.0 | 39 | 1.0 | 1.1 |
| 17BCD1 | 82.0 | 269 | 229 | 153 | 128 | 5.1 | 41 | 2.4 | 2.5 |
| 15S-44E-13CCA1S | 47.5 | 231 | 73 | 86 | 55 | 27.3 | 158 | -0.4 | -0.3 |
| 16S-36E-10BBC1S | 27.0 | 192 | 57 | 78 | 47 | 29.8 | 135 | 0.3 | 0.3 |

¹ Values are departure from theoretical equilibrium in kilocalories; (+) values indicate supersaturation, (-) values indicate unsaturation. Calculations from computer program SOLMNEQ (Kharaka and Barnes, 1973).

² Temperature may be higher; measurement not made at vent.

³ Estimated reservoir temperature is lower than water temperature at surface.

Table 2. Estimated reservoir temperatures, magnesium corrections, and free energy of formation for selected springs and wells.

The magnesium-correction method is empirical and probably will not work equally well for all waters. As pointed out by Fournier and Potter (1979), the magnesium-corrected Na-K-Ca geothermometer is sensitive to near-surface water-rock reactions that occur in response to lowering temperatures or changing mineralogy of reservoir rocks. Such water-rock reactions will likely alter the concentrations of various dissolved constituents. For waters that have acquired additional magnesium, application of the magnesium correction to the Na-K-Ca geothermometer will probably yield a calculated reservoir temperature that is too low. In general, chemical geothermometers should be used with caution when applied to magnesium-rich waters.

SUMMARY

Initial reservoir temperatures estimated by use of chemical geothermometers for thermal waters in southeastern Idaho generally resulted in poor agreement between the silica and Na-K-Ca geothermometers. Na-K-Ca-estimated reservoir temperatures for 10 springs and 3 wells ranged from 170° to 368°C. Concentrations of magnesium in these waters ranged from 7.1 to 260 mg/L. By applying a magnesium correction to the Na-K-Ca geothermometer, estimated reservoir temperatures previously reported are reduced between 39° and 268°C and result in somewhat closer agreement between the silica-estimated and Na-K-Ca-estimated reservoir temperatures. Reservoir temperatures for southeastern Idaho, as determined from the magnesium-corrected Na-K-Ca and silica geothermometers, probably do not exceed 128°C.

SELECTED REFERENCES

Fournier, R. O., and Potter, R. W. II, 1979, Magnesium correction to the Na-K-Ca chemical geothermometer: *Geochimica et Cosmochimica Acta*, v. 43, p. 1543-1550.

Fournier, R. O., and Rowe, J. J., 1966, Estimates of underground temperatures from silica content of water from hot springs and wet steam wells: *American Journal of Science*, v. 264, p. 685-695.

Fournier, R. O., and Truesdell, A. H., 1973, An empirical Na-K-Ca geothermometer for natural waters: *Geochimica et Cosmochimica Acta*, v. 36, p. 1255-1275.

Kharaka, Y. K., and Barnes, Ivan, 1973, SOLMNEQ-- Solution-mineral equilibrium computations: U.S. Geological Survey Computer Contributions, PB 215-899, 82 p.

Muffler, L. J. P., ed., 1979, Assessment of geothermal resources of the United States-- 1978: U.S. Geological Survey Circular 790, 163 p.

Young, H. W., and Mitchell, J. C., 1973, Geothermal investigations in Idaho, Part I, Geochemistry and geologic setting of selected thermal waters: Idaho Department of Water Resources, Water Information Bulletin no. 30, 43 p.