NEW IMPROVED EQUATIONS FOR Na/K AND SiO_2 GEOTHERMOMETERS BY ERROR PROPAGATION

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Abstract

We present here new improved equations for the Na/K and SiO_2 geothermometers, obtained by the theory of error propagation and statistical treatment of the data base **used** by Fournier (1979) and Fournier and Potter II (1982). The minimum and "reasonable" maximum errors associated with the use of the new geothermometric equation for Na/K range respectively from ~29°C—54°C and ~31°C—57°C for the temperature range of 150°C—350°C. These values are significantly lower than ~45°C—82°C and ~46°C—84°C found for the original Fournier equation. Similarly, the new equations for the SiO_2 geothermometer, for 20°C to 310°C, result in the minimum and "reasonable" maximum errors of ~0.5°C—4°C and −1.8°C—18°C respectively, which are much lower than −1.7°C—19°C and ~2.3°C—55°C for the original regression. Finally, an application of the Na/K geothermometer to actual field data shows a better performance of our new equation.

1. INTRODUCTION

Without exception, a physical or a chemical parameter measured by any experimental technique has an associated experimental or analytical error (probable error), whether systematic (resulting from faulty instrument, its calibration or from bias on behalf of the experimenter) or random (that make the result different from the "true" value with a reproducible discrepancy).

Data reduction and error analysis have been fundamental in physical sciences (e.g., Bevington, 1969). The evaluation and treatment of these errors have also become a routine matter in some branches of Earth Sciences, such as isotope geology and geochronology (e.g., York, 1967, 1969; Lanphere and Dalrymple, 1967; Brooks *et al.,* 1972; Russell, 1977; Faure, 1986), major element geochemistry and modelling (e.g., Bryan *et* ***al.,*** 1968; Wright and Doherty, 1970; Verma *et* ***al.***, 1991), trace element geochemistry (e.g., Kleeman, 1967; Ingamells, 1974; Verma and Schilling, 1982), and compilation of international geochemical reference samples (e.g., Govindaraju, 1980; Gladney and Burns, 1983; Abbey, 1986; Velasco and Verma, 1993).

In geothermal research involving the application of geothermometers to hydrothermal systems, such criteria have not been generally applied (e.g., Buntebarth, 1984; Henley *et al.,* 1984). It is only very recently that the geothermometers have been looked at from the standpoint of deviation between a regression curve and the actual data (Nieva and Nieva, 1987) or totai propagated analytical and regression errors (Santoyo and Verma, 1991, 1993).

In the present work, we derive newly revised and improved geothermometric equations for two chemical geothermometers (Na/K and SiO_2), with significantly reduced total propagated errors. This has been achieved through statistical tests of the data population and application of the theory of error propagation to each of these geothermometers. We report here these new equations and compare their performance with the original ones proposed by Fournier (1979) and Fournier and Potter II (1982). Our choice of these two rather old geothermometric equations is based on the fact that these are still among the most widely used equations in geothermal exploration.

2. PREVIOUS WORK

There are several sources of errors or uncertainties associated with the use of chemical geothermometers, such as, errors of the regression coefficients of the geothermometric equations, accuracy and precision of the analytical determinations of the chemical species in a given sample, sampling errors, calibration errors of the geothermometers for high temperature hydrothermal systems, and errors related to the geologic and thermodynamic processes of the chemical equilibria involved in the reactions (Santoyo and Verma, 1993). These different errors affect the interpretation of the final predicted temperatures and are propagated according to certain rules summarized by Bevington (1969) in the chapter on propagation of errors of his book. Because several aspects related to the geologic and thermodynamic processes have been discussed by Henley *et al.* (1984) and Giggenbach (1988), we have not included them in our present paper.

As a first step, we have evaluated the effect of analytical errors in Na/K and SiO_2 geothermometers (Santoyo and Verma, 1991). We have expanded this work by combining the analytical errors with those associated with the regression analysis of the geothermometric equations (Santoyo and Verma, 1993).

3. METHODOLOGY

We describe very briefly the procedure we have followed for evaluating the two geothermometers (Na/K and SiO_2) and proposing new improved equations.

3.1 Na/K geothermometer

The Na/K geothermometer proposed by Fournier (1979) on the basis of well data from many locations around the world (n = 36) is:

$$t = \frac{A_1}{\log(Na/K) + A_2} - 273.15 \qquad (1)$$

where t = temperature in °C, Na and K are the concentration of these cations in ppm and n is the number of the available data employed in the regression. The regression coefficients of eq. (1) are: $A_1 = 1217 \pm \sigma_{A1}$ and $A_2 = 1.483 \pm \sigma_{A2}$, where $\sigma_{A1} = 93.9$ and $\sigma_{A2} = 0.2076$ are the standard deviations of these regression coefficients (Santoyo and Verma, 1993).

The propagated combined error (σ_t) in the temperature t for this equation is (Santoyo and Verma, 1993):

$$\sigma_t = \frac{A_1}{\log(Na/K)+A_2} \cdot \left[\frac{\sigma_{A1}^2}{A_1^2} + \frac{\frac{1}{(\ln 10)^2} \cdot \left[\frac{\sigma_{Na}^2}{Na^2} + \frac{\sigma_K^2}{K^2}\right] + \sigma_{A2}^2}{(\log(Na/K)+A_2)^2}\right]^{1/2} \qquad (2)$$

A limiting case for estimating the minimum error of this geothermometer ($\sigma_{t\ min}$) will be when the analytical errors of sample determination $\sigma_{Na} = \sigma_K = 0$. The above equation reduces to:

$$\sigma_{t-min} = \frac{A_1}{\log(Na/K)+A_2} \cdot \left[\frac{\sigma_{A1}^2}{A_1^2} + \frac{\sigma_{A2}^2}{(\log(Na/K)+A_2)^2}\right]^{1/2} \qquad (3)$$

Santoyo and Verma (1993) used eq. (2) and (3) to evaluate this geothermometer (eq. 1). Here we use them to evaluate our new equation (eq. 7 in the "RESULTS" section), derived by minimizing the errors associated with the regression coefficients of the existing equations.

Our procedure is to first estimate the average deviation (1σ) of all the data points with respect to the originally proposed geothermometric equation (*eq.* 1). Then we use a statistical criterion of rejecting all those data points lying outside:

> the $\pm 4\sigma$ deviation from the original equation, derive the new geothermometric equation using a BMDPAR subroutine (Dixon, 1981) and the new average 4σ deviation, and repeat this procedure until no more data points are rejected (*4σ method)*.

Thus we have obtained a new equation for this geothermometer (eq. 7 in the "RESULTS" section). The total propagated errors of this new equation are then compared with those associated with the originally proposed geothermometric equation (eq. 1).

3.2 SiO_2 geothermometer

The SiO_2 geothermometer is based on the regression of experimental data of silica solubility and temperature (n = 32; Fournier and Potter II, 1982):

$$t = C_1 + C_2S + C_3S^2 + C_4S^3 + C_5\log S \qquad (4)$$

where t = temperature in °C in the range of 20°C to 330°C, S is the concentration of SiO_2 in a sample in mg/kg (ppm), and Ci are the regression coefficients as follows (Santoyo and Verma, 1993):

$C_1 = -42.1981 \quad \pm \sigma_{C1} \; (= 1.3454)$
$C_2 = 0.288313 \quad \pm \sigma_{C2} \; (= 1.337\text{x}10^{-2})$
$C_3 = -3.6686\text{x}10^{-4} \quad \pm \sigma_{C3} \; (= 3.152\text{x}10^{-5})$
$C_4 = 3.1665\text{x}10^{-7} \quad \pm \sigma_{C4} \; (= 2.421\text{x}10^{-8})$
$C_5 = 77.034 \quad \pm \sigma_{C5} \; (= 1.21637)$

At first sight, Fournier and Potter II (1982) fit of the regression equation to the experimental data appears to be perfect. However, the associated errors in the regression coefficients, particularly in the higher order terms (quadratic and cubic), are very large (8.6% and 7.6% respectively), as is seen from the above error data estimated by Santoyo and Verma (1993). Furthermore, such a complicated regression (eq. 4) and a "perfect" fit to the data points implicitly and perhaps erroneously assumes that the data of the silica solubility experiment have *no* analytical errors.

The propagated error (σ_t) of eq. (4) can be estimated by the general equation:

$$\sigma_t = [\sigma_{C1}^2 + (S^2\sigma_{C2}^2 + C_2{}^2\sigma_S^2) + (S^4\sigma_{C3}^2 + 4C_3{}^2S^2\sigma_S^2) + (S^6\sigma_{C4}^2 + 9C_4{}^2S^4\sigma_S^2) + ((\log S)^2\sigma_{C5}^2 + (C_5{}^2/(\ln 10)^2)(\sigma_S^2/S^2))]^{1/2} \qquad (5)$$

and the minimum error ($\sigma_{t\text{-}min}$) is given when $\sigma_S = 0$:

$$\sigma_{t\text{-}min} = [\sigma_{C1}^2 + S^2\sigma_{C2}^2 + S^4\sigma_{C3}^2 + S^6\sigma_{C4}^2 + (\log S)^2\sigma_{C5}^2]^{1/2} \qquad (6)$$

In order to obtain new improved equations for this geothermometer, we have attempted to fit:

(i) a simpler equation to the silica solubility data (Fournier and Potter II, 1982) in the temperature range of 20°C—210°C, and

(ii) a linear equation for the data from 210°C to 330°C.

Although the SiO_2 geothermometer is based on controlled laboratory experimental data, rather than the worldwide well data of the Na/K geothermometer, we have applied the same strict statistical criterion of rejecting only those data points lying outside the $\pm 4\sigma$ deviation from the geothermometric equation, derive the new equation and the new average 4σ deviation, and repeat this procedure until no more data points are rejected (*4σ method*).

Thus, we have obtained two new equations (eq. 8 and 9 in the next section) for this geothermometer applicable for temperatures between 20°C—210°C and >210°C—310°C. The total propagated errors of these new equations are then derived according to the theory of error propagation and the results are compared with the originally proposed geothermometric equation (eq. 4).

4. RESULTS

4.1 Na/K geotherniometer

The data points used by Fournier (1979) as well as his geothermometric equation are plotted in Figure 1. The new equation after rejecting the "outlier" data is also shown in Figure 1 for the 4σ *method.*

The new equation is ($n = 33$ for the 4σ *method):*

$$t = \frac{1289(\pm 65)}{\log(Na/K) + 1.635(\pm 0.145)} - 273.15 \qquad (7)$$

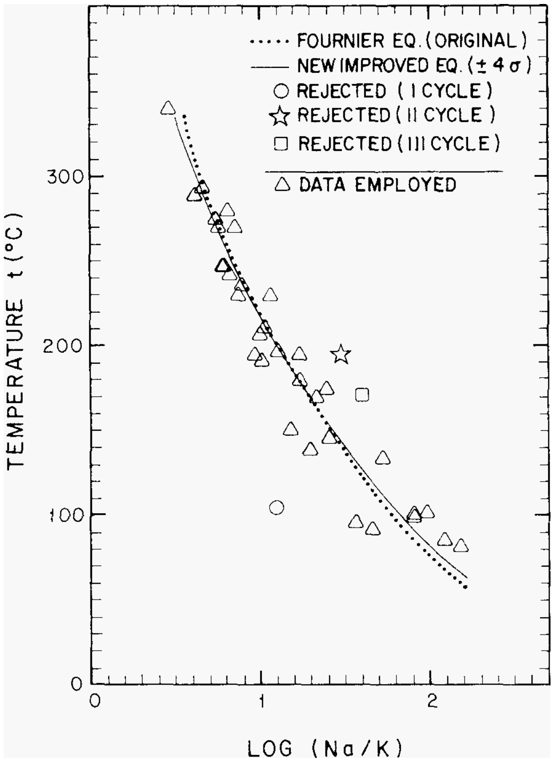

Figure 1. Log(Na/K) — temperature plot for the data used in the Na/K geothermometer. The original equation (Fournier, 1979) proposed on the basis of these data is shown by dotted curve. The continuous curve is the new geothermometric equation for the 4σ *method.* Three data were successively eliminated as "outliers", these rejected data are also shown for reference.

We have evaluated the errors associated with the use of this new equation (eq. 7). Figure 2 compares them with the original equation (Fournier, 1979; Santoyo and Verma, 1993). For temperatures ranging from 150°C to 350°C, our results show that the minimum total propagated error ($\sigma_{t\text{-min}}$) of the new geothermometric equation vanes from −29°C to ~54°C. These values are significantly lower than for the original Fournier equation for which we found minimum error values from −45°C to 82°C (Figure 2). The total propagated errors (σ_t) for the new equation are also much lower (~31°C—57°C) than the Fournier (1979) regression (~46°C—84°C; Figure 2).

Thus, the minimum total propagated error ($\sigma_{t\text{-min}}$; eq. 3) of the new equation for the temperature range of 150°C to 350°C varies from 15% to 20%, which is considerably lower than the corresponding error (23% to 30%) of the original Fournier equation (eq. 1). Similarly, the "reasonable" maximum error (σ_t; eq. 2) associated with the use of the new geothermometer for the same temperature range is 16%—20%, much lower than 24%—30% estimated for the original Fournier equation.

The propagated analytical errors for the hypothetical case of no errors in the regression coefficients ($\sigma_{A1} = \sigma_{A2} = 0$) are also shown in Figure 2. These errors are relatively small (< 10°C) for the case of $\sigma_{Na} = \sigma_K = 5\%$ but can reach somewhat higher values (−20°C) for $\sigma_{Na} = \sigma_K = 10\%$. However, note that our new equation still results in somewhat lower error values (vs and vs' curves always lie below the f and f' curves; Figure *2)* throughout the temperature range.

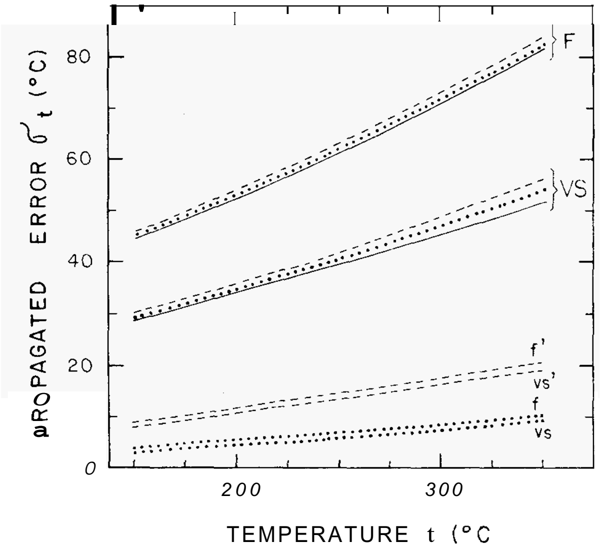

Figure 2. Predicted temperature (t) — propagated error (σ_t) plot for the Na/K geothermometer. F, f, and f' = Fournier (1979); VS, vs, and vs' = this work. Upper curves (grouped as F and VS) are for total propagated errors of the regression coefficients (σ_{A1} and σ_{A2}) and the analytical errors (σ_{Na} and σ_K) (dotted curves here are for $\sigma_{Na} = \sigma_K = 5\%$ and dashed curves for $\sigma_{Na} = \sigma_K = 10\%$, whereas continuous curves represents $\sigma_{t\text{-min}}$). Lower curves (denominated f, vs, f', and vs') are for propagated analytical errors, assuming no errors in the regression coefficients ($\sigma_{A1} = \sigma_{A2} = 0$). The curves f and vs are for $\sigma_{Na} = \sigma_K = 5\%$ (dotted curves) and f' and vs' for $\sigma_{Na} = \sigma_K = 10\%$ (dashed curves).

4.2 SiO_2 geothermometer

The data points ($n = 32$) used by Fournier and Potter II (1982) and their geothermonietric equation are plotted in Figure 3.

The first new geothermometric equation ($n = 20$) is:

$$t = C_1 + C_2 S + C_3 S^2 + C_4 \log S \qquad (8)$$

where t = temperature in °C in the range of 20°C to 210°C, S is the concentration of SiO_2 in a sample in mg/kg (ppm), and Ci are the regression coefficients as follows:

$C_1 = -44.119 \quad \pm \sigma_{C1}$ (= 0.438)
$C_2 = 0.24469 \quad \pm \sigma_{C2}$ (= 0.00573)
$C_3 = -1.7414\times10^{-4} \quad \pm \sigma_{C3}$ (= 1.365×10^{-5})
$C_4 = 79.305 \quad \pm \sigma_{C4}$ (= 0.427)

The 4σ *method* did not reject any data.

The second is a linear equation for the remaining data from 210°C to 330°C (two highest temperature data were successively eliminated by the *4σ method;* the applicable temperature range is therefore >210°C—310°C). This second equation for the SiO_2 geothermometer (n = 11) is as follows:

$$t = C_1 + C_2S \tag{9}$$

The regression coefficients are as follows:

$$C, = 140.82 \qquad \pm \sigma_{C1} \; (= 0.00)$$
$$C, = 0.23517 \qquad \pm \sigma_{C2} \; (= 0.00179)$$

The total propagated error (σ_t) of eq. **(8)** can be estimated by:

$$\sigma_t = [\sigma_{C1}^2 + (S^2\sigma_{C2}^2 + C_2{}^2\sigma_S^2) + (S^4\sigma_{C3}^2 + 4C_3{}^2 S^2\sigma_S^2)$$
$$+ ((\log S)^2 \sigma_{C4}^2 + (C_4{}^2/(\ln 10)^2)(\sigma_S^2/S^2))]^{1/2} \tag{10}$$

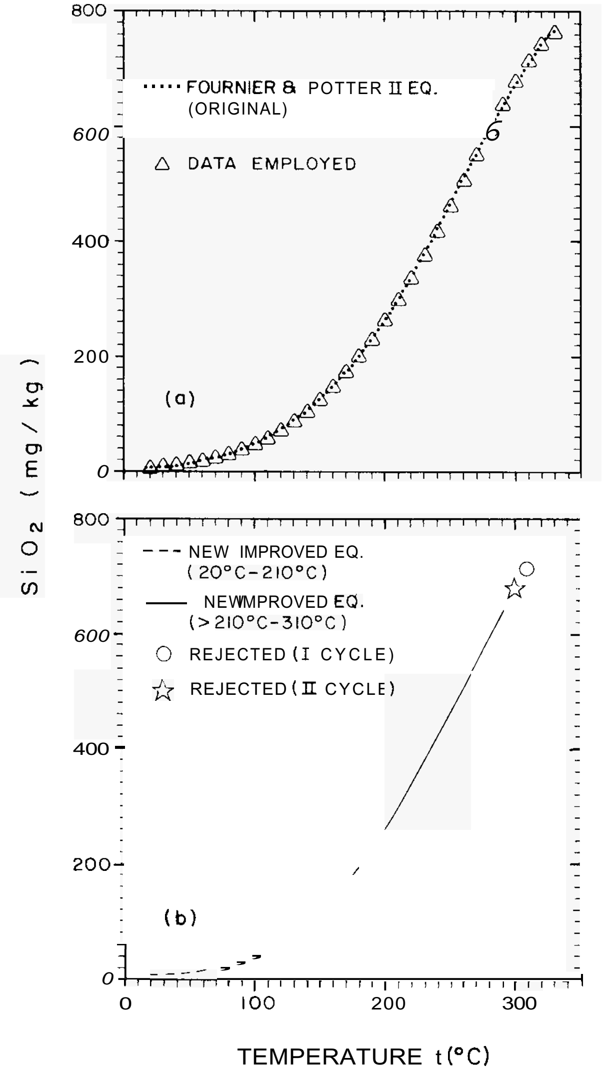

Figure **3.** SiO_2 concentration (mg/kg) — temperature (t) plot for the data points used in the SiO_2 geothermometer. (a) The original equation (Fournier and Potter II, 1982) is shown by dotted curve. (b) The dashed and continuous curves are the new geothermometric equations (eq. **8** and 9 obtained by the *4σ method)* for the temperature range of 20°C—210°C and >210°C—310°C respectively.

and the minimum error ($\sigma_{t\text{-min}}$) is given when $\sigma_S=0$:

$$\sigma_{t\text{-min}} = [\sigma_{C1}^2 + S^2\sigma_{C2}^2 + S^4\sigma_{C3}^2 + (\log S)^2\sigma_{C4}^2]^{1/2} \tag{11}$$

Similarly, the total propagated error (σ_t) of eq. (9) can be estimated by:

$$\sigma_t = [S^2\sigma_{C2}^2 + C_2{}^2\sigma_S^2]^{1/2} \tag{12}$$

and the minimum error ($\sigma_{t\text{-min}}$) is given when $\sigma_S=0$:

$$\sigma_{t\text{-min}} = S\sigma_{C2} \tag{13}$$

We have evaluated the errors associated with the use of these new equations (8 and 9) and compared them with the performance of the original eq. (4) by Fournier and Potter II (1982) in Figure 4 (a and b).

For temperatures ranging from 20°C to 310°C, our results show that the minimum error ($\sigma_{t\text{-min}}$) of the new geothermometric equations varies from ~0.5°C to −4°C. These values are considerably smaller than for the original Fournier and Potter **II** equation, for which we found minimum error values from −1.7°C to ~ 19°C (Figure 4a). The total propagated errors (σ_t) for the new equations (for analytical error in SiO_2, σ_S from *5%* to 10%) are also much lower (−1.8°C—18°C) than the original regression (~2.3°C—55°C; Figure 4a).

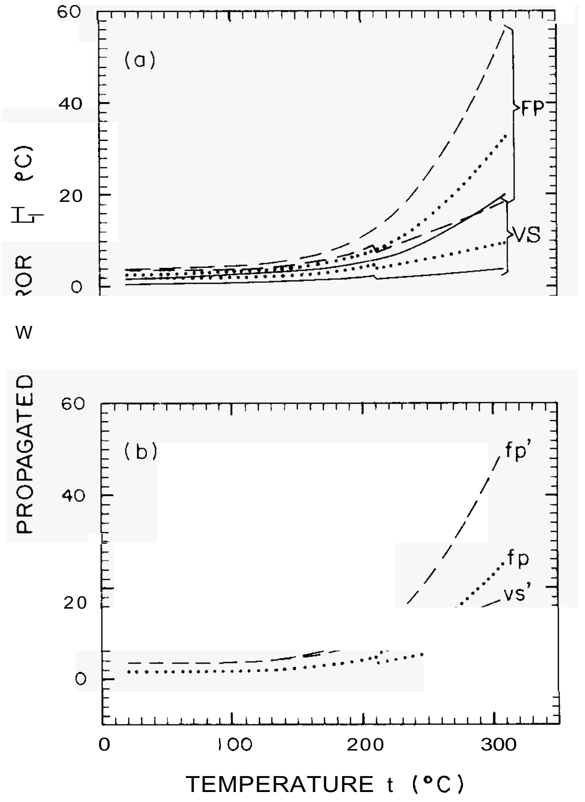

Figure 4. Predicted temperature (t) —propagated error (σ_t) plot for the SiO_2 geothermometer. Dotted curves refer to the case of a, = **5%** and dashed curves are for σ_S = 10%. (a) Total propagated error in the regression coefficients (σ_{Ci}) and the analytical error (σ_S). Continuous curves are for $\sigma_{t\text{-min}}$. **VS** = Verma and Santoyo (this work); FP = Fournier and Potter II. (b) Propagated analytical error, assuming no error in the regression coefficients (σ_{Ci} = 0) [fp (σ_S = *5%)* and fp' (σ_S = 10%) = Fournier and Potter II; vs and vs' = this work).

Thus, the minimum errors ($\sigma_{t\text{-min}}$) of the new equations (eq. 8 and 9) for the temperature range of 20°C to 310°C vary from 0.8% to 2.8%, which are considerably lower than the corresponding error (2.2% to 8.3%) of the original Fournier and Potter II equation (eq. **4).** Similarly, the "reasonable" maximum errors (σ_t) associated with the use of the new geothermometers for the same temperature range are 1.7% to 17.8%, which are consistently lower than 2.7% to 18.8% estimated for the original equation.

The propagated analytical errors for the hypothetical case of no errors in the regression coefficients ($\sigma_{C_i} = 0$) are shown in Figure 4b. These errors are relatively small (< -9°C for the new equations and <25°C for the original one) for the case of a, = *5%,* but can reach somewhat higher values (up to $-$ 18°C for the new equations and -55°C for the original one) for $\sigma_S = 10\%$.

5. APPLICATION TO ACTUAL FIELD DATA

In order to further evaluate the performance of our new improved equation (eq. 7) for the Na/K geothermometer in comparison with the original equation (eq. 1), we have computed the corresponding temperatures from the chemical data (compiled by Nieva and Nieva, 1987) from hot springs and wells in Mexico (Cerro Prieto) and other countries. In Figure *5,* the relative % temperature deviation $\{100 * (t_{vs} - t_f)/t_m\}$ of the new and old equations is plotted as a function of the measured temperature (t_m). The negative % deviation values are for samples for which the temperature **(f,)** predicted by the new equation (eq. 7) is closer to the measured temperature **(t_m).** On the other hand, the positive % deviation values correspond to samples for which the temperature (t,) by original equation (eq. 1) falls closer to the measured temperature (t_m). We conclude that the temperatures predicted by the new equation are in general closer to the measured temperatures, because most of the data fall in the negative % deviation field in Figure 5.

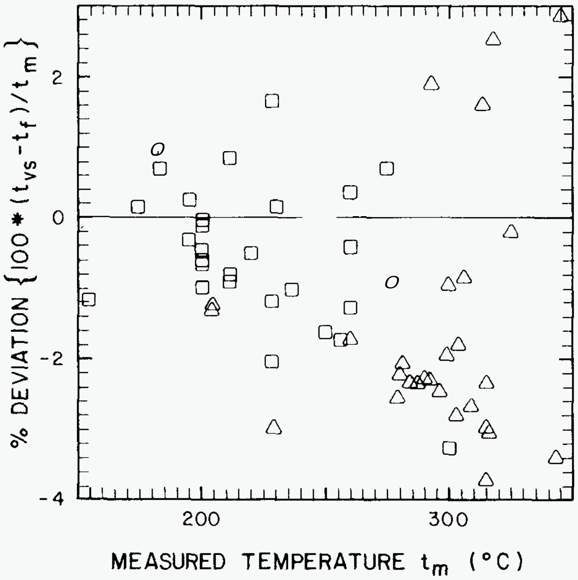

Figure 5. **A** plot of % deviation $\{100 * (t_{vs} - t_f)/t_m\}$ as a function of the measured temperature (t_m) in hot springs and wells (t_{vs} = temperature computed from the new equation and t, = temperature from the original Foumier equation). The symbols are: triangles for Mexico (Cerro Prieto) and squares for other countries.

We have not attempted to evaluate from field data the performance of our new equations (eq. 8 and 9) for the SiO_2 geothermometer. This is because, in the lower temperature range of 20°C—210°C, the new (eq. 8) and original (eq. **4)** equations should give very similar temperature values, as there were no "outliers" in this part of the regression (see Figure **4).** For the higher temperature range (>210°C—310°C), the new equation (eq. 9), because of its simplicity, is likely to be more useful in comparison with the original equation (linear regression of eq. 9 ***versus*** the original more complicated eq. **4).**

6. DISCUSSION

We have clearly demonstrated that the existing geothermometric equations for the Na/K and SiO_2 geothermometers result in very large total propagated errors which are perhaps unacceptable in modern geothermal exploration. We have also presented our new improved equations for these geothermometers and shown by the application of the theory of error propagation that they should perform much better than Fournier (1979) and Foumier and Potter **II** (1982) equations. In fact, we have applied both sets of equations—the new as well as the original equation for the Na/K geothermometer—to actual field data, which once again confirms that our new equation performs better than the original.

In future work, we plan to apply this methodology to chemical geothermometers of Fouillac and Michard (1981) and Fournier (1990), and to gas geothermometers (CO_2, H_2S and H_2) proposed by Arnórsson and Gunnlaugsson (1985), in order to evaluate the associated total propagated errors. We will also attempt to obtain corresponding revised and improved equations with considerably reduced,errors and evaluate their performance with actual field data.

This approach **is** likely to provide an additional tool to the field geologist or geochemist, by which he/she will be able to make better decisions regarding the temperature field distribution in an area under exploration. Furthermore, this kind of work shows an entirely new way of explaining, at least partly, the discrepancies in the temperatures predicted by different geothermometers.

Such an approach will be particularly useful in geothermal exploration when combined with other recent techniques of temperature field simulations from cooling of a magma chamber for the entire volcanic history of the geothermal areas (Verma and Andaverde, in press, this volume).

7. CONCLUSIONS

We have clearly demonstrated that our new equations (eq. **7** for the Na/K and eq. 8 and 9 for the SiO_2 geothermometers) result in very significantly reduced propagated errors, in comparison with the originally proposed equations for these two geothermometers by Fournier (1979) and Fournier and Potter **II** (1982). Further, from actual field data we have also shown that in most cases the new equation predicts temperatures closer to the actually measured values than the original Na/K geothermometer. We therefore strongly recommend the use of these improved geothermometric equations for geothermal exploration.

We have also shown that the application of the theory of error propagation in geothermal research is a novel and rewarding scientific and technical approach. This could eventually lead to a significant progress in the development of new techniques for geothermal exploration, particularly when employed in conjunction with other recent developments of temperature field simulations from magma chambers (Verma and Andaverde, in press, this volume).

8. ACKNOWLEDGEMENTS

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