# Hot or cold: a review of geothermometry at the Kawerau and Ngā Tamariki fields, Taupo Volcanic Zone, New Zealand

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**Keywords:** Geothermometer, silica, NaK, NaKCa, enthalpy deficit, Kawerau, Ngā Tamariki

#### **ABSTRACT**

Geothermometers are widely employed to determine reservoir enthalpy in both exploration and production scenarios. This paper evaluates the conditions under which silica and cation geothermometers provide temperatures, with case examples from the Kawerau and Nga Tamariki reservoirs. Geothermometry temperatures are presented in conjunction with tracer flow testing (TFT) and downhole survey results (i.e. PTS). Notably, at both fields, enthalpy deficit conditions are identified, where enthalpy determined from quartz solubility (i.e. Fournier and Potter, 1982a,b) exceeds TFT and PTS values. In this paper, an iterative spreadsheet-based approach is demonstrated for correcting enthalpy deficit. The spreadsheet method presented here provides comparable outputs to the WATCH geothermal chemical speciation software package, with corrected T<sub>Qtz</sub> using either approach within <1°C. At both Kawerau and Ngā Tamariki, corrected quartz thermometry provides valid characterization of near-well reservoir conditions, as established by comparison to feedzone PTS temperatures. At Kawerau, cation geothermometer (NaK, NaKCa) results are lower than T<sub>Otz</sub> and PTS temperatures. Lower cation geothermometer temperatures likely indicate incomplete equilibration of cation ratios as fluids transit from lower temperature injection zones to production areas, while quartz temperatures demonstrate that enthalpy remains stable in production areas. These examples highlight that correcting for enthalpy deficit improves the accuracy of quartz geothermometry. In cases where equilibrium is not attained, geothermometers may be used to diagnose the impact of ongoing changes in reservoir state due to production, reinjection, or marginal fluid incursion. Incorporating geothermometry into routine monitoring can enable better conceptual understanding of changes in reservoirs over time.

### 1. INTRODUCTION

## 1.1 Background

Geothermometers provide an estimate of the temperatures at which geothermal fluids have equilibrated in the subsurface. From a reservoir management standpoint, selection and application of a suitable geothermometer enables quantification of changes in enthalpy in response to development and operation. Broadly, geothermal geothermometers have been applied based on mineral solubility, gas ratios, or isotopic equilibria (Nicholson, 1993). The application of a geothermometer in a given reservoir should take into account fluid chemistry, host rock mineralogy, probable residence times, and likely temperature ranges.

#### 1.2 Silica geothermometers

Silica geothermometry, based upon the activity of silicic acid (H<sub>4</sub>SiO<sub>4</sub>) in solution, is widely used to calculate temperatures

in geothermal reservoirs. Experimental work from the 1950s onwards has resulted in a number of published thermometers (e.g. Arnórsson, 1975; Fournier and Potter, 1982a,b), which express temperature as a function of the solubility of quartz (e.g. Fournier and Potter, 1982a,b) or other polymorphs favoured at lower temperatures, such as chalcedony (e.g. Fournier, 1977). The quartz thermometer presented in Fournier and Potter (1982a,b), and utilized in this paper, can be applied to estimate reservoir temperature in discharging wells over the range of 250 to 330°C. The thermometer is defined below as a function of the molal concentration of silica, where:

 $T_{Qtz} = A*(SiO_2) - B*(SiO_2)^2 + C*(SiO_2)^3 + D*LOG(SiO_2) - 42.198$  A = 0.28831 B = 0.00036686 C = 0.00000031665 D = 77.034

# 1.3 Cation geothermometers

The NaK geothermometer reflects the temperature dependent reactions governing Na-K cation exchange between sodic and potassic minerals (i.e. albite-adularia). A number of NaK thermometers have been developed and applied historically (e.g. Fournier, 1979; Giggenbach et al., 1988). Sodiumpotassium geothermometry (i.e. T<sub>NaK</sub>) is most accurate at fields with near-neutral, low-Ca fluids, at temperatures over 100°C. A geothermometer based upon Na-K-Ca cation exchange is suitable in high enthalpy fields (Fournier and Truesdell, 1973), but can be impacted by reactions that add or remove Ca from geothermal fluid (e.g. precipitation or dissolution of calcite and/or anhydrite).

One of the primary advantages of cation ratio thermometers (e.g.  $T_{NaK}$ ,  $T_{NaKCa}$ ) is that they are not subject to the abundance of any one component in solution, whereas  $T_{Qtz}$  is affected by the absolute concentration of Si in fluid. However, longer equilibration times for  $T_{NaK}$  and  $T_{NaKCa}$  (~0.3 years at 250°C) complicate application in reservoirs with shorter residence times and variable fluid inputs (e.g. injection returns, downflows), where the apparent geothermometer temperatures may not reflect equilibrium with fluid in production areas (Nicholson, 1993). In comparison,  $T_{Qtz}$  can reach equilibrium in 1-100 hours at temperatures over 250°C (Nicholson, 1993; Lovelock, 1995).

# 1.4 Well-head chemistry sampling and tracer flow testing

Routine monitoring of reservoir chemistry typically involves collection of steam and brine samples in conjunction with Tracer Flow Testing (TFT). Such an approach is relatively low-cost and can be carried out multiple times annually without interruption to production. During tracer flow tests, the mass flow rate of vapour and liquid phases are quantified and applied to determine discharge enthalpy. TFT

methodology is described in detail elsewhere (Hirtz, 2001; Broaddus et al., 2010). In order to concentrations of chemical species (e.g. solutes in brine, gases) in the reservoir, measurements on brine or gas collected during two-phase sampling are renormalised relative to total well discharge (i.e. brine plus steam).

With respect to using wellhead chemistry sampling to infer reservoir conditions, some degree of uncertainty is expected. Silica temperatures can be adversely impacted due to sampling artefacts (e.g. evaporation of the sample during collection, or storage) or issues with TFT constraints upon brine and steam fractions. In reservoirs experiencing 2-phase conditions, excess enthalpy (excess steam) measured by TFT will result in a lower total discharge silica concentration and lower calculated quartz temperatures. Conversely, under enthalpy deficit conditions, where TTFT<TQtz, an overestimate of silica in total discharge leads to calculation of inaccurately high reservoir temperature. The need to correct for enthalpy excess and/or deficit has been established elsewhere (e.g. Lovelock, 1995), and is evaluated at two geothermal fields in this paper.

#### 1.5 Case Study

#### 1.5.1 Sampling locales

In this paper, the performance of quartz and cation geothermometers are compared to measured PTS values for feedzone temperature at two liquid reservoirs in the Taupo Volcanic Zone (Figure 1). The Kawerau Geothermal System, located in the northeast TVZ, covers an area of approximately 35 km<sup>2</sup>. Kawerau has been developed since the 1950s and is presently utilised by three main tappers (Mercury, NTGA, Eastland) for both electrical generation and industrial steam supply. Since 2008, Mercury NZ has operated a 100MWe flash geothermal power station at Kawerau. In this study, data from Kawerau wells KA45A and PK07 are presented. The Ngā Tamariki Geothermal System is located approximately 25 kilometers northeast of Lake Taupo. Mercury has operated an 85 MWe binary power station at Ngā Tamariki since 2013, which makes use of a deep high-enthalpy resource. Two wells from Ngā Tamariki were selected for this study (NM07, NM13).

# 1.5.2 Correcting for enthalpy deficit

In this paper, quartz geothermometer temperatures are calculated using three different approaches. In approach 1, concentrations of elements in brine are recalculated as concentrations relative to total discharge (i.e. brine plus steam) using TFT constraints. Total discharge silica concentrations are then applied to determine the quartz geothermometer temperature in the reservoir.

Given the potential shortcomings in case 1, where application of a TFT-based steam fraction can lead to overestimation (or underestimation) of total discharge silica concentration, a spreadsheet-based correction process is demonstrated. In the spreadsheet approach, brine chemistry is renormalised to total discharge via a multistep iterative process. To test the results from the spreadsheet correction process, concentrations of constituents in brine (e.g. silica) were also recalculated at reservoir conditions using the WATCH speciation software package, which also follows an iterative solving approach. WATCH was developed in the 1970s-1980s (e.g. Arnórsson, et al., 1982), and later updated. The software operates by solving mass balance and mass action equations for chemical equilibria between various species.

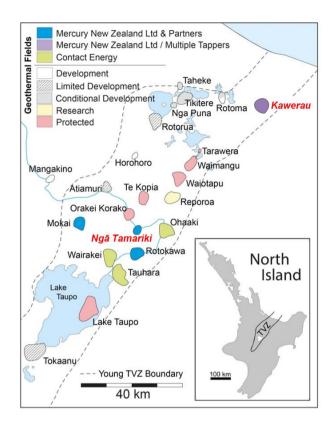


Figure 1: Locations of the Kawerau and Ngā Tamariki fields within the Taupo Volcanic Zone.

### 2. METHODOLOGY

# 2.1 Sampling and TFT methodology

Sampling at wells was carried out for both brine and steam on 2-phase pipelines using standard methodology. Following sample collection, tracer flow testing was carried out to measure enthalpy in both the liquid and steam phases. Measurement of anions, cations, silica, pH, steam condensates, and gases were carried out in accordance with procedures specified by the NZ Geothermal Analytical Laboratory (NZGAL), an IANZ-accredited testing facility.

# ${\bf 2.2}\ Calculation\ of\ total\ discharge\ silica\ concentrations$

The spreadsheet procedure for calculation of quartz temperatures follows a multistep process, in which a modified steam fraction is calculated to satisfy the silica concentration result for a given brine sample. The process is outlined below in Table 1. The calculations in steps 1-5 outlined in Table 1 below are carried out multiple times (4-7 iterations), and the final liquid correction factor is applied to determine final silica temperature (i.e.  $T_{\rm Qtz}$ ). The final modified liquid fraction (Liq $_{\rm mod}$  parameter in Table 1, Step 4) is applied to brine chemistry results (e.g. Cl, B etc.) to calculate molal concentrations of species in the reservoir.

Table 1: Spreadsheet calculation steps to correct enthalpy deficit influence upon quartz geothermometry.

| Step 1: | Calculate T <sub>Qtz</sub> from TFT parameters. Si                                      |
|---------|---|
|         | concentration (mg/kg) in brine (Si <sub>brine</sub> ) is multiplied                     |
|         | by the TFT-determined liquid fraction (Liq <sub>TFT</sub> ) to                          |
|         | determine silica concentration in total discharge                                       |
|         | (Si <sub>TD</sub> ). T <sub>Qtz</sub> is calculated by applying Si <sub>TD</sub> to the |
|         | Fournier and Potter (1982a,b).  |
| Step 2: | Calculate enthalpies at T <sub>Qtz</sub> (step 1) for steam (H-                         |
|         | stm <sub>Otz</sub> ) and liquid conditions (H-liq <sub>Otz</sub> ).                     |
| Step 3: | Calculate enthalpy deficit (HD) fraction, using TFT                                     |
|         | enthalpy (H <sub>TFT</sub> ) and quartz enthalpies calculated in                        |
|         | step 2:   |
|         | $HD = (H_{TFT} - H - liq_{Qtz}) / (H - stm_{Qtz} - H - liq_{Qtz})$                      |
|         | If this value is negative, enthalpy deficit conditions                                  |
|         | exist, while a positive value indicates excess steam,                                   |
|         | as encountered in 2-phase wells.  |
| Step 4: | Calculate modified liquid fraction (Liq <sub>mod</sub> ).                               |
|         | $Liq_{mod} = Liq_{TFT}/(1 - HD)$  |
| Step 5: | Recalculate T <sub>Qtz</sub> using Liq <sub>mod</sub> , following steps 1-4             |
|         | above.  |

The effect of this correction process upon calculated  $T_{Qtz}$  is demonstrated for two samples from Kawerau well PK07 in Figure 2, which stabilize after 4-5 calculation iterations. In this study, seven correction iterations were used for all well chemistry calculations based upon the observation that values typically converge to the WATCH (version 2.4) output value at, or before, this step; correcting seven times is not a strict requirement, however.

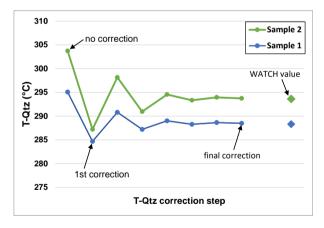


Figure 2: Example of spreadsheet correction steps to address enthalpy deficit for two samples collected at Kawerau well PK07. For comparison, WATCH-corrected quartz temperatures are also shown (diamond).

### 2.3 Cation geothermometry

Brine sample concentrations for Na, K, and Ca are normalized to total discharge using TFT constraints for brine and steam fractions. Calculation of  $T_{\rm NaK}$  was made using the equation in Arnórsson et al., 1983. Calculation of  $T_{\rm NaKCa}$  was made using the relationship in Fournier and Truesdell (1973).

#### 3. RESULTS AND DISCUSSION

# 3.1 Evaluation of spreadsheet method relative to WATCH outputs for $T_{\text{Otz}}$

Quartz geothermometry results are plotted for Kawerau and Ngā Tamariki wells (Figures 3-5). In Figure 3, uncorrected  $T_{Qtz}$  results ( $T_{Qtz}$  TFT) and spreadsheet corrected ( $T_{Qtz}$  corrected) are compared by difference relative to WATCH outputs for  $T_{Qtz}$  at Kawerau wells (KA45A, PK07) and Ngā Tamariki wells (NM07, NM13). For all wells surveyed, corrected  $T_{Qtz}$  values determined using either WATCH or the spreadsheet method presented here are within error of one another. On average, uncorrected  $T_{Qtz}$  results (' $T_{Qtz}$  TFT' in Figure 3) at NM07 are 6.9°C greater than WATCH outputs, while uncorrected results at NM13 are 8.2°C greater. At Kawerau, uncorrected results at KA45A are 4.2°C greater, while uncorrected results at PK07 are 6.0°C greater on average.

In order to demonstrate the effect of each calculation approach for Totz, results for well NM07 are plotted in timeseries in Figure 4. The plot includes enthalpy deficit corrected Totz values (both WATCH and spreadsheet methods), uncorrected T<sub>Qtz</sub>, PTS results, and TFT temperatures. The close overlap of WATCH outputs and spreadsheet-corrected T<sub>Qtz</sub> methods is evident. Notably, corrected results (WATCH or spreadsheet approach) provide a reasonable approximation of reservoir temperature, as highlighted by close agreement with PTS downhole temperatures. At well NM07, both the spreadsheet corrected Totz and WATCH results for 2013-2014 are 290°C on average, which is within error of the 2014 downhole temperature of 287°C. In contrast, the uncorrected average quartz temperature in 2013-2014 is 296°C. In 2020-2021, the spreadsheet corrected T<sub>Qtz</sub> at NM07 was 291°C on average, while WATCH results were 292°C. Temperatures determined using either correction approach closely matched the 2021 PTS result of 288°C, while uncorrected T<sub>Otz</sub> values over the 2020-2021 interval were higher, with a mean value of 299°C.

# 3.2 Comparison of $T_{Qtz}$ and cation geothermometer techniques at Kawerau and $Ng\bar{a}$ Tamariki

At both fields,  $T_{Qtz}$  provides reasonable approximation of reservoir conditions (Figures 4-5). Quartz temperatures calculated using the spreadsheet iterative approach demonstrated in this paper are compared to  $T_{NaK}$  and  $T_{NaKCa}$  in Figure 5 for Kawerau well KA45A and  $Ng\bar{a}$  Tamariki well NM07. Notably, cation geothermometers (e.g. NaK, NaKCa) exhibit declining temperatures over time. At Kawerau (KA45A), the offset of  $T_{NaK}$  and  $T_{NaKCa}$  relative to  $T_{Qtz}$  and PTS values is most pronounced (Figure 5).

At KA45A, a PTS result in 2008 indicates downhole temperature of 268°C, while  $T_{Qtz}$  in 2013-2014 was 279°C on average. During the 2008-2009 timeframe  $T_{\rm NaKCa}$  was 267°C, and  $T_{\rm NaK}$  was 245°C. Initially,  $T_{\rm NaKCa}$  recorded temperatures which most closely matched observed downhole conditions. However, a pronounced decline trend in  $T_{\rm NaKCa}$  from 2009-2021 is not reflected in  $T_{\rm Qtz}$  or PTS temperature. In 2021, KA45A recorded a PTS result of 267°C. In 2020-2021,  $T_{\rm Qtz}$  at KA45A was 274°C on average, while both cation thermometers showed evidence of decrease over time with  $T_{\rm NaKCa}$  registering an average temperature of 243°C and  $T_{\rm NaK}$  at 222°C on average.

At well NM07, Ngā Tamariki field, a PTS result in 2014 indicates a downhole temperature of 287°C, while  $T_{Qtz}$  in 2013-2014 was 290°C on average. During the 2013-2014 timeframe  $T_{NaK}$  was 300°C and  $T_{NaKCa}$  was 286°C. Over the

course of nine years of operation, feedzone temperatures remained largely stable, with the PTS result in 2021 registering 288°C. In 2020-2021,  $T_{\rm Qtz}$  at NM07 was 291°C on average, while  $T_{\rm NaKCa}$  showed evidence of decline, with an average temperature of 280°C. Over this interval,  $T_{\rm NaK}$  also showed some evidence of decline with a mean temperature of 295°C, but continues to be elevated relative to the other thermometers presented.

#### 3.3 Interpretation

Comparison of results to known downhole conditions provides a first order assessment of the likelihood that a geothermometer continues to reflect conditions in the production area for a given well. For both Kawerau and Ngā Tamariki, quartz thermometry (corrected for enthalpy deficit) continues to record reservoir temperatures that are most similar to PTS downhole temperature results. At Kawerau, cation thermometers exhibit some degree of temperature decline over time, which is not reflected in feedzone temperatures recorded by PTS. For the wells surveyed here, quartz temperatures and PTS generally indicate relatively stable enthalpy conditions. Stable T<sub>Qtz</sub> likely reflects the shorter time required for SiO<sub>2</sub> to reach quartz equilibrium at temperatures greater than 250°C. However, careful observation of quartz results should take into account effects imparted by elevated silica due to injection returns and/or incursion of marginal fluid in equilibrium with lower temperature silica polymorphs (e.g. chalcedony). A comprehensive analysis of quartz equilibrium conditions is beyond the scope of this paper, but should be considered during future well monitoring.

The decline in cation thermometer temperatures at Kawerau indicate that T<sub>NaK</sub> and T<sub>NaKCa</sub> may become less accurate indicators of temperature near production areas as development of the field progresses. Dissolution and/or precipitation of anhydrite and calcite may impact NaKCa geothermometry. Furthermore, these cation thermometers have relatively lengthy equilibration times (~0.3 years), and at Kawerau may have come to indicate temperatures that are intermediate between injection and production sites. In this case, cation thermometers may present an opportunity to better understand changes in the heat-up of reinjected fluids as they transit back to production zones.

#### CONCLUSIONS

In this study, geothermometry outputs associated with well chemistry monitoring programs at the Kawerau and Ngā Tamariki reservoirs are presented. Based upon 9-plus years of sampling, recommendations are made with respect to correction and interpretation of geothermometry results. At both fields, correction of enthalpy deficit leads to closer agreement of T<sub>Qtz</sub> data with direct downhole temperature determinations. The iterative spreadsheet-based approach for correcting enthalpy deficit closely matches calculations made using the WATCH chemical speciation program. Following development, declines in cation ratio geothermometer temperatures, which are not recorded in PTS or quartz enthalpy, may reflect thermal conditions intermediate between injection and production areas. This effect is more pronounced at Kawerau. It may be informative to evaluate both silica and cation ratio temperature trends in the context of reservoir tracer test outputs to establish whether the timing and degree of temperature offset between thermometers is consistent with changes in injection strategy.

#### **ACKNOWLEDGEMENTS**

Ed Mroczek is thanked for feedback and insight during this investigation. Mercury is thanked for allowing the publication of this data. Useful discussions related to sampling methodology and interpretation of results were also provided by Farrell Siega, Kelly Melia, Gabriel Petrar, and Alan Eastwood.

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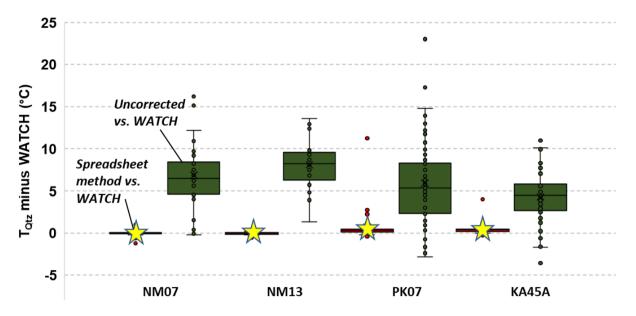


Figure 3: Quartz temperature comparison at Nga Tamariki (NM07, NM13) and Kawerau (PK07, KA45A) with results presented as differences relative to WATCH outputs. Results corrected using the enthalpy deficit spreadsheet method presented in this paper (star symbol) closely overlap WATCH outputs. Uncorrected  $T_{\rm Qtz}$  values, determined using TFT liquid-steam fractions applied to silica concentrations in brine, exceed WATCH outputs and reflect enthalpy deficit conditions at all four wells.

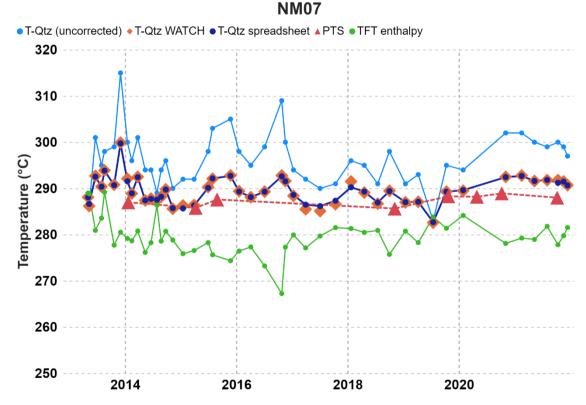


Figure 4: Timeseries plot illustrating the close agreement of WATCH (orange diamond) and spreadsheet-based corrections (dark blue) of enthalpy deficit for  $T_{Qtz}$  at well NM07. For comparison, TFT enthalpy provides an underestimate of reservoir temperature, as established by PTS, while uncorrected  $T_{Qtz}$  values (light blue) are higher and more variable.



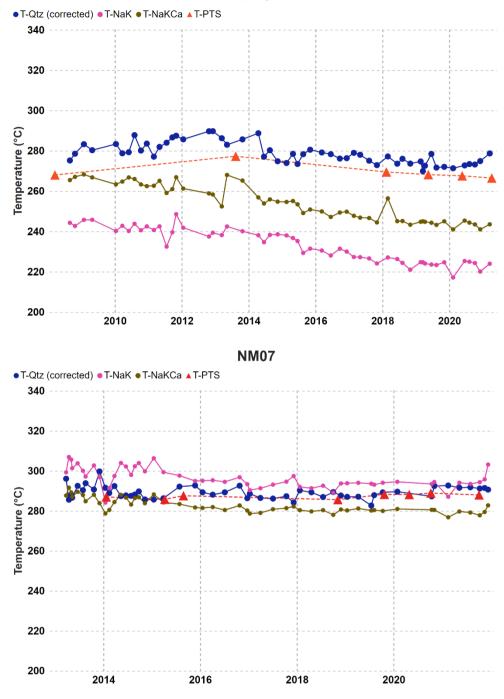


Figure 5: Comparison of silica (quartz) and cation (NaK, NaKCa) thermometers relative to measurements of downhole temperature (PTS) over time. Quartz results are corrected for enthalpy deficit using the spreadsheet method presented in this paper. Upper panel: Kawerau (KA45A) well example; Lower panel: Ngā Tamariki (NM07) example.