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A New Improved Proposal of the *Na/K* Geothermometer to Estimate Deep Equilibrium Temperatures and their Uncertainties in Geothermal Systems

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ABSTRACT

Cation geothermometers based on *Na/K* ratios are tools commonly used for predicting subsurface temperatures of geothermal systems under exploration and exploitation. Temperature estimates of cation geothermometers are usually inconsistent due to errors in calibrations, coefficients and chemical analyses. Large differences are still found between measured and predicted temperatures of geothermal wells. Such a problem has motivated several authors to develop new equations to reduce the geothermometer uncertainties. In light of these discrepancies, a new improved *Na/K* geothermometer has been developed using a world geochemical database together with advanced geochemometric techniques. The new improved *Na/K* geothermometer is given by the following equation:

$$t^{o}C = \frac{876.3(\pm 26.26)}{\log\left(\frac{Na}{K}\right) + 0.8775(\pm 0.0508)} - 273.15$$

where the numbers in parentheses are the coefficient errors; and *Na* and *K* are concentrations (in mg/L or mg/kg). The calibration of the geothermometer and validation, as well as some application examples are outlined in the present work.

1. INTRODUCTION

The estimation of deep equilibrium temperatures is a fundamental task commonly required for the exploration and exploitation of geothermal systems. The reliable knowledge of underground temperatures is part of an integral methodology constituted by geochemistry, geological, and geophysics studies (Verma, 1985; Verma et al., 1990; Verma y Rodríguez-González, 1997; Verma y Andaverde, 1996, 2007). Deep equilibrium temperatures are usually estimated by using geothermometers, which include chemical (both solutes and gases), isotopic, clay minerals, and fluid inclusions (Arnórsson, 1983; Nicholson, 1993; D'Amore and Arnórsson, 2000). These tools have been used in geothermal industry for almost 50 years. Chemical geothermometers rely on either concentration of a solute or gas or concentration ratio of two or more solutes or gases and equilibrium conditions of temperature-dependent water-rock interaction processes (Verma et al., 2008). A large number of solute geothermometers have been proposed, among which the cation (or alkalai metal) geothermometric tools have had a major applicability (Verma, 2002). Cation geothermometers are based on ion exchange reactions with equilibrium constants that depend on temperature changes.

Among the cation geothermometric tools, the *Na/K* ratio geothermometer is the most used equation in geothermal exploration and exploitation. The preferential use of this geothermometer has relied on the experience gained in many active geothermal fields. It may be due to fact that common geochemical processes, such as mixing of geothermal waters with superficial waters and degassing of geothermal waters during ascent towards the surface, do not significantly affect the *Na/K* ratio (Arnórsson, 1985; Pope et al., 1987; Pang and Reed, 1998). Furthermore, the determination of *Na* and *K* cations in geothermal waters is a simple analytical task (Nicholson, 1993). Although, ion exchange reactions with minerals (mainly clay minerals), enrichment processes of some cations, or the lack of equilibrium between solutes and alteration minerals could affect its application (D'Amore et al., 1987; Palandri and Reed, 2001). Nevertheless, given the good applicability of most *Na/K* geothermometers these problems have not been of much concern in practice. *Na/K* ratios are controlled by the equilibrium between geothermal fluids and alkali feldspar minerals, with a dependency on temperature (Orville, 1963; Stefánsson and Arnórsson, 2000). The thermodynamic assumptions of the *Na/K* geothermometer have been widely studied by many authors (e.g., Arnórsson, 2000; Arnórsson and Stefánsson, 1999).

The *Na/K* geothermometer has been gradually improved over the last 30 years, from qualitative observations of high temperature, to more precise calibrations to provide more reliable temperature estimates (e.g., White, 1957; Ellis and Mahon, 1967; Ellis, 1970; Fournier and Truesdell, 1973; Truesdell, 1976; Fournier, 1979; Tonani, 1980; Arnórsson, 1983; Giggenbach, 1988; Verma and Santoyo, 1997; Arnórsson, 2000; Bayram, 2001, Can, 2002; Díaz-González and Santoyo, 2008; Díaz-González et al., 2008; and Serpen et al., 2009): see Table 1. Most of these equations have been derived from either experimental thermodynamic data or geothermal fluid geochemical databases. From the practical point of view, it may often be of advantage to calibrate empirically geothermometers rather than to use experimental thermodynamic data because the errors involved in deriving thermodynamic data could also produce large deviations in temperature estimates (Arnórsson et al., 1983). Although the large number of available equations, when more than two geothermometers are used in either exploration or exploitation geochemical tasks, temperature estimates are generally inconsistent (Verma et al., 2006a, 2008). Several error sources have been identified with the use of the *Na/K* geothermometer.

Table 1. Na/K Geothermometers for Geothermal Exploration (modified after Verma, 2002 and Verma *et al*., 2008a).

Reference	Equation (t °C) ♣	Geothermometer Code **
Fournier and Truesdell, 1973	$\{777/(\log(Na/K)+0.700)\}-273.15$	TNKFT73
Truesdell, 1976	$\{855.6/(\log(Na/K)+0.8573)\}-273.15$	TNKT76
Fournier, 1979	$\{1217(\pm 93.9)/(\log(Na/K)+1.483(\pm 0.2076))\}-273.15$	TNKF79
Tonani, 1980	$\{833/(\log(Na/K)+0.780)\}-273.15$	TNKT80
Arnórsson *et al*., 1983b	$\{933/(\log(Na/K)+0.993)\}-273.15$	TNK1A83
Arnórsson *et al*., 1983b	$\{1319/(\log(Na/K)+1.699)\}-273.15$	TNK2A83
Nieva-Nieva, 1987	$\{1178/(\log([Na]/[K])+1.239)\}-273.15$	TNKNN87
Giggenbach, 1988	$\{1390/(\log(Na/K)+1.75)\}-273.15$	TNKG88
Verma and Santoyo, 1997	$\{1289(\pm 76)/(\log(Na/K)+1.615(\pm 0.179))\}-273.15$	TNKVS97
Arnórsson, 2000b	$733.6-770.551(\log([Na]/[K]))+378.189(\log([Na]/[K]))^2-95.753(\log([Na]/[K]))^3+9.544(\log([Na]/[K]))^4$	TNKA00
Bayram, 2001	$\{2.0446/(\log(Na/K)+126.01)\}-273.15$	TNKB01
Can, 2002	$\{1052/(1+exp(1.714(\log(Na/K)+0.252)))\}+76$	TNKC02
Díaz-González *et al*., 2008	$\{883/(\log(Na/K)+0.908)\}-273.15$	TNK1DSR08
Díaz-González *et al*., 2008	$(1273.2*(\tanh(-0.4144*\log(Na/K)-0.5642))+1156.9)$	TNK2DSR08
Díaz-González *et al*., 2008	$\{883(\pm 15)/(\log(Na/K)+0.894(\pm 0.032))\}-273.15$	TNK3DSR08

♣ Concentrations of *Na* and *K* are in mg/kg (element symbols are used for this purpose); Concentrations in molal unit are indicated by square brackets, viz. [*Na*] and [*K*].

** Applicability conditions: TNKT76 is applicable for temperature is applicable for fluids with TMEQ>8.0, *%Mg*≤3.5 and for temperatures >125°C, where the abbreviations are: TMEQ = *Na+K+Ca+Mg*, all in milliequivalents/kg; *%Mg* = 100Mg/TMEQ; TNKVS97 is applicable for temperatures 80-350ºC; TNKA00 is applicable for dilute to moderately saline waters and for temperature range 0-350°C; TNKB01 temperature range 91-516°C; TNKC02 applicable for the temperature range used for calibration, approximately 100-350°C; TNK1DSR08, TNK2DSR08 and TNK3DSR08, the database for proposing both geothermometric equations was for temperatures between 30-350°C, this being the applicable range.

Some uncertainties could come from variations in the mineralogy of reservoir rocks that react with the fluid, whereas other could arise from the equilibrium conditions assumed with particular minerals in the deep geothermal system. Large differences are also reported in comparison studies between measured and predicted temperatures of geothermal wells (Verma et al., 2008). Temperature uncertainties are also attributed to errors coming from calibrations, regression coefficients, and fluid sampling or chemical analyses (Verma and Santoyo, 1997). All these problems have motivated authors to develop new versions of the geothermometer for reducing their uncertainties. In the light of these discrepancies, a new *Na/K* geothermometer was developed using a worldwide geochemical database and geochemometric advanced techniques.

2. Na/K GEOTHERMOMETER

The thermodynamics of the *Na/K* geothermometer is briefly described. In high-temperature systems, the temperature-dependent variation of *Na* and *K* in geothermal waters is due to ion exchange of these elements between coexisting alkali feldspars, according to the reaction (Nicholson, 1993):

$$K^+ + Na - feldspar = K - feldespar + Na^+ \quad (1)$$

The equilibrium constant (K_{eq}) of this reaction is given in terms of the thermodynamic activities:

$$K_{eq} = \frac{a_{K-feldespar}\, a_{Na^+}}{a_{Na-feldespar}\, a_{K^+}} \quad (2)$$

If minerals K-feldspar and Na-feldspar are pure phases, then $a_{K-feldespar} = 1$ and $a_{Na-feldespar} = 1$, and

$$K_{eq} \approx \frac{a_{Na^+}}{a_{K^+}} \quad (3)$$

where a_i is activities of the solute species i. The temperature dependence of log K_{eq} can be approximated by using the van't Hoff equation:

$$\log K_{eq} = \frac{\Delta H^o}{2.303RT} + C \quad (4)$$

In Eq. (4), ΔH^o is the standard enthalpy of reaction at absolute temperature *T(K)*, and *R* is the universal gas constant. Eq. (4) assumes a linear relationship between *log* K_{eq} and *1/T*, if ΔH^o maintains constant over a temperature interval of 0-300°C (Fournier, 1991). Eq. (4) is therefore modified using the assumption of Eq. (3):

$$\log\left(\frac{a_{Na^+}}{a_{K^+}}\right) = \frac{\Delta H^o}{2.303R} \cdot \frac{1}{T(K)} + C \quad (5)$$

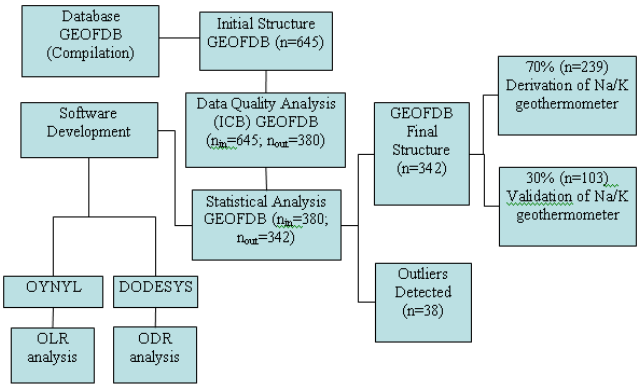
The ratio of *Na/K* activities may be approximated by the ratio of concentrations, and solving for temperature (*t* in °C). From this assumption, Eq. (5) becomes in the classical equation of the Na/K geothermometer:

$$t°C = \frac{b}{\log\left(\frac{Na}{K}\right) + a} - 273.15 \quad (6)$$

where a and b coefficients are inferred from linear regression between *log* K_{eq} and *1/T*. A list of some equations is summarised in Table 1. Coefficient errors are also compiled, which have been quantified by some authors (e.g., Verma and Santoyo, 1997; Díaz-González et al., 2008).

3. GEOCHEMOMETRIC METHODOLOGY

In a previous geochemical study, Verma and Santoyo (1997) developed a new version of the *Na/K* geothermometer using the geochemical database proposed by Fournier (1979) with 36 well data from some geothermal sites around the world. The new equation was obtained by a statistical methodology consisting of an outlier detection/rejection (ODR), ordinary linear regression (OLR), and error propagation theory concepts (Bevington and Robinson, 2003). This statistical methodology enabled these authors to lower the regression coefficient errors, and the uncertainties of the temperature estimates. For the present study, we have applied a new geochemometric methodology to a large and a more representative geochemical database (Fig. 1). The new geothermal fluid database (GEOFDB) was created using stable bottomhole temperature (BHT) measurements and geothermal brine compositions of wells from worldwide geothermal fields. A total number of 645 samples were compiled (from papers reported in the literature) and initially evaluated by calculating ion charge balances (ICB), which enabled to select data with ICB<10% for a better geothermometer calibration. 380 samples were surprisingly selected from this analysis, and re-evaluated with both the methodology proposed by Eqs. (1-6) and a new variant of the geochemometric method suggested by Verma and Santoyo (1997). The ODR algorithm, originally proposed by Barnett and Lewis (1994) and used by Verma and Santoyo (1997) for linear regressions (or bivariate samples) was suitable for statistical samples of n<100 data. However, when a statistical sample is greater than 100 data (e.g., GEOFDB, n=380), the algorithm must not be directly used because there are no available critical values for its application. This constraint enabled a new geochemometric methodology based on univariate samples to be developed for the correct regression analysis of the GEOFDB (n=380). For the ordinary linear regression (OLR), the computer code OYNYL was used (Verma et al., 2006b). For solving the ODR problem, thirty-three statistical discordance tests were applied to univariate samples given by *"studentized residuals"* derived from the regressions. An iterative geochemometric process coupling OLR (between *log Na/K* and *1/T*) with univariate statistical tests was used for ODR.



Flow diagram of the work methodology.

Normalised univariate samples of the *"smaller studentized residuals"* enabled the outliers to be clearly detected, and therefore rejected (i.e., *"larger studentized residuals"*). This

analysis was carried out using the computer code DODESYS (Verma and Díaz-González, in preparation).

4. RESULTS AND DISCUSSION

After applying the new geochemometrical methodology, three computing cycles were used for deriving the new *Na/K* geothermometer equation. The overall numerical process is schematically shown in Figs. 2 (A-C). In each cycle, the *log Na/K* and *1/T* data set together with the best OLR (red dash line) are plotted. The regression parameters obtained in each cycle and the data number used are also included. Normalised "studentized residuals" were computed by regression equations for detecting and rejecting discordant outliers.

From cycle I, 32 discordant outliers were detected and rejected (Fig. 2A). The normal distribution showing the statistical treatment is plotted in Fig. 3A. For the cycle II, 6 discordant outliers were rejected: Figs. 2B and 3B. Finally, no outliers were detected in the cycle III (Figs. 2C and 3C).

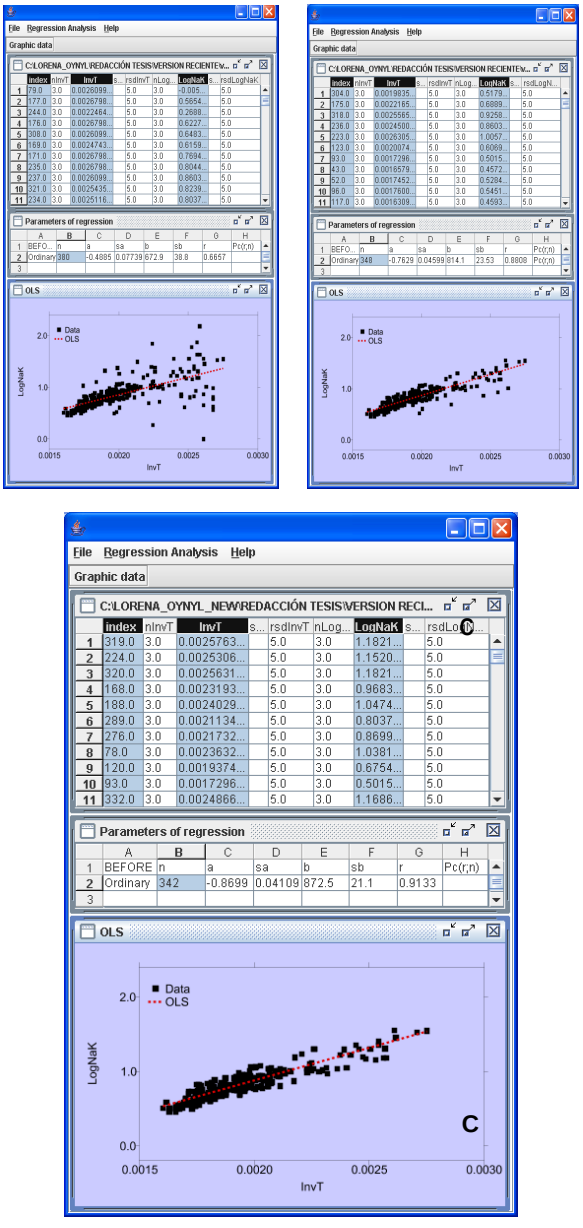


Fig 1: Iterative numerical process used for the sample detection-rejection showing from the initial stage of GEOFDB (n=380 data) to the final structure (n=342).

A total number of 38 outliers were rejected to obtain the final structure of GEOFDB with 342 data pairs (*log Na/K* and *1/T*).

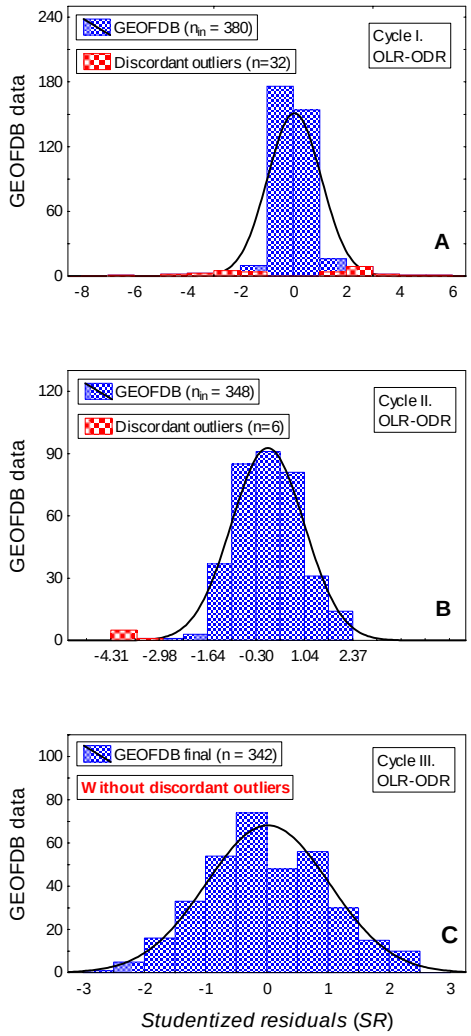


Fig 2: Statiscal results provided by DODESYS software using an iterative analysis based on OLR and ODR.

The thirty-eight outliers detected were related to low- to medium temperature samples which could probably present some problems in fluid sampling, chemical analysis or temperature measurements. From the final structure of the GEOFDB, 239 samples (70 %) were randomly selected to derive the new *Na/K* geothermometer equation (Fig. 4). The remaining 103 data pairs were used for the validation (accuracy evaluation) of the new geothermometer version.

The new improved Na/K geothermometer is given by the following equation:

$$t^{o}C = \frac{876.3(\pm 26.26)}{log\left(\frac{Na}{K}\right) + 0.8775(\pm 0.0508)} - 273.15 \qquad (7)$$

where the numbers in parentheses are the coefficient errors; and *Na* and *K* are concentrations (in mg/L or mg/kg).

5. GEOTHERMOMETER VALIDATION

The validation process was finally achieved through a statistical comparison between BHT measurements and geothermometric temperature (GT) estimates obtained from: (i) the *Na/K* geothermometers most commonly used in geothermal industry; and (ii) the new improved *Na/K* geothermometer: Eq. (7) (this work). Data validation was carried out using the remaining part of the GEOFDB (30%: n=103 data). This data set and the corresponding references used are available upon the direct request to the authors. The new *Na/K* geothermometer was successfully validated and applied to estimate equilibrium temperatures in 103 geothermal wells, which showed a much better agreement with the measured temperatures, than those estimates provided by the previous *Na/K* geothermometers developed for the geothermal industry.

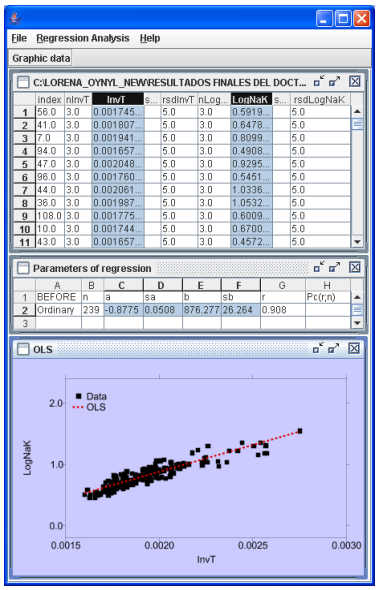


Fig 3: Regression parameters and optimum data set (n=209) used for the final derivation of the new geothermometer of *Na/K*

Statistical comparative analysis. This process was performed using a linear regression analysis between the geothermometric temperature (GT) estimates (t_g) and the BHT measurements (t_m). The intercept and slope values of the linear regressions were used as a main statistical agreement criterion. Results of this analysis are presented in Table 2 and Figs. 5 y 6).

Table 2. Linear regression parameters (intercept and slope) computed between the geothermal temperature estimates (t_a) and BHT measurements (t_m). Confidence limits were calculated with a 95% of confidence level.

Code	Intercept		Slope		Slope Confidence limits	
	a	s_a	*b*	s_b	Upper	Lower
TNKSD10 (this work)	-0.005	11.178	1.003	0.045	0.884	1.122
TNKFT73	-28.199	12.447	1.102	0.05	0.97	1.234
TNKT76	50.95	13.942	0.704	0.06	0.544	0.864
TNKF79	67.101	8.39	0.771	0.034	0.682	0.86
TNKT80	-11.276	12	1.069	0.049	0.942	1.197
TNK1A83	55.521	12.277	0.701	0.057	0.549	0.852
TNK2A83	128.366	14.859	0.549	0.054	0.405	0.693
TNKG88	93.622	7.706	0.712	0.031	0.63	0.794
TNKVS97	77.13	7.953	0.733	0.032	0.649	0.818
TNKA00	44.531	9.055	0.814	0.037	0.718	0.911
TNKB01	41.046	10.286	0.934	0.042	0.825	1.044
TNKC02	57.183	8.729	0.774	0.035	0.681	0.866
TNK1DSR08	1.105	10.861	0.976	0.044	0.861	1.092
TNK2DSR08	29.279	9.339	0.869	0.038	0.77	0.968
TNK3DSR08	1.566	11.043	0.992	0.045	0.875	1.109

As can be ideally expected, a total agreement between geothermometric temperatures (GT) estimates and BHT measurements is obtained when the intercept and slope values are equal to 0 and 1, respectively. These conditions are closely approached with the estimates provided by the new improved *Na/K* geothermometer (TNKSD10: Eq. 7). Verma and Santoyo (1997) demonstrated that the coefficient errors are the most important uncertainties of the *Na/K* geothermometer. Since the coefficient errors of the new improved equation are also smaller than those related to previous equations, it is fully expected than the global uncertainties of the new equation would be smaller.

CONCLUSIONS

A new precise calibration of the Na/K geothermometer was developed using a geochemical database of geothermal fluids. This new geochemical tool was successfully validated through a comparative study with actual BHT measurements logged in 103 producer wells from several geothermal fields of the world. The obtained results showed that TNKSD10 (Eq. 7) provides geothermometric temperature estimates more precise and reliable than those predicted by previous Na/K geothermometers.

The new geothermometer (Eq. 7) constitutes an improved tool that will benefit to the world geothermal industry for future exploration and exploitation tasks. Statistical comprehensive analyses of uncertainties in developing and applying new geothermometric tasks requires to be considered, and not ignored, for a better and reliable estimation of deep equilibrium temperatures. The development of more efficient and reliable geothermometry tools will help the exploration and exploitation of geothermal resources. A statistically correct use of the gothermometry tools is also likely to provide better and more reliable estimates of the energy budget of a given area, and thus, could exert constraints on the economic aspects of geothermal energy exploitation.

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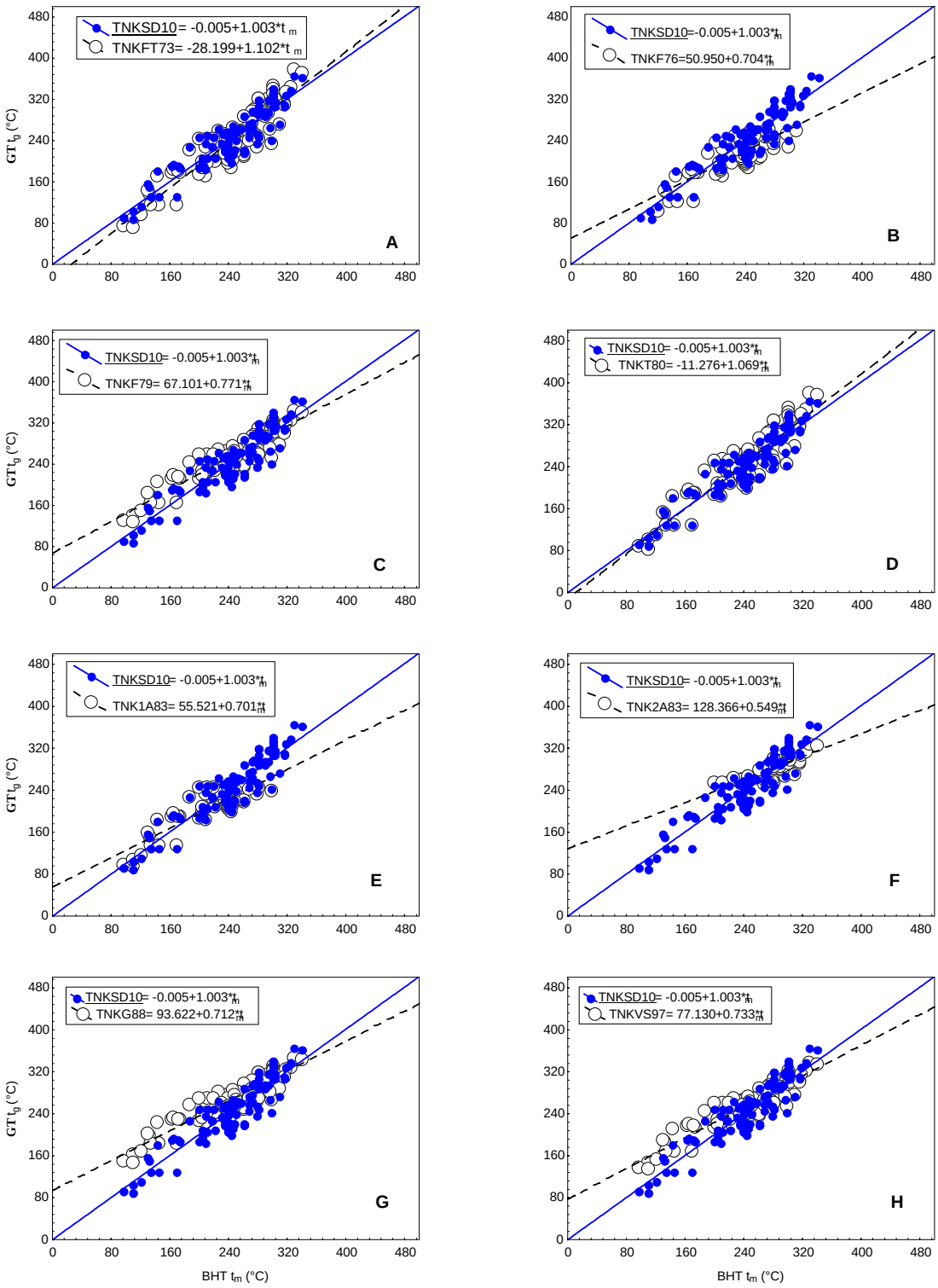

Fig. 5: Linear regression analysis between BHT measurements and geothermometric temperature estimates obtained with: (i) the *Na/K* geothermometers most commonly used in geothermal industry (TNKFT73, TNKT76, TNKF79, TNKT80, TNK1A83, TNK2A83, TNKG88 y TNKVS9), and (ii) the new improved *Na/K* geothermometer: TNKDS10. Data validation was randomly carried out using the remaining part of the GEOFDB (30%: n=103 data)

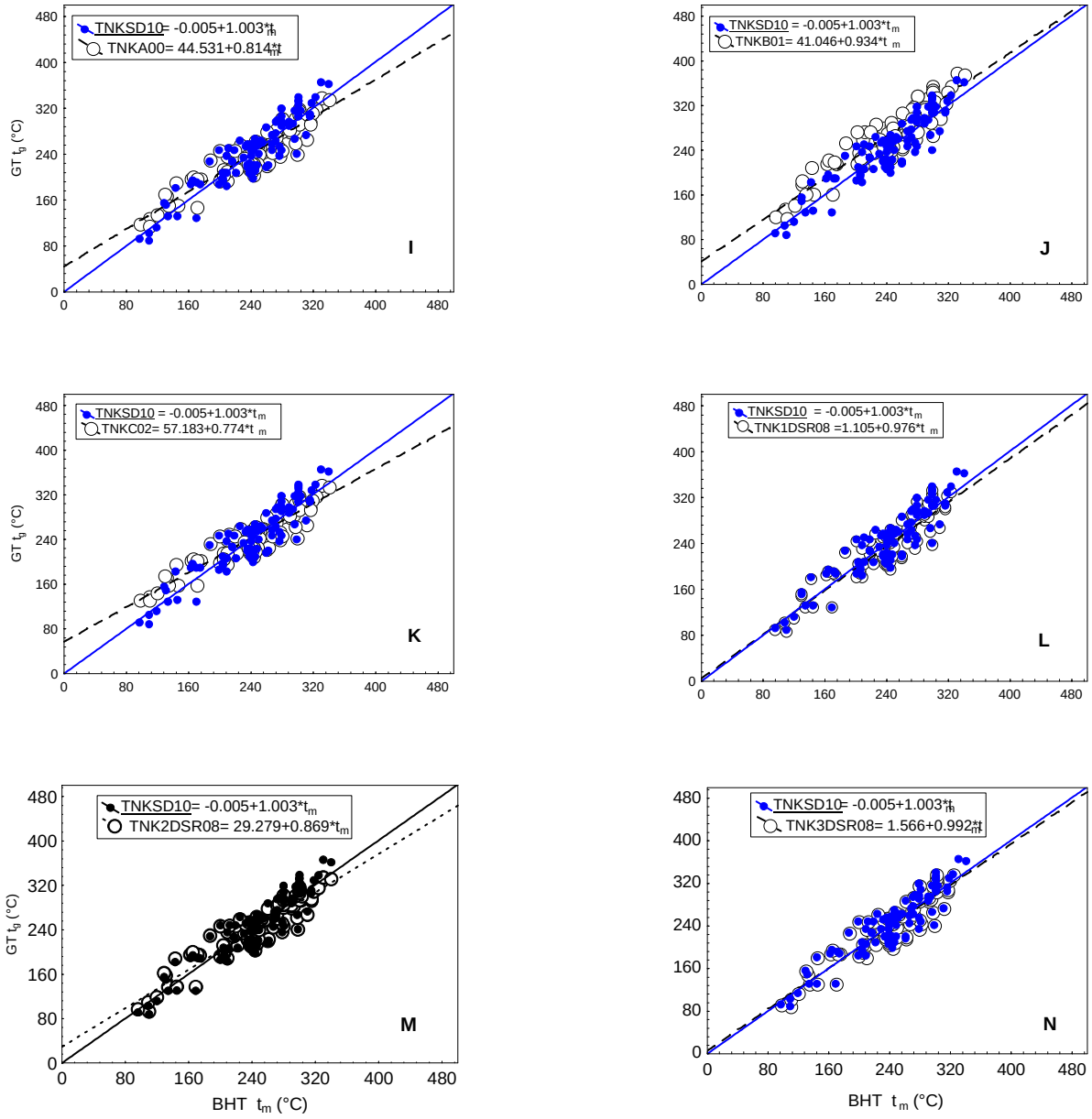

Fig 6: Linear regression analysis between BHT measurements and geothermometric temperature estimates obtained with: (i) the *Na/K* geothermometers most commonly used in geothermal industry (TNKA00, TNKB01, TNKC02, TNK1DSR08, TNK2DSR08 y TNK3DSR08), and (ii) the new improved *Na/K* geothermometer: TNKDS10