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SolGeo: A new computer program for solute geothermometers and its application to Mexican geothermal fields

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Abstract

The freely available computer program Solute Geothermometers (SolGeo) was written and tested using geochemical data and reported geothermometric temperatures from several geothermal wells from around the world. Subsurface temperatures for the Mexican geothermal fields of Cerro Prieto, Las Tres Vírgenes, Los Azufres, and Los Humeros were estimated based on different solute geothermometers and found to be generally in close agreement with measured well temperatures when considering errors in the calculations and measurements. For Los Humeros wells it was concluded that a better agreement of chemical geothermometric temperatures is observed with static formation than with bottom-hole temperatures (BHTs). It was also found that the widely used Na–K geothermometric equations generally give more consistent and more reliable temperature estimates than the other geothermometers, which should therefore be applied with caution.

Keywords: Geothermal; Geochemistry; Mexico; Computer software; Geothermal exploration; Geothermometry

1. Introduction

A plethora of geothermometric equations put forth for estimating subsurface temperatures from solute concentrations in geothermal waters are difficult to use without suitable computer software. In the 1970s, Truesdell (1976) reported computer program GEOTHERM, which was

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capable of calculating temperatures from seven geothermometric equations (see also Henley et al., 1984). Since then, numerous new equations have been proposed and used in geothermometric temperature calculations (see D'Amore and Arnórsson, 2000, or Verma, 2002, for relatively recent compilations of such equations).

Commercial program AquaChem (Version 5.1.33; http://www.swstechnology.com/software_product.php?tab=3&ID=1#index) contains 18 geothermometric equations (four for Na–K; one for K–Mg; one for Mg–Li; three for Na–Li; two for Na–K–Ca; four for quartz; three for sulfate-waters) and provides for modifying regression coefficients corresponding to most of the programmed equations, but does not allow changes to the sign (+ or −) of the coefficients. More recent equations such as those proposed by Nieva and Nieva (1987), Fournier (1991), Verma and Santoyo (1997), and Can (2002) are absent from AquaChem. El-Naqa and Zeid (1993) presented a computer program (GEOTHERM) for applying Na–K, Na–K–Ca, and silica (or quartz) geothermometers, but so far temperatures computed using this program have not been reported in the published literature.

Most geochemists use some kind of spreadsheets or hand calculators that probably lead to frequent errors, as discussed below. Therefore, there is a special need for developing freely available software that could facilitate these computations in an easy, friendly, efficient, and reliable way. With this need in mind, we developed computer program Solute Geothermometers (i.e., SolGeo) that includes 35 geothermometric equations for solute geothermometers (Table 1). A salient feature of the program is that the concentration of each chemical variable is converted to the measurement units required by each geothermometric equation (see Table 1 for these requirements) using updated values of atomic weights (e.g. Vocke, Jr., 1999; Verma et al., 2003; Wieser, 2006) and proper geothermal water density calculations and corrections (McCutcheon et al., 1993; Nicholson, 1993). Here, we present validation of SolGeo from a worldwide geothermal database and results from application to four Mexican geothermal fields.

2. SolGeo: a new computer program

Computer program SolGeo (for Solute Geothermometers) was written in Visual Basic 6.0; the main functions of the code are summarized in Fig. 1. It accepts input data as an Excel (*.xls) or a Statistica (*.sta; Version 5) file (example files are available from any of the authors on request). Thirty-five geothermometric equations and their respective applicability constraints used in SolGeo are listed in Table 1.

For each sample, the chemical variables Cl, HCO_3, SO_4, Na, K, Li, Ca, Mg, and SiO_2 (indicated without the respective charge) are compiled in an input file, and the units (mg/kg, mg/l, or the sometimes ambiguously used ppm) in a single column as reported in the literature reference. The input file also has a provision to include relative standard deviation (R.S.D.) data (analytical errors expressed as R.S.D.%) for Na, K, Li and SiO_2, if the information is available. Otherwise, typical values of 2% R.S.D. are used as default values in the error propagation module as inferred by some workers (e.g. Arnórsson, 2000; Santoyo et al., 2005).

An important feature of SolGeo is the data validation option that checks the input file for probable typographical errors such as characters in place of numbers and negative concentration values. The program also computes "% ionic balance" in several different ways according to the availability of ionic species data; either all of them (i.e. anions Cl, HCO_3, and SO_4; cations Na, K, Li, Ca, and Mg) or without Li and/or Mg if not reported. However, because of the presence of other charged species in solution that generally are not routinely determined, the use of the ionic balance as the sole indicator of data quality should be done with caution.

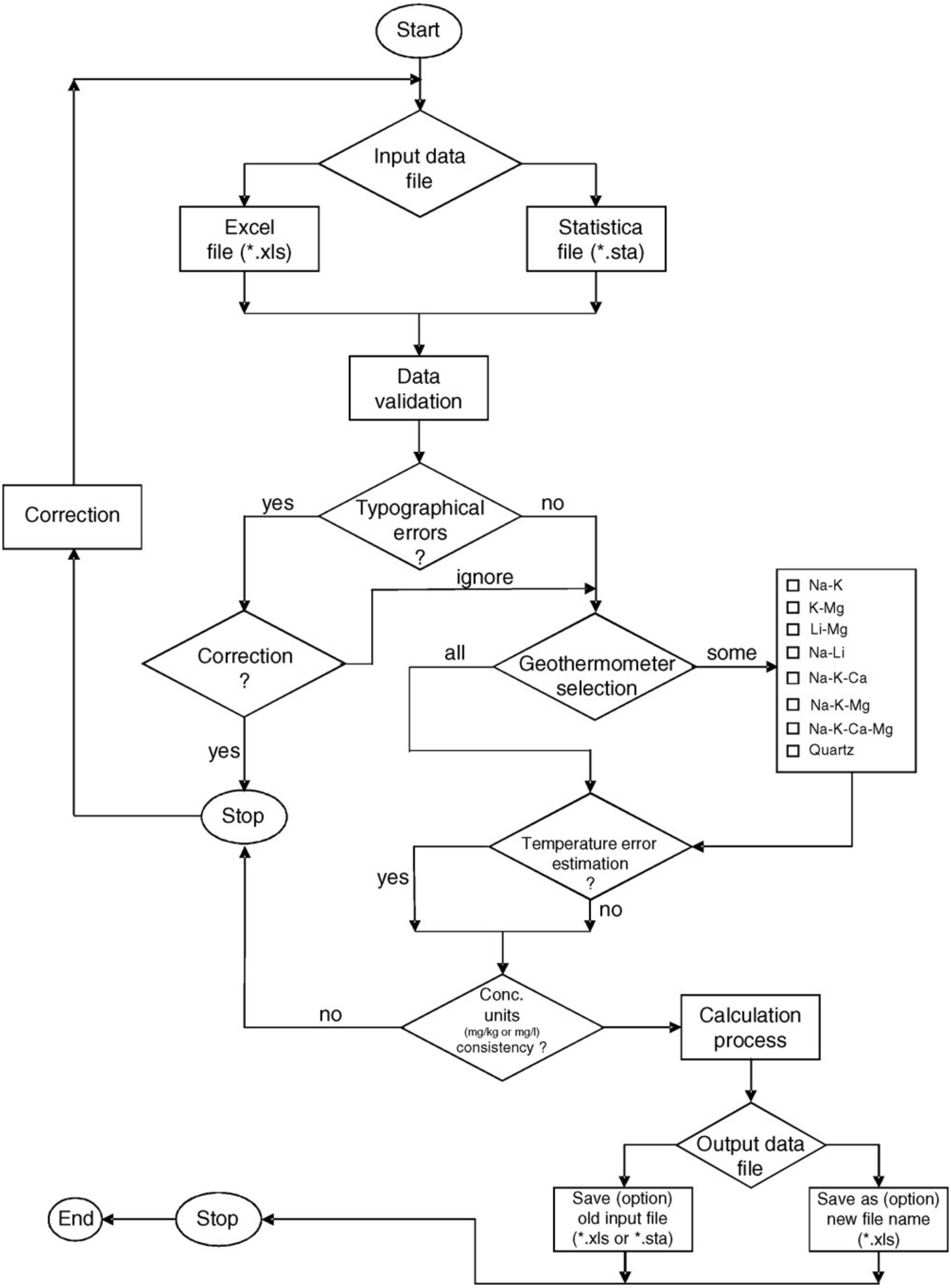

Fig. 1. Flow chart for program SolGeo.

Table 1

Solute geothermometers for geothermal exploration (modified after Verma, 2002) programmed in SolGeo

Geothermometer	Equation to obtain temperatures (in °C)[a]	Ref. [b]	Eq. no.	Geothermometer abbreviation [c]
Na–K (Fournier–Truesdell)	$\{777/[\log(Na/K)+0.700]\}-273.15$	FT73	1	TNKFT73
Na–K (Truesdell)	$\{855.6/[\log(Na/K)+0.8573]\}-273.15$	T76	2	TNKT76
Na–K (Fournier)	$\{1217(\pm 93.9)/[\log(Na/K)+1.483)]\}-273.15$	F79	3	TNKF79 ± ENKF79
Na–K (Tonani)	$\{833/[\log(Na/K)+0.780]\}-273.15$	T80	4	TNKT80
Na–K (Arnórsson-1)	$\{933/[\log(Na/K)+0.993]\}-273.15$	A83	5	TNKA83
Na–K (Arnórsson-2)	$\{1319/[\log(Na/K)+1.699]\}-273.15$	A83	6	TNK2A83
Na–K (Nieva–Nieva)	$\{1178/[\log(Na_m/K_m)+1.239]\}-273.15$	NN87	7	TNKNN87
Na–K (Giggenbach)	$\{1390/[\log(Na/K)+1.75]\}\ 273.15$	G88	8	TNKG88
Na–K (Verma–Santoyo)	$\{1289(\pm 76/[\log(Na/K)+0.615)]\}-273.15$	VS97	9	TNKVS97 ± ENKVS97
Na–K (Arnórsson)	$733.6-770.551[\log(Na_m/K_m)]+378.189[\log(Na_m/K_m)]^2$ $-95.753[\log(Na_m/K_m)]^3+9.544[\log(Na_m/K_m)]^2$	A00	10	TNKA00
Na–K (Can)	$\{1052/[1{=}\exp(1.714(\log(Na/K)+0.252))]\}+76$	C02	11	TNKC02
Na–K (DíazGonzález–Santoyo–Reyes-1)	$\{883(\pm 15)/[\log(Na/K)+0.894(\pm 0.032)]\}-273.15$	DSR07	12	TNKDSR08 ± ENKDSR08
Na–K (DíazGonzález–Santoyo–Reyes-2)	$\{833/[\log(Na/K)+0.908]\}-273.15$	DSR07	13	TNK2DS08
K–Mg (Giggenbach)	$\{4410/[14.0-\log(K^2/Mg)]\}-273.15$	G88	14	TKMG88
K–Mg (Fournier-1)	$\{2330/[7.35-\log(K^2/Mg)]\}-273.15$	F91	15	TKMF91
K–Mg (Fournier-2)	$\{1077/[4.033+\log(K^2/Mg)]\}-273.15$	F91	16	TKM2F91
Li–Mg (Kharaka–Mariner-1)	$\{2200/[5.47-\log(Li/(Mg^{0.5}))]\}-273.15$	KM89	17	TLMKM89
Li–Mg (Kharaka–Mariner-2)	$\{1910/[4.63-\log(Li/(Mg^{0.5}))]\}-273.15$	KM89	18	TLM2KM89
Na–Li (Fouillac–Michard-1)	$\{1000(\pm 47)/[\log(Na_m/Li_m)+0.38(\pm 0.11)]\}-273.15$	FM81	19	TNLFM81 ± ENLFM81
Na–Li (Fouillac–Michard-2)	$\{1195(\pm 75)/[\mathrm{Log}(Na_m/Li_m)-0.19(\pm 0.25)]\}-273.15$	FM81	20	TNL2FM81 ± ENL2FM81
Na–Li (Kharaka–Mariner)	$\{1590/[\log(Na/Li)+0.779]\}-273.15$	KM89	21	TNLKM89
Na–Li (Verma–Santoyo-1)	$\{1049(\pm 44)/[\log(Na_m/Li_m)+0.44(\pm 0.10)]\}-273.15$	VS97	22	TNLVS97 ± ENLVS97
Na–Li (Verma–Santoyo-2)	$\{1267(\pm 35)/[\log(Na_m/Li_m)+0.07(\pm 0.10)]\}-273.15$	VS97	23	TNL2VS97 ± ENL2VS97
Na–K–Ca (Fournier–Truesdell)	$\{1647/[\log(Na_m/K_m)+\beta(\log((Ca_m)0.5/Na_m)+2.06)+2.47]\}-273.15$	FT73	24	TNKCFT73
Na–K–Ca (Kharaka-Mariner)	$\{1120/[\log(Na/K)+\beta(\log(Ca0.5/Na)+2.06)+1.32]\}-273.15$	KM89	25	TNKCKM89
Na–K–Mg (Nieva–Nieva)	$\{11140/[6\log(Na_m/K_m)+\log(Mg_m/(Na_m)2)+18.30]\}-273.15$	NN87	26	TNKMNN87
Na–K–Ca–Mg (Nieva–Nieva-1)	$\{16000/[3\log(Na_m/K_m)+3\log(Ca_m/(Na_m)2)-$ $\log(Mg_m/(Na_m)2)+44.67]\}-273.15$	NN87	27	TNKCMN87
Na–K–Ca–Mg (Nieva–Nieva-2)	$\{10080/[5\log(Na_m/K_m)+2\log(Ca_m/(Na_m)^2)$ $-\log(Mg_m/(Na_m)^2)+16.65]\}-273.15$	NN87	28	NKCM2N87

Quartz (Fournier-1)	$[1309/(5.19 - \log S)] - 273.15$	F77	29	TSF77
Quartz (Fournier-2)	$[1522/(5.75 - \log S)] - 273.15$	F77	30	TS2F77
Quartz (Fournier–Potter)	$-42.198(\pm 1.345) + 0.28831(\pm 0.01337)S - 3.6686 \times 10^{-4}$ $(\pm 3.152 \times 10^{-5})S^2 + 3.1665 \times 10^{-7}(\pm 2.421 \times 10^{-7})S^3 + 77.034(\pm 1.216)\log S$	FP82	31	TSFP82 ± ESFP82
Quartz (Verma–Santoyo-1)	$-\{44.119(\pm 0.438)\} + \{0.24469(\pm 0.00573)\}S - \{1.7414 \times 10^{-4}$ $(\pm 1.365 \times 10^{-5})\}S^2 + \{79.305(\pm 0.427)\}\log S$	VS97	32	TSVS97 ± ESVS97
Quartz (Verma–Santoyo-2)	$[140.82(\pm 0.00)] + [0.23517(\pm 0.00179)]S$	VS97	33	TS2VS97 ± ES2VS97
Quartz (Arnórsson-2)	$-55.3 + 0.3659S - 5.3954 \times 10^{-4}S^2 + 5.5132 \times 10^{-7}S^3 + 74.360 \log S$	A00	34	TS2A00
Quartz (Verma)	$\{[1175.7(\pm 31.7)]/[4.88(\pm 0.08) - \log S]\} - 273.15$	V00	35	TSV00

A00, Arnórsson (2000); temperature range: 0–350 °C, directly applicable for dilute to moderately saline waters; A83, Arnórsson et al. (1983); the first equation (Arnórsson-1) is applicable for 25–250 °C, whereas the second (Arnórsson-2) is for 250–350 °C; C02, Can (2002); concentrations are in mg/kg; applicable for the temperature range used for calibration, approximately 100–350 °C; DSR07, Díaz-González et al. (in press); the database for proposing both geothermometric equations was for temperatures between 30 and 350 °C; F77, Fournier (1977); all geothermometers given by this author are applicable for 0–250 °C; quartz (Fournier-1) for no steam loss; quartz (Fournier-2) for maximum steam loss (silica concentrations in water initially in equilibrium with quartz after adiabatic boiling to 100 °C); F79, Fournier (1979); applicable for temperatures >150 °C; certainly not recommended for temperatures <100 °C when this geothermometer might give anomalously high temperatures; note the errors in the regression coefficients were reported by Verma and Santoyo (1997); F91, Fournier (1991); K–Mg (Fournier-1) geothermometer is applicable for $\log(K^2/Mg) > 1.25$, whereas K–Mg (Fournier-2) is for $\log(K^2/Mg) < 1.25$. Note that in the present work, most geothermometric temperatures calculated by K–Mg (Fournier-2; equation 16 above) were found to be negative values; the change of the + sign to the − sign in this equation resulted in a lesser number of negative geothermometric temperatures, but the problem still persisted; FM81, Fouillac and Michard (1981); Na–Li (Fouillac–Michard-1) geothermometer is applicable for $Cl < 0.3$ mol/kg, Na–Li (Fouillac–Michard-2) for $Cl > 0.3$ mol/kg; the errors in the regression coefficients were reported by Verma and Santoyo (1997); FP82, Fournier and Potter II (1982) presented a modified geothermometric equation after Fournier's earlier work; the errors in the regression coefficients were reported by Verma and Santoyo (1997); FT73, Fournier and Truesdell (1973); the equations were apparently not reported by the authors explicitly but were inferred by Arnórsson (1991); concentrations are in mg/kg in the Na–K geothermometer, but in mol/kg (molal) in the Na–K–Ca geothermometer; β, 4/3 for $t < 100$ °C, β, 1/3 for $t > 100$ °C and β, 1/3 for $t < 100$ °C and $\log(Ca^{0.5}/Na) < 0$; Mg correction is recommended for Na–K–Ca (Fournier–Truesdell) geothermometer; see Fournier (1991) or D'Amore and Arnórsson (2000) for details. Because a very large number of temperature estimates for the Na–K–Ca geothermometer (TNKCFT73) were negative (see Fig. 4), we decided to include a parallel equation using mg/kg, as suggested in Fournier (1991), and added a new column TNKCF73M in the output file; G88, Giggenbach (1988); for Na–K (Giggenbach) geothermometer, the Na–K pair reaches equilibrium slower than the K–Mg pair used in the K–Mg (Giggenbach) geothermometer, and therefore the earlier pair should provide more reliable results; KM89, Kharaka and Mariner (1989); the concentrations are in mg/l (which is close to, but not identical to mg/kg); Li–Mg (Kharaka–Mariner-1) is for all waters; Li–Mg (Kharaka–Mariner-2) is particularly useful for oil-field waters; use Na–K–Ca (Kharaka–Mariner) geothermometer only when no Mg data are available, β, 1/3 for all samples; NN87, Nieva and Nieva (1987); the abbreviations are: TMEQ, $Na + K + Ca + Mg$, all in meq/kg; $\%Mg = 100Mg/TMEQ$; the conditions are: (a) for Na–K (Nieva–Nieva) geothermometer, $TMEQ > 8.0$, $\%Mg \leq 3.5$, $t_{Na-K} > 125$ °C; (b) for Na–K–Mg (Nieva–Nieva), $TMEQ < 8.0$, $\%Mg > 3.5$, $Mg^{0.5}/Na \leq 1.7$, $Ca^{0.5}/Na \leq 2.6$, $t_{Na-K} \leq 125$ °C; (c) for Na–K–Ca–Mg (Nieva–Nieva-1), $TMEQ < 8.0$, $\%Mg > 3.5$, $Mg^{0.5}/Na > 1.7$, $t_{Na-K} \leq 125$ °C; (d) for Na–K–Ca–Mg (Nieva–Nieva-2), $TMEQ < 8.0$, $\%Mg \leq 3.5$, $Mg^{0.5}/Na > 1.7$, $Ca^{0.5}/Na > 2.6$, $t_{Na-K} \leq 125$ °C. TCCGNN87 is one of these temperatures (TNKNN87, TNKMNN87, TNKCMN87, or NKCM2N87) depending on conditions; T76, Truesdell (1976) cited in Henley et al. (1984); applicable in the 100–275 °C range; T80, Tonani (1980); this reference was not available to us, and, therefore, correctness of the equation could not be checked; this equation was reported by Fournier (1991), Arnórsson (1991), and D'Amore and Arnórsson (2000), from where it has been reproduced; V00, Verma (2000); silica value should be corrected iteratively for the vapor fraction in the geothermal reservoir. This is only possible if enthalpy information is available for a given well. Therefore, SolGeo provides only an approximate temperature for this geothermometer. A more appropriate computer program for this particular geothermometer is available from Verma; VS97, Verma and Santoyo (1997); note that errors were estimated for each regression parameter in this and other equations; the Na–Li (Verma–Santoyo-1) geothermometer is for $Cl < 0.3$ mol/kg, the Na–Li (Verma–Santoyo-2) geothermometer is for $Cl > 0.3$ mol/kg. Quartz (Verma–Santoyo-1) is applicable for 20–210 °C, whereas quartz (Verma–Santoyo-2) should be used for 210–330 °C.

[a] Concentrations of Na, K, Li, Ca, and Mg are in mg/kg (element symbols are used for this purpose); S is the concentration of SiO_2 in mg/kg. Concentrations in molal units are indicated by the subscript m, i.e. Na_m, K_m, Li_m, Ca_m, and Mg_m, whereas mg/l units are indicated by an underline, i.e. Na, K, and Ca.

[b] Reference (Ref.) abbreviations, along with pertinent comments, are given here.

[c] Geothermometer abbreviations are given in Table 2.

A salient feature of SolGeo is that for a given sample the concentrations of the chemical variables are converted to the units required for (a) each geothermometric equation (see Table 1) using updated and more accurate atomic weights (e.g. Vocke, Jr., 1999; Verma et al., 2003; Wieser, 2006), and (b) geothermal water density calculations and corrections (McCutcheon et al., 1993; Nicholson, 1993). For chemical data reported in mg/l or ppm (taken as equivalent to mg/l following the common analytical practice; see also Nicholson, 1993), the density calculations are carried out in a loop. When the data are given in mg/kg, the density calculations are simpler. The program also provides an output for density data as well as for all concentrations that were recalculated into mol/kg units.

Another important feature of SolGeo is the calculation of total propagated errors for geothermometric temperatures (Bevington and Robinson, 2003; see also Verma, 2005 for approximations and applicability conditions). At present, it is possible to estimate total propagated errors for 10 geothermometric equations (i.e. three Na–K, four Na–Li, and three SiO_2 equations; see the last column in Table 1). All abbreviations used in Table 1 and in the input or output files are explained in Table 2.

SolGeo (with a few example files and a Readme file) is available on request from the authors for use by those interested in applying this tool for geothermal and other geological applications.

3. Geochemical databases for program validation and application

Geochemical data on well waters and measured bottom-hole temperatures (BHTs) were compiled from the following geothermal fields: (1) Berlin, El Salvador (D'Amore and Mejia, 1999); (2) Fushime, Japan (Okada et al., 2000); (3) Geysir, Iceland (Pasvanoglu, 1998); (4) Kizildere, Turkey (Gôkgôz, 1998); (5) Miravalles, Costa Rica (Fung, 1998); (6) Salihli, Turkey (Tarcan et al., 2000); (7) Seferihisar, Turkey (Tarcan and Gemici, 2003); (8) Takigami, Japan (Furuya et al., 2000); (9) Xiaotangshang, China (Xiaoping, 1998). Well chemical and temperature data were also compiled from Nieva and Nieva (1987) for Czechoslovakia, Chile, El Salvador, Hungary, Iceland, Japan, New Zealand, Turkey, U.S.A., and U.S.S.R. Similarly, the data compiled and used by Can (2002) were included in the database. A total of 311 samples were compiled in a worldwide database for evaluating the functioning and use of SolGeo.

For the application of the program to Mexican geothermal fields, well data were compiled on: (1) Cerro Prieto, Baja California (Mañon et al., 1987; Nieva and Nieva, 1987; Hurtado, 1990; Sampedro et al., 1990; Verma and Santoyo, 1997); (2) Las Tres Vírgenes, Baja California Sur (Tello Hinojosa, 2005; Verma et al., 2006a); (3) Los Azufres, Michocán (Kruger et al., 1985; Nieva and Nieva, 1987; Ochoa Pérez and Meza de Luna, 1989; González-Partida et al., 2005); (4) Los Humeros, Puebla (López Mendiola and Munguía Bracamontes, 1989; Viggiano Guerra and Quijano León, 1989; Tello Hinojosa, 1992; Prol-Ledesma, 1998; González Partida et al., 2001). A total of 268 samples were compiled for evaluating the application of geothermometers to all the Mexican fields where geothermal fluids are presently being used in electricity generation.

4. Results and discussion

We processed both the worldwide and the Mexican databases with SolGeo. The information from the worldwide database was used for performance validation by comparing geothermometric temperatures given in the literature (t_{lit}) against SolGeo computed temperatures (t_{SolGeo}); the results are shown in Fig. 2 in the form of "Difference" values (see the figure caption for explanation). In Table 3 are listed the miscalculated samples showing greater than ±4 °C difference

Table 2
Geothermometer abbreviations used in program SolGeo

Geothermometer abbreviation	Explanation
TNKFT73	Temperature from Na–K geothermometer of Fournier and Truesdell (1973)
TNKT76	Temperature from Na–K geothermometer of Truesdell (1976)
TNKF79 ± ENKF79	Temperature from Na–K geothermometer of Fournier (1979) and its error estimate
TNKT80	Temperature from Na–K geothermometer of Tonani (1980)
TNKA83	Temperature from Na–K geothermometer-1 of Arnórsson et al. (1983)
TNK2A83	Temperature from Na–K geothermometer-2 of Arnórsson et al. (1983)
TNKNN87	Temperature from Na–K geothermometer of Nieva and Nieva (1987)
TNKG88	Temperature from Na–K geothermometer of Giggenbach (1988)
TNKVS97 ± ENKVS97	Temperature from Na–K geothermometer of Verma and Santoyo (1997) and its error estimate
TNKA00	Temperature from Na–K geothermometer of Arnórsson (2000)
TNKC02	Temperature from Na–K geothermometer of Can (2002)
TNKDSR08 ± ENKDSR08	Temperature from Na–K geothermometer-1 of Díaz-González et al. (in press) and its error estimate
TNK2DS08	Temperature from Na–K geothermometer-2 of Díaz-González et al. (in press)
TKMG88	Temperature from K–Mg geothermometer of Giggenbach (1988)
TKMF91	Temperature from K–Mg geothermometer-1 of Fournier (1991)
TKM2F91	Temperature from K–Mg geothermometer-2 of Fournier (1991)
TLMKM89	Temperature from Li–Mg geothermometer-1 of Kharaka and Mariner (1989)
TLM2KM89	Temperature from Li–Mg geothermometer-2 of Kharaka and Mariner (1989)
TNLFM81 ± ENLFM81	Temperature from Na–Li geothermometer-1 of Fouillac and Michard (1981) and its error estimate
TNL2FM81 ± ENL2FM81	Temperature from Na–Li geothermometer-2 of Fouillac and Michard (1981) and its error estimate
TNLKM89	Temperature from Na–Li geothermometer-1 of Kharaka and Mariner (1989)
TNLVS97 ± ENLVS97	Temperature from Na–Li geothermometer-1 of Verma and Santoyo (1997) and its error estimate
TNL2VS97 ± ENL2VS97	Temperature from Na–Li geothermometer-2 of Verma and Santoyo (1997) and its error estimate
TNKCFT73	Temperature from Na–K–Ca geothermometer of Fournier and Truesdell (1973), mol/kg unit
TNKCF73M	Temperature from Na–K–Ca geothermometer of Fournier and Truesdell (1973), mg/kg unit
TNKCKM89	Temperature from Na–K–Ca geothermometer of Kharaka and Mariner (1989)
TNKMNN87	Temperature from Na–K–Mg geothermometer of Nieva and Nieva (1987)
TNKCMN87	Temperature from Na–K–Ca–Mg geothermometer-1 of Nieva and Nieva (1987)
NKCM2N87	Temperature from Na–K–Ca–Mg geothermometer-2 of Nieva and Nieva (1987)
TSF77	Temperature from quartz geothermometer-1 of Fournier (1977)
TS2F77	Temperature from quartz geothermometer-2 of Fournier (1977)
TSFP82 ± ESFP82	Temperature from quartz geothermometer of Fournier and Potter II (1982) and its error estimate
TSVS97 ± ESVS97	Temperature from quartz geothermometer-1 of Verma and Santoyo (1997) and its error estimate
TS2VS97 ± ES2VS97	Temperature from quartz geothermometer-2 of Verma and Santoyo (1997) and its error estimate
TS2A00	Temperature from quartz geothermometer-2 of Arnórsson (2000)
TSV00	Temperature from quartz geothermometer of Verma (2000)

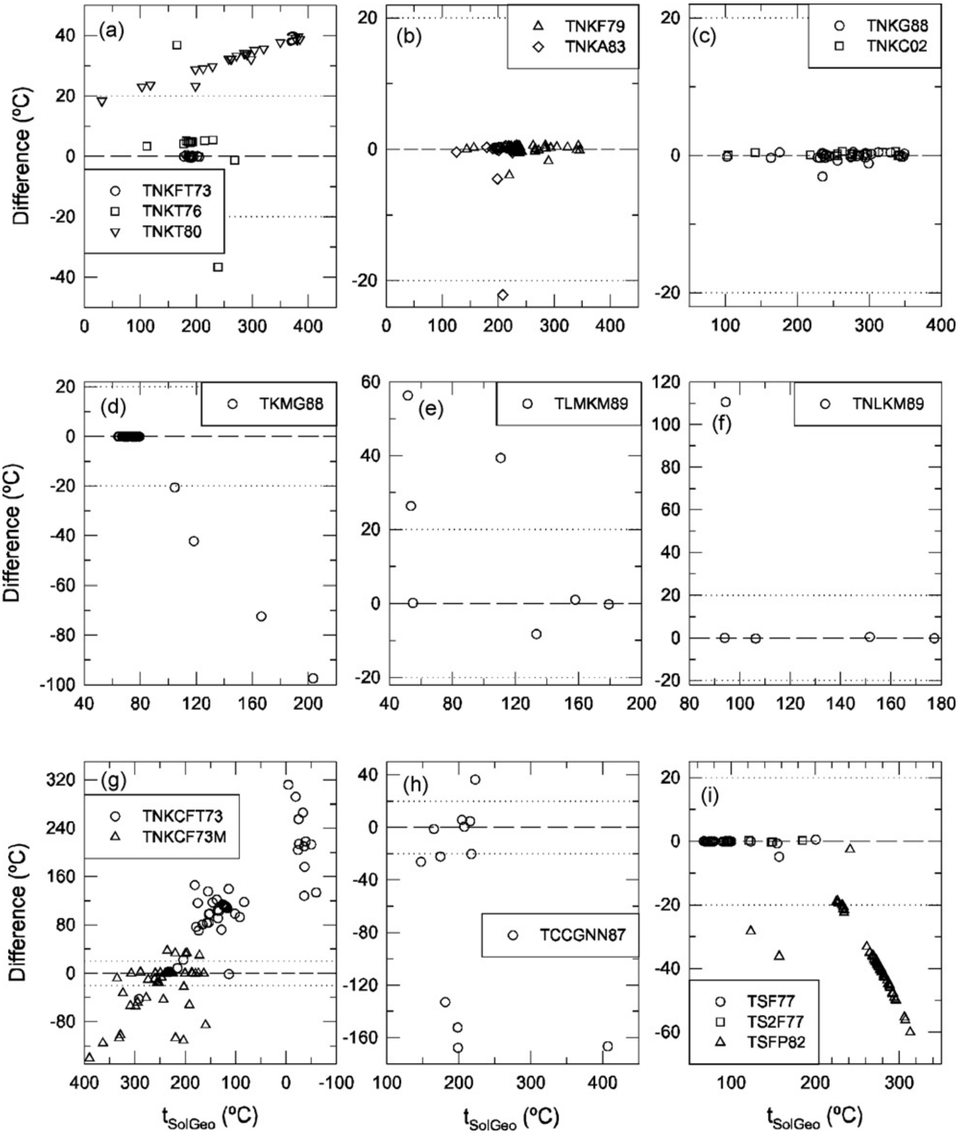

Fig. 2. Differences [Difference = ($t_{\text{lit}} - t_{\text{SolGeo}}$)] between geothermometric temperatures reported in the literature (t_{lit}) and those calculated by SolGeo software (t_{SolGeo}) using the worldwide database. Note samples falling right on the horizontal "zero-difference dashed" line in each diagram (i.e. at difference = 0) show no (or negligible) temperature difference. Dotted lines at Difference = +20 °C and −20 °C are also shown for reference (see text for more details). (a) Na–K geothermometers of Fournier and Truesdell (1973), Truesdell (1976), and Tonani (1980); (b) Na–K geothermometers of Fournier (1979) and Arnórsson et al. (1983); (c) Na–K geothermometers of Giggenbach (1988) and Can (2002); (d) K–Mg geothermometer of Giggenbach (1988); (e) Li–Mg geothermometer of Kharaka and Mariner (1989); (f) Na–Li geothermometer of Kharaka and Mariner (1989); (g) Na–K–Ca geothermometer of Fournier and Truesdell (1973) with two different measurement units mol/kg and mg/kg, see Tables 1 and 2; (h) Cationic composition geothermometer (CCG) of Nieva and Nieva (1987); (i) quartz geothermometers of Fournier (1977) and Fournier and Potter II (1982). Geothermometer abbreviations are given in Table 2.

Table 3
Comparison of SolGeo geothermometric temperatures against those reported in the literature for geothermal fields worldwide

Geothermometer abbreviations[a]	Number of miscalculated samples (total number of samples) Literature source[b]
TNKT76	***8*** (8) Go98, ***3*** (4) DM99, ***2*** (4) P98
TNKT80	***5*** (5) P98, ***16*** (16) C02
TNKA83	***1*** (4) P98, ***1*** (4) T00
TKMG88	***4*** (4) P98
TLMKM89	***2*** (5) P98, ***2*** (2) T00
TNLKM89	***1*** (5) P98
TNKCFT73	***12*** (12) NN87, ***82*** (82) Fu98, ***8*** (8) Go98, ***5*** (5) P98, ***7*** (7) DM99, ***3***(4) T00
TNKCF73M	***5*** (12) NN87, ***1*** (82) Fu98, ***8*** (8) Go98, ***5*** (5) P98, ***4*** (7) DM99, ***3***(4) T00
TCCGNN87	***10*** (12) NN87
TSF77	***1*** (4) T00
TSFP82	***62*** (62) Fu98, ***8*** (8) Go98, ***2*** (3) DM99, ***2*** (2) T00

[a] Geothermometer abbreviations are given in Table 2.

[b] Number of samples processed by a given author is given in parentheses, whereas the number of samples with more than ±4 °C difference between SolGeo and reported temperatures is shown in italic boldface. For example, ***8*** (8) Go98 mean that all the eight samples processed by Go98 showed such large differences whereas ***3*** (4) DM99 mean that three out of four samples processed by DM99 showed such significant differences. Note that the papers reporting only correctly calculated samples are *not* included in this table. The literature sources are: C02, Can (2002); DM99, D'Amore and Mejia (1999); Fu98, Fung (1998); Go98, Gôkgôz (1998); NN87, Nieva and Nieva (1987); P98, Pasvanoglu (1998); T00, Tarcan et al. (2000).

between t_{lit} and t_{SolGeo}. Similarly, the computed t_{SolGeo} for the worldwide database were compared against measured BHTs to evaluate geothermometer performance; see Figs. 3 and 4. The results for the Mexican database are presented in Figs. 5 and 6.

4.1. SolGeo performance evaluation using the worldwide database

Most samples (Fig. 2) compiled by numerous authors (Fung, 1998; Gôkgôz, 1998; Pasvanoglu, 1998; Xiaoping, 1998; D'Amore and Mejia, 1999; Tarcan et al., 2000; Can, 2002; Tarcan and Gemici, 2003) plot on the horizontal "zero-difference dashed line" in Fig. 2a–i, showing that SolGeo temperatures match those reported for the respective geothermometers. For example, all results are in total agreement with SolGeo calculations for the Na–K geothermometers of Fournier and Truesdell (1973; Fig. 2a) and Can (2002; Fig. 2c). Similarly, results for the Na–K geothermometers of Fournier (1979; Fig. 2b) and Giggenbach (1988; Fig. 2c), for the Na–Li geothermometer of Kharaka and Mariner (1989; Fig. 2f), and for the quartz geothermometer of Fournier (1977; Fig. 2i) are also in agreement, with the exception of one or two samples.

An unexpectedly large number of samples plot far from the zero-difference dashed line (Fig. 2a–i), for example, those for Na–K geothermometry of Tonani (1980) (inverted triangles, Fig. 2a), along with two samples for Truesdell (1976) geothermometer (squares, Fig. 2a). Tonani (1980) geothermometric temperatures were reported by Pasvanoglu (1998) and Can (2002). We do not understand why the Tonani temperatures calculated by these two authors are different from those given by SolGeo, particularly since Pasvanoglu (1998) reported Truesdell (1976) geothermometric temperatures identical to SolGeo results (squares, Fig. 2a), and Can (2002) did so for Fournier (1979) (triangles, Fig. 2b) and Giggenbach (1988) (circles, Fig. 2c). Similarly, it is not clear why three samples out of a total of four reported by D'Amore and Mejia (1999), but not all, show Truesdell (1976) geothermometric temperatures different from those computed using

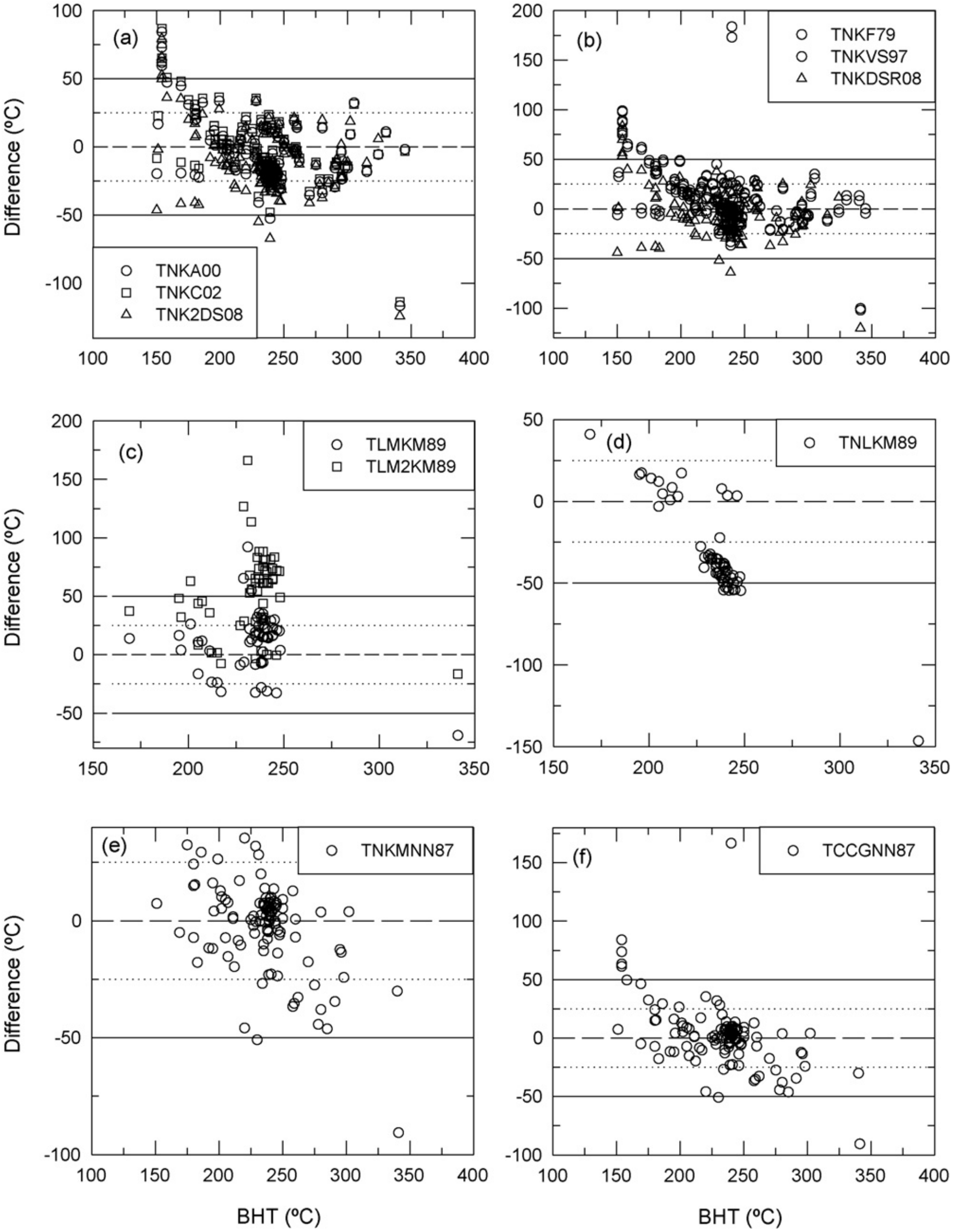

Fig. 3. Differences [Difference = ($t_{\mathrm{SolGeo}} - \mathrm{BHT}$)] between SolGeo geothermometric temperatures (t_{SolGeo}) and bottom-hole temperatures (BHTs) using the worldwide database. Only geothermometers with relatively small differences are included in the figure. Note samples falling right on the zero-difference dashed line in each diagram (at Difference = 0) show no (or negligible) temperature differences. Dotted lines at Difference = +25 °C and −25 °C and solid lines at Difference = +50 °C and −50 °C are also shown for reference (see text for more details). (a) Na–K geothermometers (Arnórsson, 2000; Can, 2002; Díaz-González et al., in press); (b) Na–K geothermometers (Fournier, 1979; Verma and Santoyo, 1997; Díaz-González et al., in press); (c) Li–Mg geothermometer (Kharaka and Mariner, 1989); (d) Na–Li geothermometer (Kharaka and Mariner, 1989); (e) Na–K–Mg geothermometer (Nieva and Nieva, 1987); (f) Cationic composition geothermometer (Nieva and Nieva, 1987). Geothermometer abbreviations are given in Table 2.

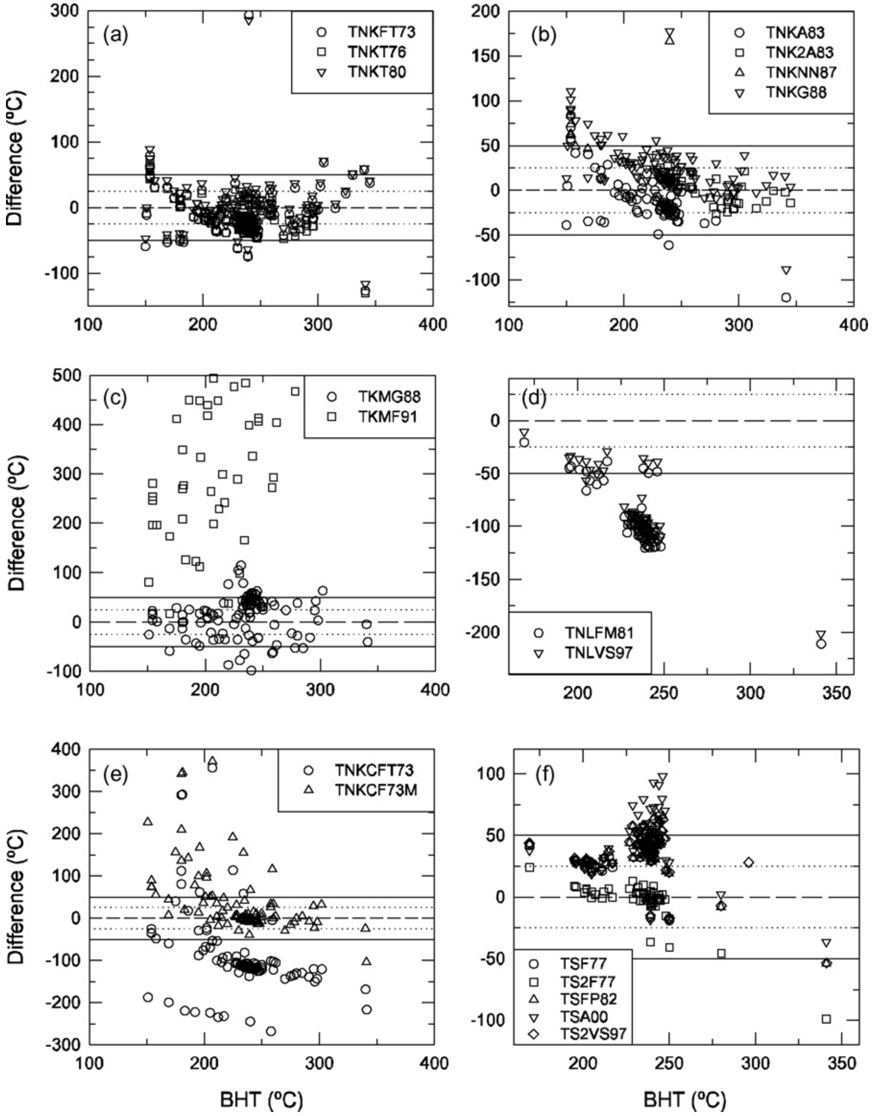

Fig. 4. Differences [Difference = ($t_{\mathrm{SolGeo}} - \mathrm{BHT}$)] between SolGeo geothermometric temperatures (t_{SolGeo}) and BHTs using the worldwide database. Geothermometers with greater differences are included in this figure; they were not included in Fig. 3. See text for more details. (a) Na–K geothermometers (Fournier and Truesdell, 1973; Truesdell, 1976; Tonani, 1980); (b) Na–K geothermometers (Arnórsson et al., 1983; Nieva and Nieva, 1987; Giggenbach, 1988); (c) K–Mg geothermometers (Giggenbach, 1988; Fournier, 1991), note the y-scale up to 500 °C excludes several unrealistically high Fournier (1991) values; (d) Na–Li geothermometers (Fouillac and Michard, 1981; Verma and Santoyo, 1997); (e) Na–K–Ca geothermometer (Fournier and Truesdell, 1973), for TNKCF73M see Tables 1 and 2 and (f) quartz geothermometers (Fournier, 1977; Fournier and Potter II, 1982; Verma and Santoyo, 1997; Arnórsson, 2000). Geothermometer abbreviations are given in Table 2.

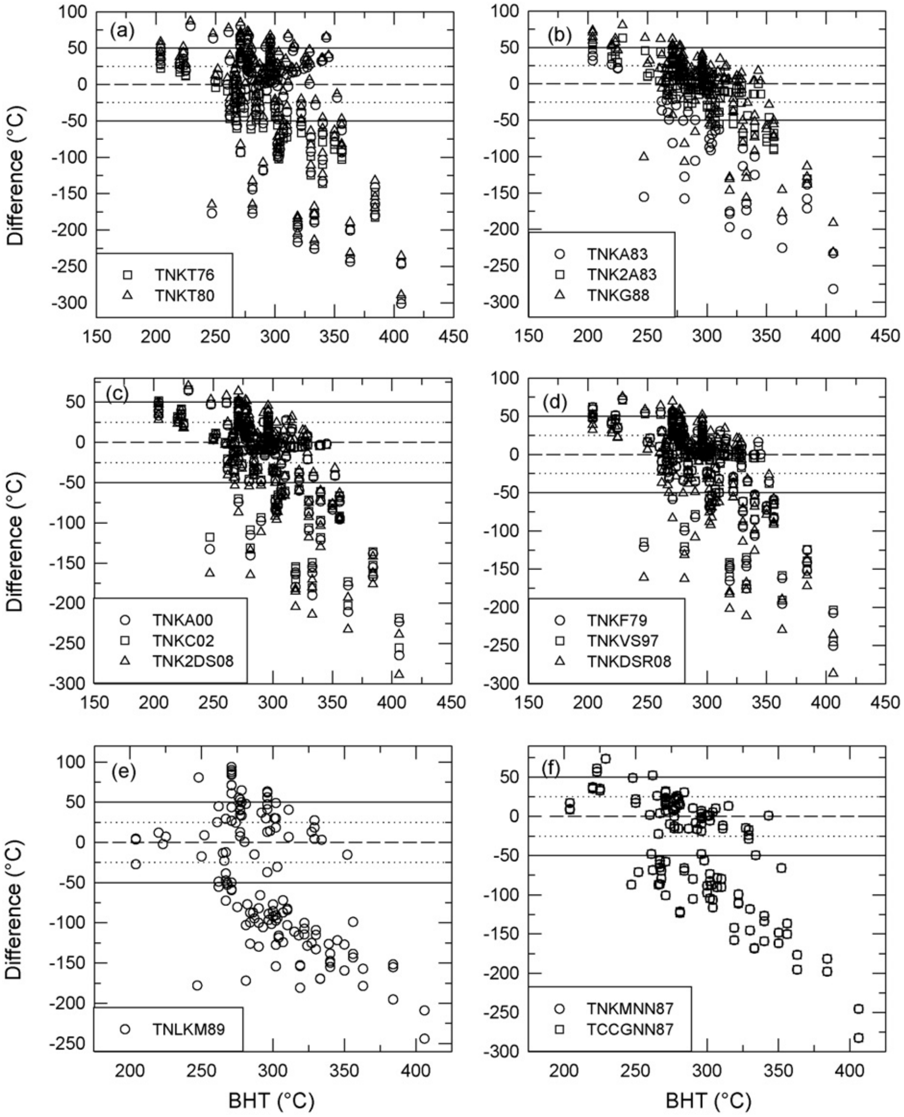

Fig. 5. Differences [Difference = (t_{SolGeo} − BHT)] between SolGeo geothermometric temperatures (t_{SolGeo}) and BHTs using the Mexican database; see caption of Fig. 3 for more details. (a) Na–K geothermometers (Fournier and Truesdell, 1973; Truesdell, 1976; Tonani, 1980); (b) Na–K geothermometers (Arnórsson et al., 1983; Giggenbach, 1988); (c) Na–K geothermometers (Arnórsson, 2000; Can, 2002; Díaz-González et al., in press); (d) Na–K geothermometers (Fournier, 1979; Verma and Santoyo, 1997; Díaz-González et al., in press); (e) Na–Li geothermometer (Kharaka and Mariner, 1989); (f) Na–K–Mg and cationic composition geothermometers (Nieva and Nieva, 1987). Geothermometer abbreviations are given in Table 2.

SolGeo (see Table 3). The Na–K geothermometer of Arnórsson et al. (1983) generally presented reliable calculations (Fig. 2b; Table 3).

The temperatures of all four samples reported by Pasvanoglu (1998) that were based on the K–Mg geothermometer of Giggenbach (1988) show large inconsistencies (−20 to −97 °C) with

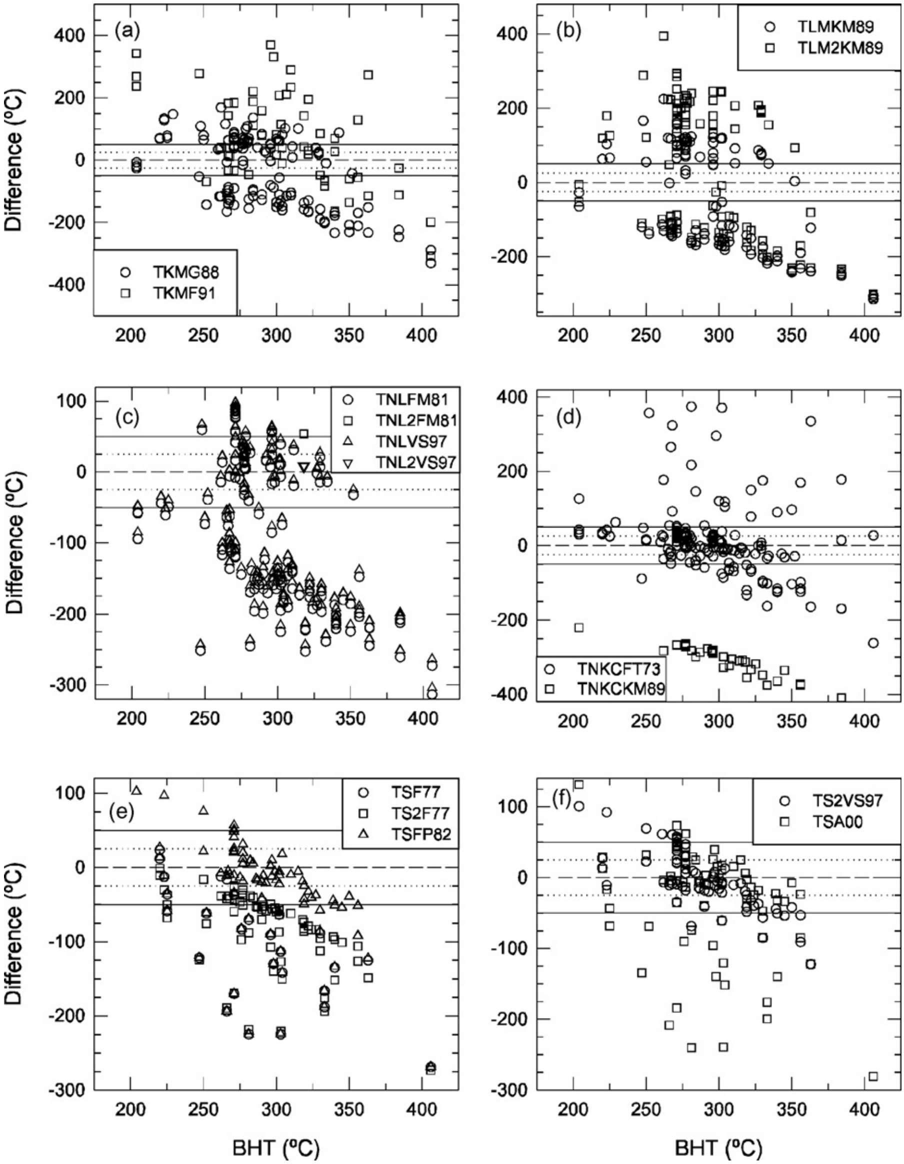

Fig. 6. Differences [Difference = (t_{SolGeo} − BHT)] between SolGeo geothermometric temperatures (t_{SolGeo}) and BHTs using the Mexican database. See caption of Fig. 4 for more details. (a) K–Mg geothermometers (Giggenbach, 1988; Fournier, 1991) note the *y*-scale up to 500 °C excludes several unrealistically high Fournier (1991) values; (b) Li–Mg geothermometer (Kharaka and Mariner, 1989); (c) Na–Li geothermometers (Fouillac and Michard, 1981; Verma and Santoyo, 1997); (d) Na–K–Ca geothermometesr (Fournier and Truesdell, 1973; Kharaka and Mariner, 1989); (e) quartz geothermometers (Fournier, 1977; Fournier and Potter II, 1982); (f) quartz geothermometers (Verma and Santoyo, 1997; Arnórsson, 2000). Geothermometer abbreviations are given in Table 2.

SolGeo results (circles plotting far from the zero-difference dashed line in Fig. 2d), whereas the temperatures of all 53 samples reported by Xiaoping (1998) are consistent with SolGeo results (circles on the dashed line in Fig. 2d). Large inconsistencies in the reported temperatures of Pasvanoglu (1998) may be the result of an incorrect formula, which has "$(K/\sqrt{Mg})$" instead of "$(K^2/\sqrt{Mg})$".

Temperatures estimated using the Li–Mg geothermometer of Kharaka and Mariner (1989) for three samples reported by Pasvanoglu (1998) plot on the zero-difference dashed line (Fig. 2e) whereas other results (two from Pasvanoglu, 1998; two from Tarcan et al., 2000) show significant differences (Table 3). The reason for these discrepancies seems to be calculation or transcription errors when using spreadsheets. Similarly, for the Na–Li geothermometer of Kharaka and Mariner (1989), Pasvanoglu (1998) reported one sample (out of five) with an erroneous result (Fig. 2f; Table 3).

The Na–K–Ca geothermometer of Fournier and Truesdell (1973), used by numerous authors, gave highly contradictory results especially when concentrations were given in mol/kg (see numerous circles in Fig. 4e that show negative differences, which imply unexpectedly low geothermometric temperatures; Table 3). The same geothermometer showed better agreement when mg/kg units were used (also programmed in SolGeo; see a few triangles in Fig. 4e showing negative differences; Table 3). Using the latter equation (see footnote of Table 3) fully consistent results were obtained for 81 of the 82 samples reported by Fung (1998) implying that for this geothermometer the author had used concentrations in mg/kg.

Temperatures reported by Nieva and Nieva (1987) computed using their own geothermometer (CCG) showed large calculation or transcription discrepancies for numerous samples (Table 3; Fig. 2h). Alternatively, this problem may be related to the equations and solutes (Na–K, Na–K–Ca, or Na–K–Ca–Mg) that have to chosen when using the CCG geothermometer, which depend on numerous conditions (see TCCGNN87 in the footnote of Table 1, and Nieva and Nieva, 1987).

The quartz geothermometer of Fournier and Potter II (1982) was probably incorrectly used by numerous authors (Table 3) as evidenced by samples that plot away from the zero-difference dashed line (triangles in Fig. 2i).

The existence of the discrepancies described above highlight the value of a suitable computer program, such as SolGeo, when calculating geothermometric temperatures since it should help minimize errors.

4.2. Geothermometer performance evaluation using the worldwide database

The solute geothermometric temperatures given by SolGeo can be evaluated by comparing them with either the measured BHTs or the static formation temperature (SFTs) estimates. The measured BHTs are usually perturbed by the drilling operations, but have been used in the calibration of solute geothermometers, instead of aquifer or equilibrium temperatures. Homogenization temperatures inferred from fluid inclusions can also represent the equilibrium temperatures of geothermal systems (e.g. González-Partida et al., 2000).

The maximum temperatures measured in geothermal wells do not always represent the aquifer temperatures at which a deep fluid had equilibrated (e.g. Fournier and Truesdell, 1973). The SFTs (also known as equilibrium or stabilized formation temperatures) are defined as the natural-state formation temperatures that exist in a geothermal system before the thermal perturbation produced by the drilling operations (e.g. Manetti, 1973; Barelli and Palamá, 1981; Deming, 1989; Santoyo et al., 2000). The SFTs are thus closer to the equilibrium reservoir temperatures that governed the initial water–rock interaction processes.

Estimated SFTs are usually calculated from three or more BHT measurements logged at the same wellbore depth but at different shut-in times after drilling completion. The BHT build-up data are extrapolated to estimate the SFTs, at any particular wellbore depth, using simplified analytical methods derived from the well-known line and cylindrical heat source methods (e.g. Dowdle and Cobb, 1975; Hasan and Kabir, 1994; Andaverde et al., 2005). In geothermal wells BHT and SFTs data may be significantly different (e.g. Andaverde et al., 2005); usually SFT > BHT.

4.2.1. Geothermometer evaluation using BHTs

We compared the SolGeo geothermometry with BHTs measured in several geothermal wells (Figs. 3a–f and 4a–f; see also the Readme document available from the authors).

The BHTs on the *x*-axes of Figs. 3 and 4 should be viewed as approximate reservoir temperatures. On the other hand, geothermometric temperatures could be characterized by similar (or sometimes smaller) errors for Na–K, Na–Li, and quartz geothermometers (Verma and Santoyo, 1997). Thus, differences of up to about 25 °C between geothermometric and well temperatures may not be statistically significant; these are schematically indicated by dotted lines in Figs. 3 and 4.

Most samples from geothermal wells around the world plot within these ±25 °C difference limits (Fig. 3a–f; see especially Fig. 3e). When the "Difference" value on the *y*-axis (Figs. 2 and 3) is positive, the SolGeo geothermometric temperatures are greater than BHT and vice versa. Large discrepancies (greater than ±50 °C arbitrarily considered to be significant) are indicated for some samples for several Na–K geothermometers (see samples with >50 °C "Difference" in Fig. 3a–b). Similarly, for Na–Li geothermometers of Kharaka and Mariner (1989) SolGeo temperatures showed large differences (Fig. 3d), but for only some samples. Finally, large discrepancies are seen for six samples (out of 47 samples) for the CCG geothermometer (Fig. 3f) of Nieva and Nieva (1987).

The geothermometers that showed larger differences as compared to those presented in Fig. 3 are grouped in Fig. 4a–e, with the exception of quartz geothermometers (Fig. 4f), which were characterized by smaller discrepancies. Unexpectedly large differences (greater than ±50 °C) between the two temperature estimates (geothermometric and BHT) are shown for some samples (Fig. 4a–b) for the Na–K geothermometers of Fournier and Truesdell (1973) and Tonani (1980), but for numerous samples when using other geothermometers (Fig. 4c–f).

Extremely large differences (greater than 500 °C) for Fournier (1991) K–Mg geothermometer temperatures (numerous samples plot outside the *y*-axis of Fig. 4c) were observed for data reported or compiled by various authors. These unduly large temperature differences correspond to samples with very low Mg concentrations (<1 mg/kg); such low contents in water samples are difficult to determine accurately using conventional analytical techniques such as flame photometry or atomic absorption spectrometry. Therefore, the application of the K–Mg geothermometer of Fournier (1991) is not recommended in routine operations unless more sophisticated analytical techniques are used instead of the conventional ones.

4.2.2. Geothermometer evaluation using static formation temperatures

Although SFTs instead of BHTs would be better for this evaluation, we were unable to obtain SFTs for the worldwide database. Furthermore, SFTs could not be estimated from the BHT values because of the lack of BHTs measured at different times (for more details, see Andaverde et al., 2005; Verma et al., 2006b,c; Espinoza-Ojeda et al., 2007). Therefore, the geothermometer evaluation using SFTs was not possible for the worldwide database.

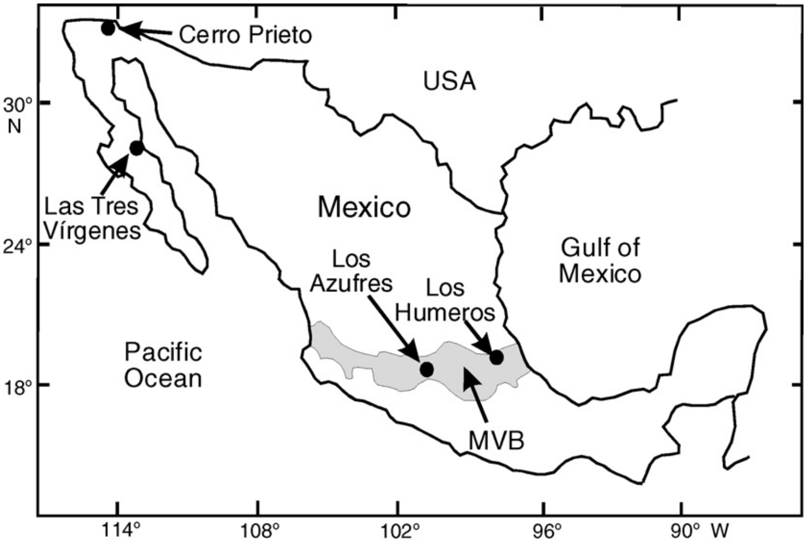

Fig. 7. Location of the four Mexican fields where geothermal fluids are used to generate electricity. MVB, Mexican volcanic belt.

4.3. *Mexican geothermal fields*

The location of the four Mexican geothermal fields producing electricity at the present time are shown in Fig. 7; the following brief summary is after Bertani (2005) and Gutiérrez-Negrín (2007). Cerro Prieto produces fluids from Tertiary sandstones to feed a total installed capacity of 720 MW_e. At Los Azufres geothermal fluids are produced mostly from Miocene–Pliocene andesites; the installed capacity in this field is 195 MW_e. Also at Los Humeros fluids are extracted from Tertiary andesites; the installed capacity is 35 MW_e. The Las Tres Vírgenes field has a total installed capacity of about 10 MW_e; its geothermal reservoir is hosted in granodiorites. The Cerro Prieto, Las Tres Vírgenes, and Los Azufres geothermal fields are liquid-dominated, whereas the Los Humeros geothermal field is vapor-dominated (Tello Hinojosa, 2005).

4.3.1. *Comparison of SolGeo and BHTs using the Mexican database*

In this section we again compare the geothermometric temperatures computed by SolGeo against BHTs, but this time against those measured in Mexican geothermal fields. Geothermometers with relatively small differences are shown in Fig. 5, whereas larger discrepancies between the two temperature estimates (geothermometers versus BHTs) are presented in Fig. 6 (compare *y*-scales in Figs. 5 and 6).

SolGeo temperatures for Na–K, Na–K–Mg, and CCG geothermometers only showed large differences (greater than ± 50 °C) for Los Humeros (Table 4). K–Mg and Li–Mg geothermometers presented substantial discrepancies for samples from all fields, while Na–Li geothermometers did so for the Cerro Prieto and Los Humeros fields. Silica geothermometers also show significant differences for Las Tres Vírgenes, Los Azufres and Los Humeros. Thus, most discrepancies were observed for Los Humeros, which may be related to the vapor-dominated nature of the field. A further explanation of these discrepancies may be related to the use of BHTs instead of SFTs.

Table 4
Comparison of SolGeo temperatures with bottom-hole temperature (BHT) measurements and static formation temperature (SFT) estimates for Los Humeros geothermal wells LH13, LH30, and LH31

Geothermometer abbreviation[a]	BHT	SFT–OLS	SFT–QR
TNKFT73	***3*** (6)	***1*** (6)	***2*** (6)
TNKT76	***3*** (6)	***1*** (6)	***3*** (6)
TNKF79	***3*** (6)	***0*** (6)	***0*** (6)
TNKT80	***3*** (6)	***0*** (6)	***2*** (6)
TNKA83	***3*** (3)	***1*** (3)	***2*** (3)
TNK2A83	***1*** (4)	***0*** (4)	***1*** (4)
TNKG88	***1*** (6)	***0*** (6)	***0*** (6)
TNKVS97	***2*** (6)	***0*** (6)	***0*** (6)
TNKA00	***3*** (6)	***1*** (6)	***2*** (6)
TNKC02	***3*** (6)	***1*** (6)	***1*** (6)
TNKDSR08	***3*** (6)	***1*** (6)	***2*** (6)
TNK2DS08	***3*** (6)	***1*** (6)	***2*** (6)
TKMG88	***6*** (6)	***6*** (6)	***6*** (6)
TKMF91	***3*** (6)	***5*** (6)	***4*** (6)
TLMKM89	***6*** (6)	***6*** (6)	***6*** (6)
TLM2KM89	***6*** (6)	***6*** (6)	***6*** (6)
TNLFM81	***6*** (6)	***6*** (6)	***6*** (6)
TNLKM89	***6*** (6)	***4*** (6)	***6*** (6)
TNLVS97	***2*** (6)	***6*** (6)	***6*** (6)
TNKCFT73	***4*** (6)	***6*** (6)	***6*** (6)
TNKCF73M	***5*** (6)	***5*** (6)	***5*** (6)
TNKMNN87	***6*** (6)	***5*** (6)	***6*** (6)
TCCGNN87	***6*** (6)	***5*** (6)	***6*** (6)
All geothermometers	***83*** (127)	***61*** (127)	***74*** (127)

In bold and italics: number of samples where the difference was greater than ±50 °C; in parenthesis: total number of samples.
SolGeo temperatures were computed from the chemical analysis data of two samples collected from each well. BHT and chemical analysis data for LH13, LH30, and LH31 were compiled from Tello Hinojosa (2005) and González Partida et al. (2001); SFT–OLS, static formation temperatures based on an ordinary least-squares linear regression model; SFT–QR, static formation temperatures based on a quadratic regression model; SFT estimates were compiled from Andaverde et al. (2005), Verma et al. (2006c), and Espinoza-Ojeda et al. (2007).

[a] Geothermometer abbreviations are given in Table 2.

4.3.2. *Comparison of SolGeo temperatures against Los Humeros bottom-hole and static formation temperatures*

In order to further understand the greater usefulness of SFTs (instead of BHTs), we compared SolGeo temperatures with both the measured BHTs and estimated SFTs (see Table 4). For these SFTs estimates, an improved Horner method was employed that used linear and quadratic regression analyses (see Andaverde et al., 2005; Verma et al., 2006a,b).

Unfortunately, SFTs data were available for only three Los Humeros wells, i.e. LH13, LH30, and LH31 (Andaverde et al., 2005; Verma et al., 2006c; Espinoza-Ojeda et al., 2007). Quartz geothermometers (Fournier, 1977; Fournier and Potter II, 1982; Verma and Santoyo, 1997; Arnórsson, 2000) were not included in this comparison because only two samples (out of six) fulfilled conditions required for proper application of these methods. Samples with greater than ±50 °C differences are compiled in Table 4. Such large discrepancies were observed for K–Mg, Li–Mg, Na–Li, Na–K–Ca, Na–K–Mg, and CCG geothermometers, but in lesser number of samples for the Na–K geothermometers (12 equations). A larger number of cases (83 out of 127) with greater than ±50 °C differences between the SolGeo temperatures and BHTs are observed in Table 4 than for either of the two SFTs estimates (SFT–OLS, 61 cases and SFT–QR, 74 cases). This implies that the SFTs based on an ordinary least-square linear (OLS) or a quadratic regression (QR) model (Andaverde et al., 2005) should be used to evaluate solute geothermometric temperatures.

Furthermore, we may also suggest that ideally both SFTs and BHTs should be reported in all geothermal studies. In fact, this was already proposed long ago by Fournier and Truesdell (1973). The reporting of SFTs and the method to compute them will be useful in the future for developing more reliable solute geothermometers calibrated based on SFTs instead of BHTs. On the other hand, the data should be evaluated by way of discordancy tests (Barnett and Lewis, 1994) using new, more precise and accurate critical values (Verma and Quiroz-Ruiz, 2006a,b; Verma and Quiroz-Ruiz, in press; Verma et al., 2008a). In addition, the final statistical samples (i.e. the remaining data after discordant outlier detection and elimination) should be used to propose new, improved equations. One of such discordancy tests was applied by Verma and Santoyo (1997) to the databases of Fournier (1979), Fouillac and Michard (1981) and Fournier and Potter II (1982) in order to propose improved equations for some solute geothermometers. Furthermore, SFTs and chemical composition data along with their uncertainty estimates would facilitate the use of weighted least-squares linear regression models (e.g. Andaverde et al., 2005; Santoyo et al., 2006; Asuero and González, 2007; Verma et al., 2008b) to obtain more reliable geothermometric equations.

4.3.3. Importance of error estimates: comparison of geothermometers with total propagated errors computed from SolGeo for the Mexican database

Santoyo and Verma (1993) and Verma and Santoyo (1997) criticized, for the first time, the validity and reliability of the Na/K geothermometer proposed by Fournier (1979) using error propagation theory (for more details on this theory see Bevington and Robinson, 2003; Verma, 2005). The errors in the regression coefficients of the geothermometric equation (estimated from ordinary least-squares linear regression of log(Na/K) and BHT data) and the typical analytical errors of the Na and K determinations were propagated to obtain the total uncertainties of the geothermometric temperatures. The regression coefficient errors were shown to be larger than the analytical errors.

SolGeo is capable of providing total propagated error estimates for (a) the Na–K geothermometers of Fournier (1979), Verma and Santoyo (1997), and Díaz-González et al. (in press), for (b) the Na–Li geothermometers of Fouillac and Michard (1981) and Verma and Santoyo (1997), and for (c) the quartz geothermometers of Fournier and Potter II (1982) and Verma and Santoyo (1997). The Mexican database was used for comparing these geothermometric temperatures (Fig. 8a–d) and to determine their errors (Fig. 9a–c).

The temperatures less than about 300 °C calculated by SolGeo (Fig. 8a–b) for the Na–K geothermometers of Fournier (1979) and Verma and Santoyo (1997) were somewhat greater than those for the Díaz-González et al. (in press) geothermometer (samples plot above the diagonal line in Fig. 8a–b). For higher temperatures (>300 °C) the inverse was true. Although the temperature differences between the Fournier and Díaz-González et al. geothermometers (−16 to +42 °C) and those between Verma-Santoyo and Díaz-González et al. geothermometers (−20 to +51 °C) were similar to the total propagated errors for these geothermometers (Fig. 9a), the systematic differences observed in Fig. 8a–b cannot be explained from these random errors. The discrepancies are probably related to the different databases used by these authors to develop their geothermometers. Fournier and Potter II (1982) and Verma and Santoyo (1997) used practically the same database

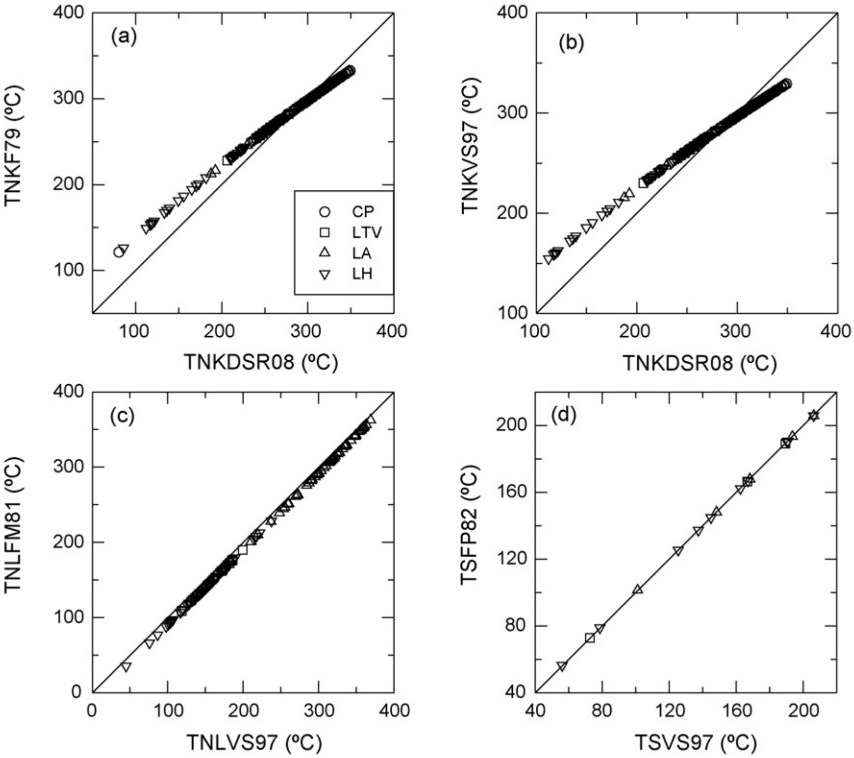

Fig. 8. Illustrating the use of SolGeo; comparing SolGeo temperatures estimated by some selected geothermometers for four Mexican geothermal fields. CP, Cerro Prieto; LTV, Las Tres Vírgenes; LA, Los Azufres; LH, Los Humeros. Note samples falling right on the diagonal line show no or negligible temperature differences. (a) Na–K geothermometers (Fournier, 1979 versus Díaz-González et al., in press); (b) Na–K geothermometers (Verma and Santoyo, 1997 versus Díaz-González et al., in press); (c) Na–Li geothermometers (Fouillac and Michard, 1981 versus Verma and Santoyo, 1997); (d) quartz geothermometers (Fournier and Potter II, 1982 versus Verma and Santoyo, 1997). Geothermometer abbreviations are given in Table 2.

whereas Díaz-González et al. (in press) established a much more extensive database in the development of their geothermometric equations. Ideally, the databases should represent the whole statistical population, which is unknown and inaccessible and whose characteristics can only be inferred from representative statistical samples (Barnett and Lewis, 1994; Verma et al., 2006d).

SolGeo temperatures for Na–Li geothermometers (Fig. 8c) of Verma and Santoyo (1997) were always slightly greater than those of Fouillac and Michard (1981) although these differences are within the estimated errors (Fig. 9b). On the other hand, the quartz geothermometers of Verma and Santoyo (1997) and Fournier and Potter II (1982) provided similar temperatures (Fig. 8d), which is again consistent with very small total propagated errors estimated for these geothermometers for temperatures below 200 °C (Fig. 9c).

4.4. Final remarks

Most of the widely used Na–K geothermometric equations proposed by various workers provide fairly consistent temperature estimates as confirmed by both the worldwide and Mexican

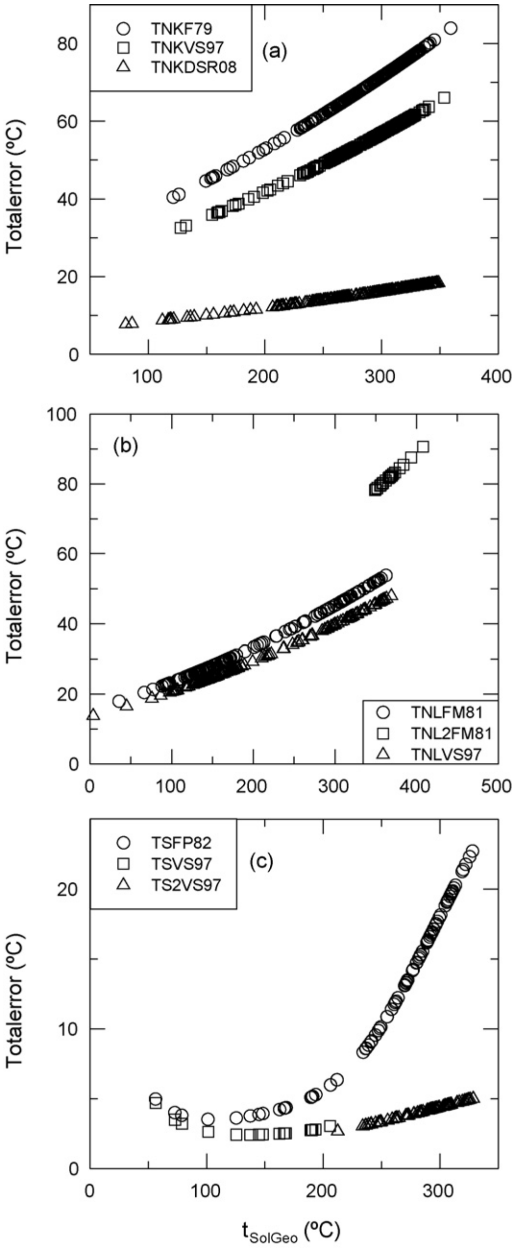

Fig. 9. Illustrating the use of SolGeo. Total propagated errors as a function of respective geothermometric temperatures t_{SolGeo}. Typical values of 2% R.S.D.% (relative standard deviation in %) were assumed as default values in the error propagation module of SolGeo as inferred by some authors (e.g. Arnórsson, 2000; Santoyo et al., 2005). (a) Estimated errors for Na–K geothermometers (Fournier, 1979; Verma and Santoyo, 1997; Díaz-González et al., in press); (b) estimated errors for Na–Li geothermometers (Fouillac and Michard, 1981; Verma and Santoyo, 1997); (c) quartz geothermometers (Fournier and Potter II, 1982; Verma and Santoyo, 1997). Geothermometer abbreviations are given in Table 2.

databases (Figs. 2 and 3; Table 4), except for some data compiled by Nieva and Nieva (1987) for the worldwide database and for the Los Humeros geothermal field. The good applicability of the Na–K geothermometers may be due to fact that the common geological processes, such as mixing of geothermal and shallow waters and the degassing of geothermal waters during their ascent towards the surface (Pang and Reed, 1998) do not significantly change the Na/K ratio (Pope et al., 1987). Furthermore, the determination of Na and K in geothermal waters is generally not a difficult analytical task. However, the application of the Na–K geothermometers can be affected to some extent by ionic exchange with minerals (particularly by clay minerals), enrichment of some cations, or the lack of equilibrium between solutes and alteration minerals present in the systems (D'Amore et al., 1987; Palandri and Reed, 2001). Nevertheless, given the good applicability of most Na–K geothermometers this problem may not be of much concern in practice.

The Li–Mg geothermometer of Kharaka and Mariner (1989) presented significant differences for Mexican geothermal fields, but not for the worldwide database. Other geothermometers (K–Mg, Na–Li, Na–K–Ca, Na–K–Mg, and Na–K–Ca–Mg) seem to provide less reliable results partly because of relatively large analytical errors associated with the determination of Li, Ca and Mg, which are generally present at low concentrations in geothermal waters. Analytical problems can thus seriously affect the results of chemical thermometry (Pang and Reed, 1998). These geothermometers should therefore be used with caution.

Finally, quartz geothermometers are susceptible to variable steam losses, which besides overestimating the temperature probably due to greater concentration of silica in the separated water, may also suggest inapplicability of most of them with the exception of those based on reservoir silica; other problems with quartz geothermometers have been pointed out by Land and Macpherson (1992) and Palandri and Reed (2001); this is why Verma (2000) proposed suitable corrections for quartz geothermometers.

5. Conclusions

In order to recognize and reduce errors when estimating subsurface temperatures in geothermal systems we developed computer program SolGeo. Here we discuss and illustrate its application to geothermal well waters from around the world, including Mexico.

It was concluded that static formation temperatures in geothermal wells should always be reported, which could be of significance when developing more reliable geothermometric equations. We suggest that K–Mg, Na–Li, Na–K–Ca, Na–K–Mg, and Na–K–Ca–Mg geothermometers should not be used or only with particular caution. We also consider that Na–K geothermometers provide more reliable data on geothermal reservoir temperatures.

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