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A MAGNESIUM CORRECTION FOR THE NA-K-Ca CHEMICAL GEOTHERMOMETER

by

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This report is preliminary and has not
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Table of Contents

Abstract.....	page	3
Introduction.....	page	3
Cation ratios involving magnesium.....	page	4
Empirical magnesium correction.....	page	11
Suggested procedure.....	page	19
References.....	page	21

Figure 1.....	page	8
Figure 2.....	page	9
Figure 3.....	page	10
Figure 4.....	page	15
Figure 5.....	page	16
Figure 6.....	page	17
Figure 7.....	page	18

Table 1.....	page	7
Table 2.....	page	14

ABSTRACT

Graphs and equations have been devised to correct for the adverse effects of magnesium upon the Na-K-Ca geothermometer. Either the graphs or equations can be used to determine temperature corrections when given waters have Na-K-Ca calculated temperatures above 70° C and values of R less than 50, where $R = \{Mg / (Mg + Ca + K)\} \times 100$ in equivalents. Waters with values of R greater than 50 probably come from relatively cool aquifers with temperatures about equal to the measured spring temperature, irrespective of much higher calculated Na-K-Ca temperatures.

INTRODUCTION

All well documented high-temperature (>175° C) waters, encountered in wells drilled into active hydrothermal systems have low concentrations of magnesium relative to the other dissolved cations. At the Reykjanes Peninsula, Iceland, where ocean water reacts with basalt at about 270°-285° C, the magnesium in the water decreases from 1,272 mg/kg to 1.0 mg/kg (Arnorsson, 1978). In the highly saline CaCl₂-rich brine from the 11D2 Salton Sea drill hole (White, 1968), 54 mg/kg Mg accounts for less than 0.1 equivalent percent of the total cations. In laboratory experiments in which chlorite, calcite, and quartz were equilibrated with water under carbon dioxide pressures of 5 and 65 atm, Ellis (1971) found dissolved magnesium concentrations ranging from about 0.5 to 1 ppm at 200° C and 0.02 to 0.05 ppm at 300° C. The above observations and the fact that many apparently low-temperature, Mg-rich waters

yield Na-K-Ca estimated temperatures (Fournier and Truesdell, 1973) well above 150°C cast considerable doubt on the usefulness of the Na-K-Ca geothermometer for Mg-rich waters. One example is ocean water (4°C) with an Na-K-Ca temperature of 173°C. This anomalously high estimated temperature for ocean water might be explained in various ways: (1) lack of water-rock equilibrium at 4°C, (2) control of the cation ratios of ocean water by water-rock equilibrium at high temperature as ocean water circulates through hot rock near crustal spreading centers, or (3) water-rock equilibrium at 4°C involving minerals not generally present in the continental systems used to formulate the original Na-K-Ca chemical geothermometer. The last explanation, a different mineral suite reacting with the water, appears to be the most plausible.

Many different Mg-bearing minerals may be involved in the water-rock reactions encountered in various hydrothermal systems. These include olivine, serpentine, montmorillonite, glauconite, chlorite, vermiculite, biotite, amphibole, pyroxene, dolomite, and Mg-bearing calcite. Furthermore, these minerals commonly occur in various structural states and/or as solid solutions. In order to apply thermodynamics rigorously to test for mineral-water equilibria at various temperatures, it is necessary to know the structural states of the solid phases and the nature of the solid solutions involved in the reactions. This information generally is not available in the early stages of a geochemical exploration program for geothermal energy.

Paces (1975) found that for relatively low-temperature waters from felsic rocks Na-K-Ca calculated temperatures commonly were higher than measured temperatures. Based on that data he formulated an empirical correction for the Na-K-Ca geothermometer based on the partial pressure of CO_2 . Unfortunately, a good estimate of the partial pressure of CO_2 deep in a hot spring system may not be possible from data obtained at the point of water discharge at the surface. Paces (1975) also recommended that the empirical CO_2 correction be used only for waters attaining a maximum temperature of 75°C . The Paces CO_2 correction and other types of corrections that we have tried based just on CO_2 do not appear to work well for waters equilibrating above 100°C . For waters equilibrating below 100°C we have found that the Mg-correction, which will be described later in this paper, generally works as well as the correction based on partial pressure of CO_2 .

CATION RATIOS INVOLVING MAGNESIUM

Fifty waters with Mg concentrations ranging from about 1 to 3,920 mg/kg and aquifer temperatures ranging from 3° to 340°C were selected from the literature (table 1) to test the temperature dependence of various cation ratios involving Mg. Figure 1 is a plot of $\text{Log} (\text{Ca}/\text{Mg})$ relative to the reciprocal of absolute temperature. There is too much scatter in the data for the Ca/Mg ratio to be used as a reliable cation geothermometer. Plots of the reciprocal of absolute temperature relative to $\text{Log} (\sqrt{\text{Mg}}/\text{Na})$, figure 2, and to $\text{Log} (\sqrt{\text{Mg}}/\text{K})$, figure 3, show less scatter than the $\text{Log} (\text{Ca}/\text{Mg})$ plot,

but still have more scatter than is desirable for establishing a cation geothermometer. Correlation coefficients and equations for the least squares straight lines through the points shown in figures 1, 2, and 3 are given in Table 2. The logarithmic expressions of the cation ratios, Na/K , $\sqrt{\text{Ca/Na}}$, $\sqrt{\text{Ca/K}}$, $\sqrt{\text{Mg/Na}}$, $\sqrt{\text{Mg/K}}$, and Ca/Mg were plotted in various combinations and proportions (25 plots), as was done in the derivation of the Na-K-Ca chemical geothermometer, without significantly reducing the scatter below that shown in figure 3. The scatter probably would be greatly diminished if the plotted points could be restricted to data from systems in which the same solid phases were involved in the reactions.

Table 1. Chemical data for waters with magnesium concentrations greater than 1 mg/kg from known temperature environments. Concentrations are in mg/kg or in mg/L depending upon the units given in the listed references.

Ref.	Well.	Na-K-Ca	Na	K	Ca	Mg	Mg*			
	Temp. °C	Temp. °C								
Czechoslovakia:										
	Marklin 1	1	3.2	31	5.5	2.5	18.0	3.6	23.5	
	Lohat 2	1	3.2	28	10.5	4.0	62.5	20.7	34.6	
Chili										
	El Tatio 1	2	211	205	4480	420	740	1.1	0.2	
	El Tatio 6	2	180	181	1900	111	99	1.3	1.4	
Hungary										
Budapest-										
	Városliget	3	100	76.6	170	16	160	35.5	25.8	
Iceland										
	Krisuvik 3	4	105		136	10.8	24.6	1.4	7.1	
	Krisuvik 7	4	30	36	30.6	1.7	18.4	10.4	47.1	
	Krisuvik 7	4	139	148	160	8.2	15.3	1.4	10.6	
	Lysuholl 1	5	40	174	414	31.1	44.0	26.6	41.5	
	Keyjanes 8	4	270	241	9854	1391	1531	1.15	0.1	
	Svartangi 3	6	236	245	6322	1012	906	1.27	0.1	
New Zealand										
	Ngaha 1	7	230	201	900	78	29	1.4	3.2	
Turkey										
	Kizildere 15	8	207	232	1173	117	6.0	1.19	2.9	
United States										
	Gen. Miss. 1	9	132	222	79000	7080	36000	3920	14.7	
	Gen. Miss. 6	9	102	113	52400	551	16800	1360	11.6	
	Gen. Miss. 9	9	141	207	53800	4430	39200	3610	12.6	
	Gen. Miss. 10	9	109	109	52100	519	22200	1660	10.9	
	Gen. Miss. 15	9	129	124	54200	863	41200	2550	9.2	
	Gen. Miss. 16	9	137	158	58300	2030	55600	3740	9.8	
	Gen. Miss. 20	9	116	120	49900	461	29500	2290	11.3	
	Gen. Miss. 21	9	116	105	50100	474	30700	2510	11.8	
	Gen. Miss. 22	9	120	115	48800	625	37200	2530	10.1	
	Gen. Miss. 23	9	131	140	59700	1340	45000	3230	10.4	
	Gen. Miss. 25	9	86	109	40100	333	4140	582	18.2	
	Gen. Miss. 26	9	109	125	53700	750	16800	1640	13.6	
	Gen. Miss. 29	9	125	128	53900	888	28900	2150	10.8	
	Gen. Miss. 30	9	127	118	53600	649	19300	2200	15.6	
	Gen. Miss. 31	9	154	244	46500	6800	30600	2970	12.6	
	Gen. Miss. 32	9	154	227	52400	5980	37400	3010	10.9	
	Gen. Miss. 33	9	154	266	29200	3830	25700	2480	12.9	
	Gen. Miss. 34	9	154	229	52000	6080	37700	3410	12.1	
	Gen. Miss. 38	9	127	133	54000	979	26500	1630	9.1	
	Gen. Miss. 39	9	129	123	61100	854	28800	1830	9.4	
	Gen. Miss. 42	9	158	214	29000	3030	25000	1470	8.4	
	Gen. Miss. 43	9	114	115	53200	635	27300	1880	10.1	
	Gen. Penn. 10	10	10.5		2	2.5	1.8	55	15	30.7
	Gen. Penn. 91	10	11.2	35	13	-6.3	92	15	20.6	
	Gen. Penn. 257	10	11.5	-9.8	4.3	0.8	54	54	62.1	
	Gen. Penn. 285	10	13	-16	0.3	1.4	56	55	61.5	
	Gen. Penn. 1040	10	10.6	0.25	5.3	1.3	56	59	63.2	
Kettleman Hills										
	323-21J	11	134	139	3090	59.4	53.8	3.31	6.1	
	47-28J	12	101	107	6240	79.4	1780	8.0	0.7	
	321-20J	11	134	165	3080	75.1	8.6	2.05	6.7	
	31-180	12	82	98	13200	88.4	797	206	28.7	
	66-70	12	97	112	13800	149	1700	88	7.6	
	61-33J	12	99	102	7780	97	5030	18.4	0.6	
Salton Sea										
	11D1	13	340	317	50400	17500	28000	54	0.2	
Yellowstone Park										
	Y-10	14	70	100	161	69	455	80	21.2	
USSR										
	Fauzhetka 4	15	195	209	986	105	52	3.5	5.2	
	OCEAN WATER	16	4	173	10560	380	400	1270	77.9	

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2. Cusicaucui, Mahon, and Ellis (1976)
3. Boldizar and Korim (1976)
4. Arnorsson, Bjornsson, and Gistason (1976)
5. Arnorsson (1975)
6. Lindal (1976)
7. Mahon (1970)
8. Kurtman (1977)
9. Carpenter, Trout, and Pickett (1974)
10. Langmuir (1971)
11. Kharska and Berry (1976)
12. Kharska and Berry (1974)
13. White (1965)
14. R.O. Fournier and R.D. Barnes (unpublished data)
15. Vakin, Polak, Sugrobov, Erlilch, Belouseou, and Pilipenko (1970)
16. White (1965)

*Equivalent percent Mg/(Mg + Ca + K)

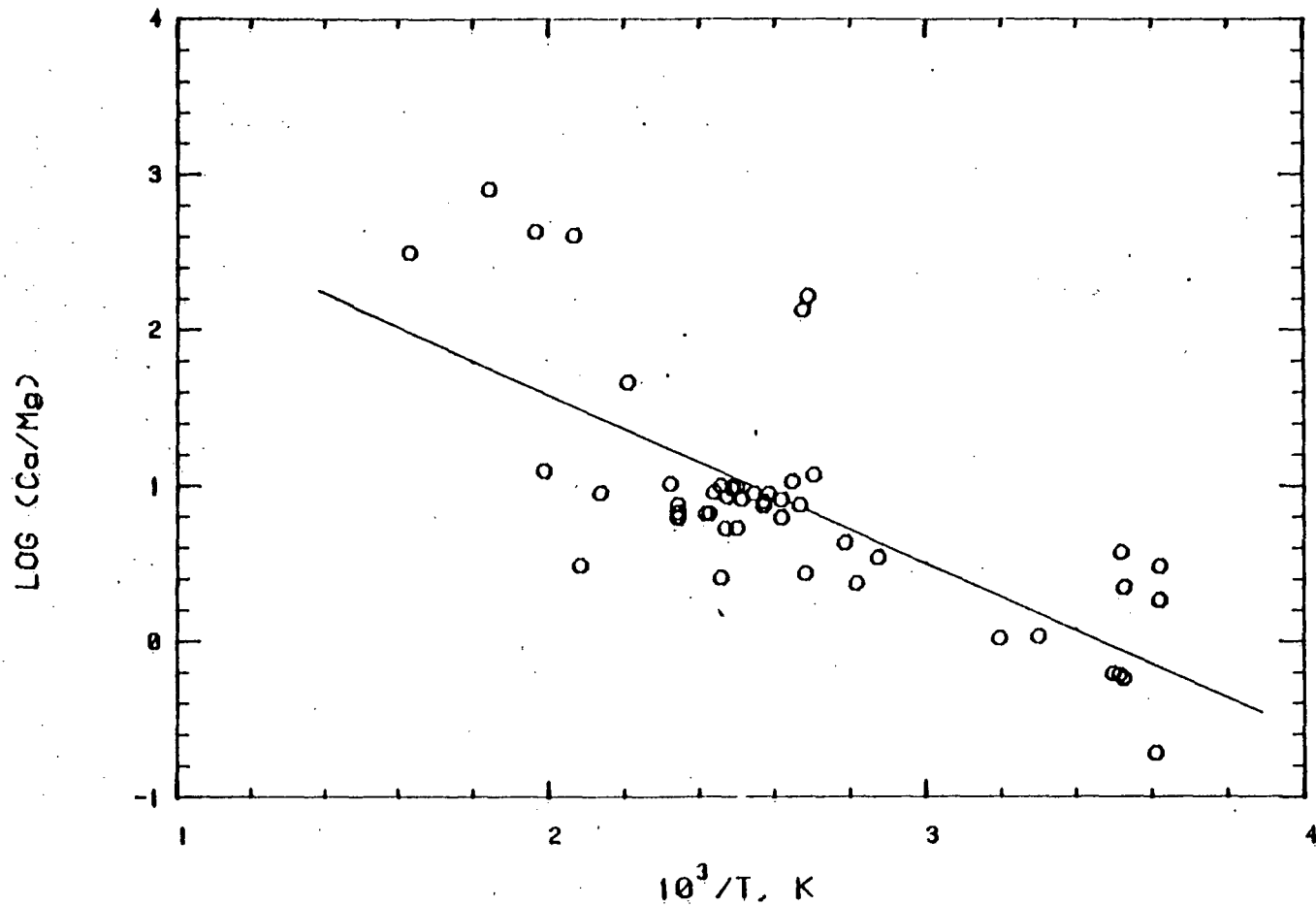


Figure 1. -- Log (Ca/Mg), using molal units, vs reciprocal of absolute temperature for well waters from known temperature environments and with Mg concentrations greater than 1 mg/kg.

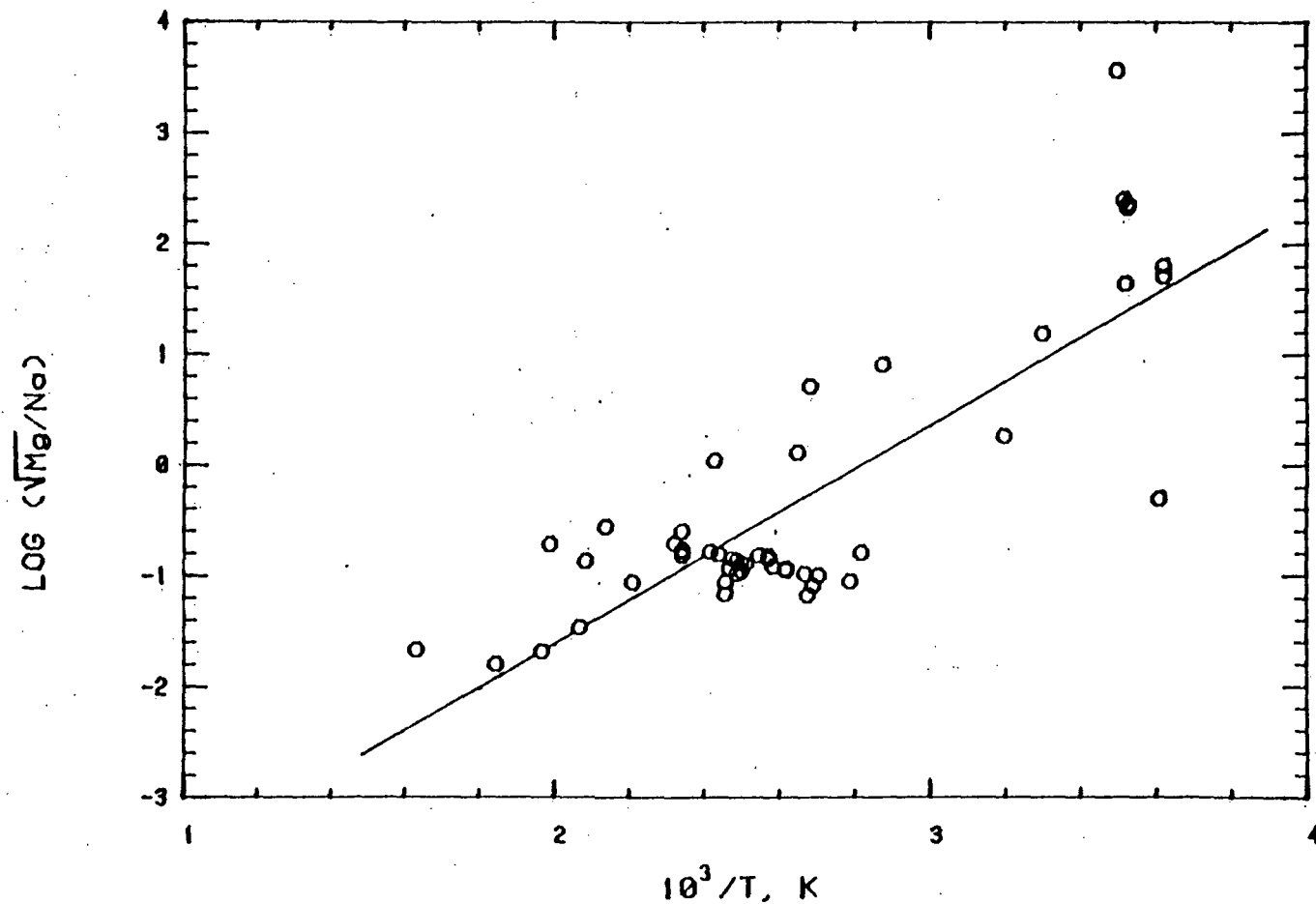


Figure 2. -- $\text{Log } (\sqrt{\text{Mg}/\text{Na}})$, using molal units, vs reciprocal of absolute temperature for well waters from known temperature environments and with Mg concentrations greater than 1 mg/kg.

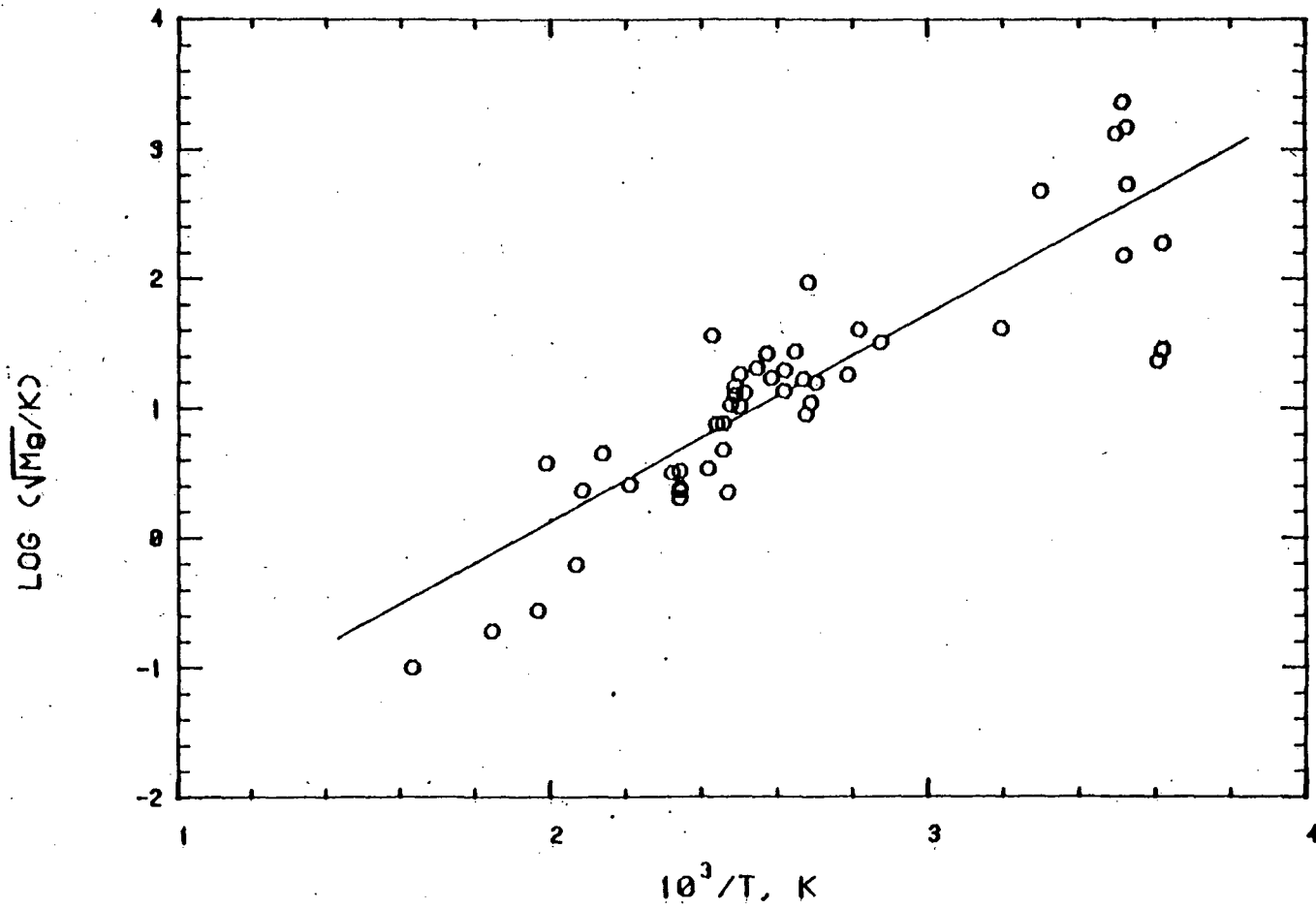


Figure 3.-- $\text{Log } (\sqrt{\text{Mg}/\text{K}})$, using molal units, vs reciprocal of absolute temperature for well waters from known temperature environments and with Mg concentrations greater than 1 mg/kg.

EMPIRICAL MAGNESIUM CORRECTION

A method of applying a magnesium correction to Na-K-Ca estimated temperatures was discovered when the data were plotted as shown in figure 4. For any given water the magnitude of the temperature correction depends both on the Na-K-Ca estimated temperature and the amount of dissolved Mg relative to the total dissolved Mg, K, and Ca. In figure 4 the dashed temperature contours can be used to obtain a temperature correction that must be subtracted from the Na-K-Ca estimated temperature in order to arrive at the actual temperature of the system. For instance, point A with an Na-K-Ca temperature of 200°C and an equivalent percent Mg/(K + Ca + Mg) of 25.0 requires a temperature correction of about 125°C.

In figure 4 the placement and curvatures of the 0°, 25° and 100°C correction curves are well constrained below 30 equivalent percent Mg. The upward projections of these curves and the positions of 150°, 200°, and 250°C correction curves are controlled by the position of the ocean water data point and the requirement that the temperature correction, Δt_{mg} , always be less than the Na-K-Ca estimated temperature. As more and better data became available, the curvatures and positions of the temperature correction curves may have to be changed.

The following equation describes most of the relations shown in figure 4:

$$\Delta t_{mg} = a_1 - b_1 R + c_1 \text{Log } R - d_1 (\text{Log } R)^2 / T - e_1 (\text{log } R)^2 / T^2 + f_1 (\text{Log } R)^3 / T^2, \quad (1)$$

where Δt_{mg} is the temperature in °C to be subtracted from the

calculated Na-K-Ca temperature, T is the calculated Na-K-Ca temperature in degrees Kelvin, R is the percent Mg/(Mg + Ca + K) in equivalents, $a_1 = 10.66$, $b_1 = 4.7415$, $c_1 = 325.867$, $d_1 = 1.0321 \times 10^5$, $e_1 = 1.9683 \times 10^7$, and $f_1 = 1.6053 \times 10^7$. We recommend that equation (1) be used only when Na-K-Ca estimated temperatures are above 70°C and when values of R are between 5 and 50. Although equation (1) appears to work well for some waters with R values above 50, the magnesium corrected temperatures of most spring waters were found to be 10° to 20°C below the measured temperatures. We corrected this difficulty by using a more complicated equation with nine terms, but the additional mathematical complications do not seem to be warranted because any water with an R value above 50 probably either equilibrated with rock at about the measured temperature (irrespective of much higher calculated Na-K-Ca temperature) or represents a non-equilibrium condition.

In the region where R values are below 5 and Δt_{mg} values are below 10, the Δt_{mg} values calculated using equation (1) diverge from our best guess of what the value of Δt_{mg} should be. This is shown in figure 5. Our best guess Δt_{mg} values at low values of R were obtained using projections of constant Na-K-Ca temperature data on a plot of R relative to Δt_{mg} . Equation 2 can be used to calculate Δt_{mg} values for waters with R values below 5:

$$\Delta t_{mg} = -a_2 + b_2 \text{Log} R + c_2 (\text{Log} R)^2 - d_2 (\text{Log} R)^2 / T - e_2 \text{Log} R / T, \quad (2)$$

where $a_2 = 1.02995$, $b_2 = 59.97116$, $c_2 = 145.049$, $d_2 = 36711.6$,
and $e_2 = 1.67516 \times 10^7$.

Figures 6 and 7, showing lines of constant R values superimposed on plots of Δt_{mg} relative to the Na-K-Ca temperature, present an alternate graphical method of calculating Δt_{mg} . Figure 6 is for values of R ranging from 5 to 50 and figure 7 is for R values from 0 to 5.

When using figures 4, 6, and 7 to correct Na-K-Ca calculated temperatures it should be kept in mind that the method is entirely empirical and should not work equally well for all waters. There are problems in calibrating the method: (1) the solid reactants are not specified or characterized structurally; (2) complexing of dissolved species is not considered (no activity coefficients are used because prior knowledge of temperature is required); (3) individual well waters may not have equilibrated at the maximum measured or estimated well temperature (water can enter a well from a higher or lower temperature aquifer); and (4) some well waters may be mixtures of two or more different waters that enter at different depths and do not equilibrate after mixing.

Table 2. Equations for the least squares best fit straight lines regressed through the data shown in figures 1, 2, and 3. Molal concentrations of Ca, Mg, Na, and K are used; T is absolute temperature; and r^2 is the correlation coefficient.

$$\text{Log (Ca/Mg)} = \frac{1708}{T} + 3.740 \quad r^2 = 0.525$$

$$\text{Log } (\sqrt{\text{Mg/Na}}) = \frac{1982}{T} - 5.583 \quad r^2 = 0.671$$

$$\text{Log } (\sqrt{\text{Mg/K}}) = \frac{1598}{T} - 3.061 \quad r^2 = 0.733$$

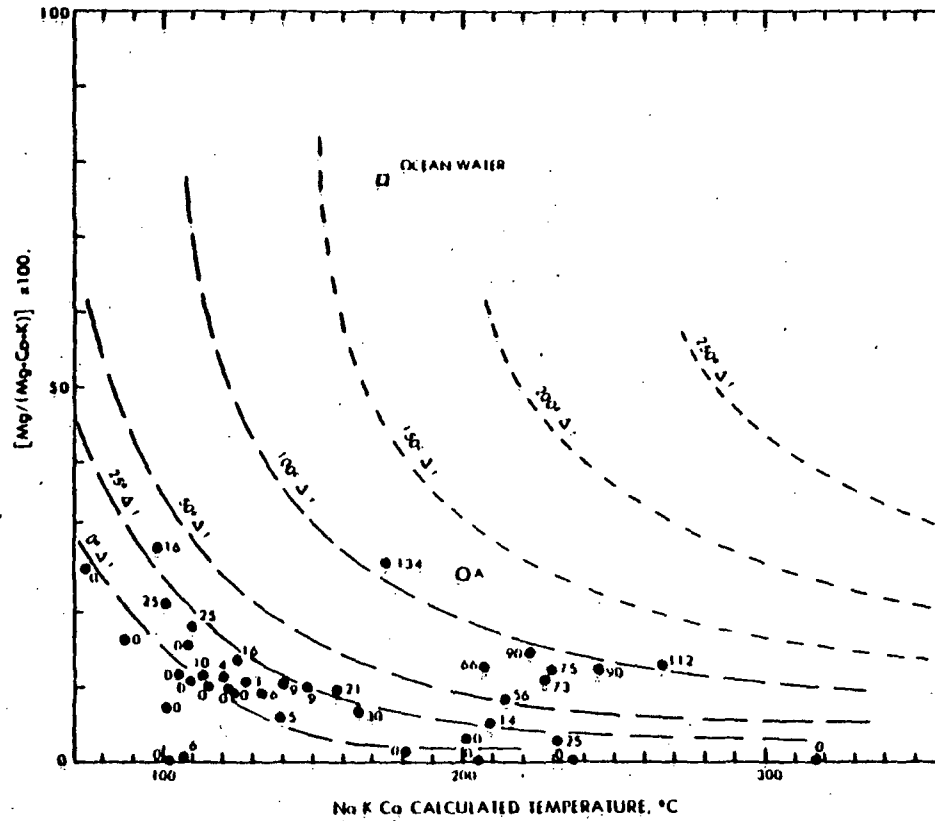


Figure 4.-- Plot of percent $Mg/(Mg + Ca + K)$, with concentrations expressed as equivalents, vs Na-K-Ca calculated temperature. The dashed curves show the temperature corrections, Δt , that should be subtracted from the calculated Na-K-Ca temperatures in order to correct for dissolved magnesium. The dots are data from well waters listed in table 1. The numbers near the data points show the difference in temperature, $^{\circ}C$, between the Na-K-Ca calculated and probably aquifer temperature.

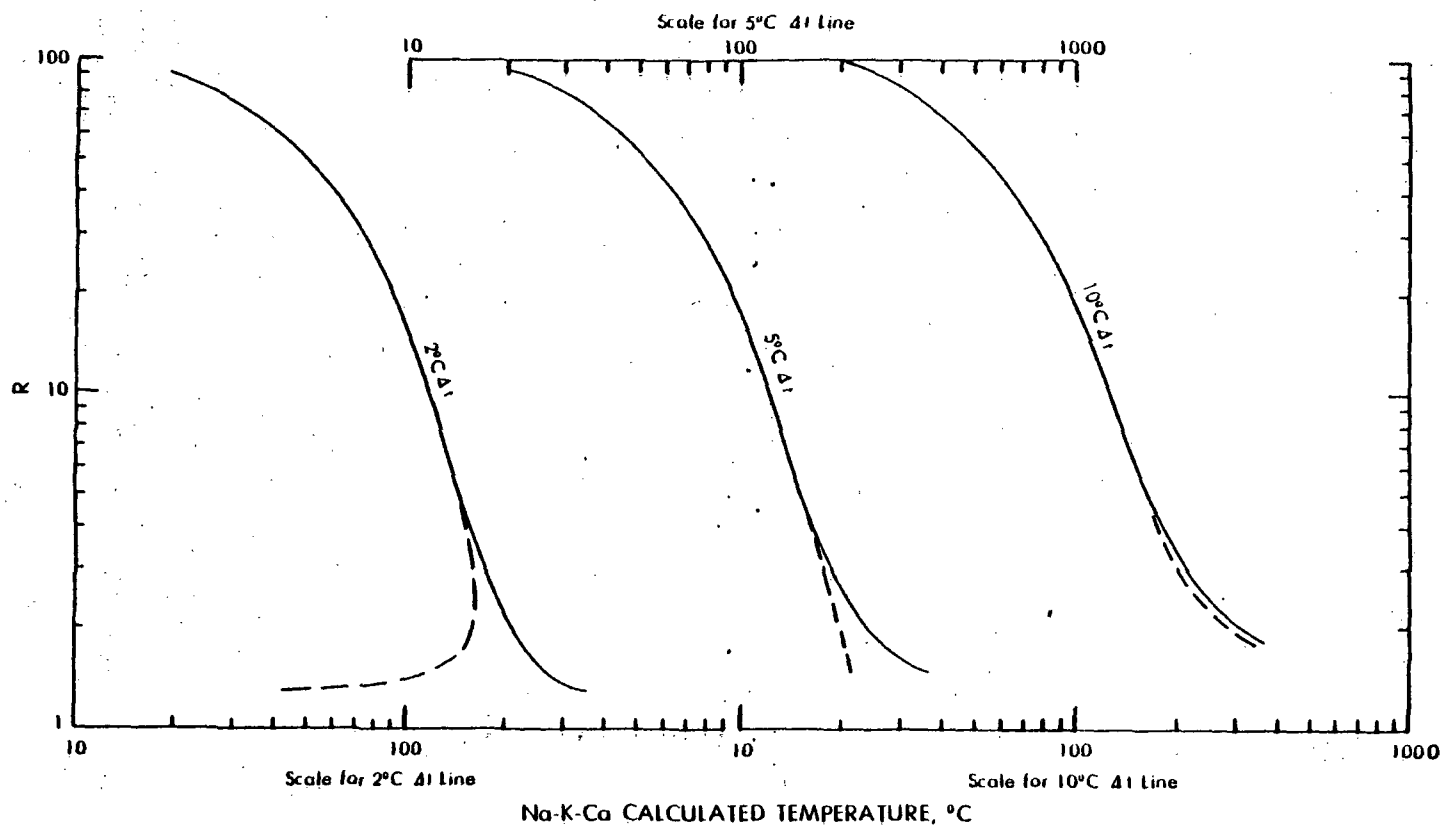


Figure 5.-- Logarithmic plot of R vs Na-K-Ca calculated temperature showing the best guess positions of the 2° , 5° , and 10° C temperature correction curves (solid lines). The dashed lines show curves calculated using equation (1). The dashed and solid curves coincide for values of R greater than 5 or when Δt is greater than 10° C.

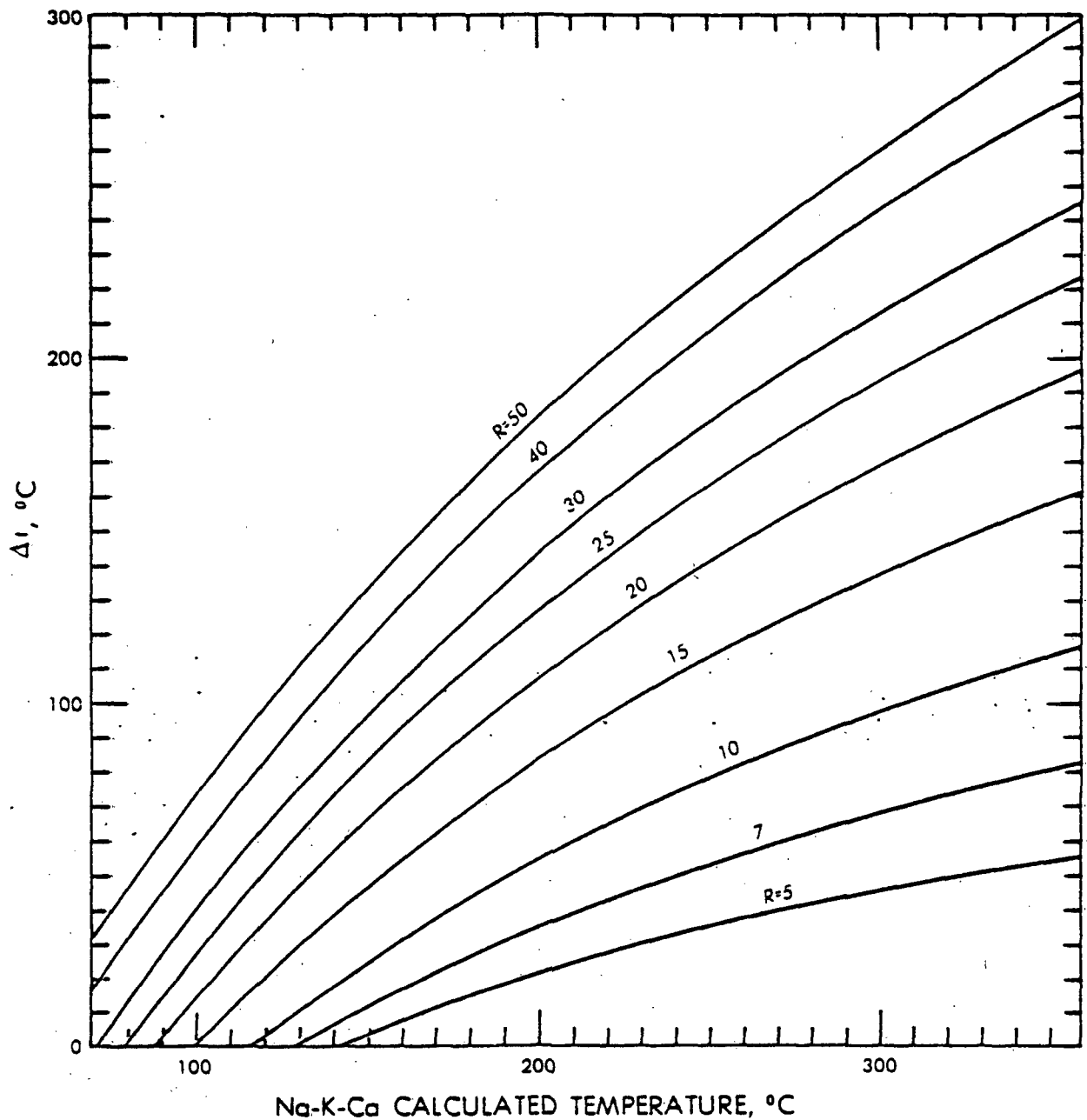


Figure 6.-- Graph for estimating the magnesium temperature correction, Δt , using Na-K-Ca calculated temperatures and R values ranging from 5 to 50. The curves were drawn using equation (1). Move directly up from the calculated Na-K-Ca temperature to the intersection (or interpolated value) of the line having the calculated R value. Move horizontally from the R value intersection and read the Δt_{mg} value on the ordinate.

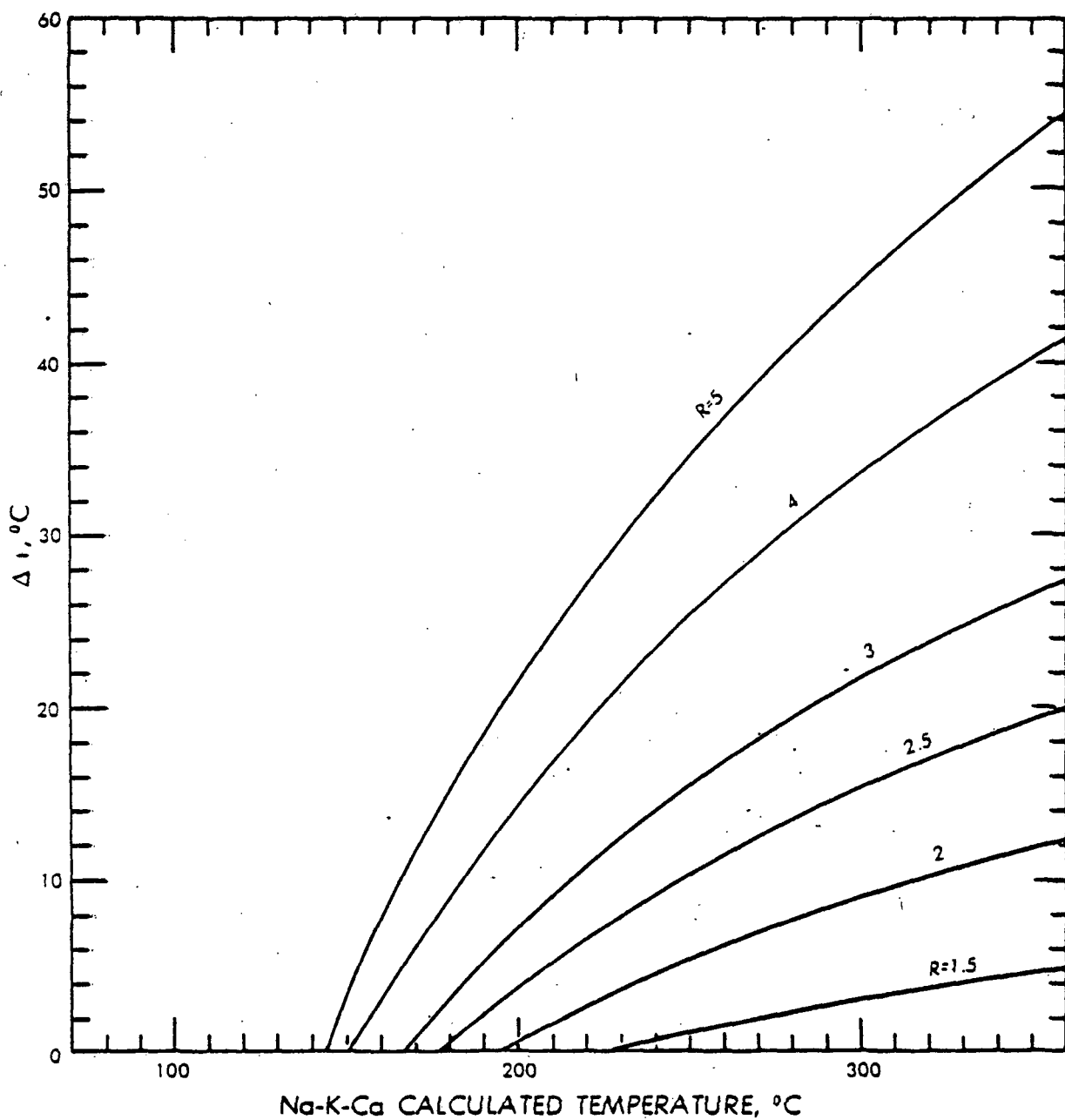


Figure 7.-- Graph for estimating the magnesium temperature correction, Δt , using Na-K-Ca calculated temperatures and R values ranging from 1.5 to 5. The curves were drawn using equation (2). Move directly up from the calculated Na-K-Ca temperature to the intersection (or interpolated value) of the line having the calculated R value. Move horizontally from the R value intersection and read the Δt_{mg} value on the ordinate.

The main intent of this paper is to provide an additional tool to distinguish waters that have equilibrated with rock at high temperatures underground from waters that result from low-temperature reactions at less than 50° to 70°C. As with all chemical geothermometers, the Mg-corrected Na-K-Ca geothermometer is sensitive to near surface water-rock reactions that occur in response to lowering temperatures or changing mineralogy of wall rocks. If a rising water picks up magnesium, application of a magnesium correction to the Na-K-Ca geothermometer probably will lead to a calculated aquifer temperature that is too low. However, high magnesium concentrations do indicate that water-rock reactions have occurred at relatively low temperature. During the low-temperature reactions it is likely that the concentrations of other dissolved constituents also will change. Therefore, chemical geothermometer results in general should be used with great caution when applied to Mg-rich waters.

SUGGESTED PROCEDURE:

1. Calculate the Na-K-Ca temperature as described by Fournier and Truesdell (1973). Do not apply a magnesium correction if that calculated temperature is below 70°C.
2. Calculate R , $\{Mg/(Mg + Ca + K)\} \times 100$, using equivalents as the units of concentration.
3. If R is greater than 50 assume that the water comes from a relatively cool underground environment with a temperature about equal to the measured water temperature, irrespective of high calculated Na-K-Ca temperatures.

4. If the calculated Na-K-Ca temperature is greater than 70°C and R is less than 50, use figure 4, 6, or 7 to calculate Δt_{mg} , the temperature in $^{\circ}\text{C}$ that should be subtracted from the Na-K-Ca calculated temperature.

5. When using a computer to calculate Δt_{mg} the following tests should be included in the program:
 - (a) Check if the Na-K-Ca calculated temperature is less than 70°C . If yes, do not proceed further with a Mg correction.
 - (b) Check if the value of R is greater than 50. If yes, assume that the water in the aquifer is relatively cold and do not proceed further with a Mg correction.
 - (c) If R is between 5 and 50 use equation (1) to calculate Δt_{mg} . Do not apply a magnesium correction if Δt_{mg} is negative.
 - (d) If R is less than 5 use equation (2) to calculate Δt_{mg} . Do not apply a magnesium correction if Δt_{mg} is negative.
 - (e) Subtract the value of Δt_{mg} $^{\circ}\text{C}$ from the calculated Na-K-Ca temperature.

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