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In-situ Temperature Determination at the Villarrica Geothermal System, Southern Chile: Implications from Laboratory Experiments for Geothermometry

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ABSTRACT

Exploring a geothermal system the determination of reservoir temperatures is a major task. Unfavorably, the uncertainties of classical solute geothermometry are still large preventing reliable reservoir temperature estimations. In this study results of laboratory experiments are presented, equilibrating two reservoir rock analogues from the Villarrica area at 140 °C. These experiments clearly show the impact of reservoir rock composition on the fluid chemistry. In order to quantify and reduce the uncertainties of geothermometric methods, we assess the performance of classical geothermometers and multicomponent geothermometry with regard to different rock compositions, by applying them to the fluids derived from the alteration experiments as well as to fluids from natural geothermal springs in the Villarrica area. It is shown that differing rock mineralogy strongly affects calculated temperatures from classical solute geothermometry. Multicomponent geothermometry is obviously more robust leading to significantly smaller temperature spreads. The here presented data are first results of ongoing research of establishing an easy-to-use modification of the multicomponent geothermometric method on basis of limited fluid analysis. Although, calculated temperatures for the Villarrica area subsurface are therefore preliminary, the approach is apparently a step into the right direction.

1. INTRODUCTION

The estimation of reservoir temperatures is a major goal in geothermal exploration. Deducing in-situ temperatures from the chemical composition of geothermal fluids emerging at the earth´s surface is a commonly used and relatively cost-effective method. Over five decades a great number of solute geothermometers have been established and constantly improved (e.g. Fournier and Rowe (1966), Giggenbach (1988), Can (2002), Sanjuan et al. (2014)). But, solute geothermometry is still afflicted with great uncertainties. In particular, exploring a geothermal systems, where only few information (reservoir lithology, borehole data, etc.) is available, the classical methods often lead to highly scattering and inconsistent calculated reservoir temperatures. Even in studies in which the individual geothermometers has been carefully selected cinsidering their applicability and validity for the expected conditions, the resulting temperatures often show variations of more than 100 K for the same sample (e.g. Pepin et al. 2015, Aquilina et al. 2002, Mutlu 1998, D'Amore et al. 1994).

Recently, a number of geochemical surveys has evaluated the in-situ temperatures of the geothermal system in the Villarrica area in Southern Chile, where numerous natural geothermal springs discharge in direct vicinity of active volcanoes. Thereby the authors have come to widely different and inconsistent results. Sánchez et al. (2013) roughly determined temperatures of 100 °C - 180 °C from cation ratio geothermometers, whereas estimations from Held et al. (in preparation), using oxygen isotope fractionation in the system SO_4^{2-}-H_2O, ranging from 80 °C - 130 °C, are significantly lower. A previous work from the authors of this paper (Nitschke et al., 2016) found the warmer temperatures of the first study as well as the cooler of the latter, but accompanied with a large variation of results for the individual springs of up to 130 K. Temperature estimations with uncertainties of that level are unsatisfactory for a reliable exploration campaign.

These uncertainties can be related to a great number of processes (e.g. dilution/mixing, boiling, immaturity, etc.). Reducing these uncertainties of geothermometry is the major subject of our ongoing research effort. In previous works, we have found strong indications for the significant influence of different reservoir lithologies on the hydrochemical compositions of the fluids effecting the calculated reservoir temperatures (Meller et al., 2016; Nitschke et al., 2015; Nitschke et al., 2016). In this study, we present results of laboratory alteration experiments, equilibrating reservoir rock analogues from the study area. Using these results, the performance of classical solute geothermometers and numerical multicomponent geothermometry is assessed and the applicability of both methods on the natural system is evaluated.

2. METHODS AND RESULTS

The Villarrica area and its geothermal system was characterized in previous works. Beside of the fluid chemistry, Held et al. (in preparation) and Sánchez et al. (2013) also investigated geological and structural aspects. It is found that the area can be divided into two major geological parts. The southern part is dominated by granitoids of the North Patagonian Batholith (NPB), whereas the northern part consists mainly of volcanic and volcano-clastic rocks of the Cura-Mallin (CM) formation. Held et al. (in preparation) finds two types of geothermal fluids, obviously linked to these changes in lithology. We select two reservoir analogues representing each geological unit, a Mesozoic tonalite (NPB) and a Cenozoic porphyric andesite (CM), to conduct long term batch reaction experiments. The aim of the experiments is to attain fluids which are in equilibrium with these rocks to evaluate the hydrochemical discrepancies due to different rock compositions. The application of classical solute geothermometers as well as a numerical multicomponent geothermometric method to these experimental fluids yield valuable insights of how different reservoir rock compositions effect geothermometry.

2.1 Laboratory Experiments

The tonalite and the andesite are chosen for the experiments as they were presumed to be the most likely reservoir rocks for the natural geothermal fluids due to their widespread occurrence and their spatial distribution. Prior to the water-rock interaction experiments, both rock samples were analyzed in detail. The mineralogical compositions derived from thin-section microscopy, X-ray diffraction and X-ray fluorescence are given in Tab. (1). Most important difference of mineralogy in terms of geothermometric applications is the absence of K-feldspar in the tonalite. Furthermore, thin section analysis (Fig. 1) reveals the occurrence of SiO_2 in different polymorphs in both rocks (only as chalcedony in the andesite and only as quartz in the tonalite).

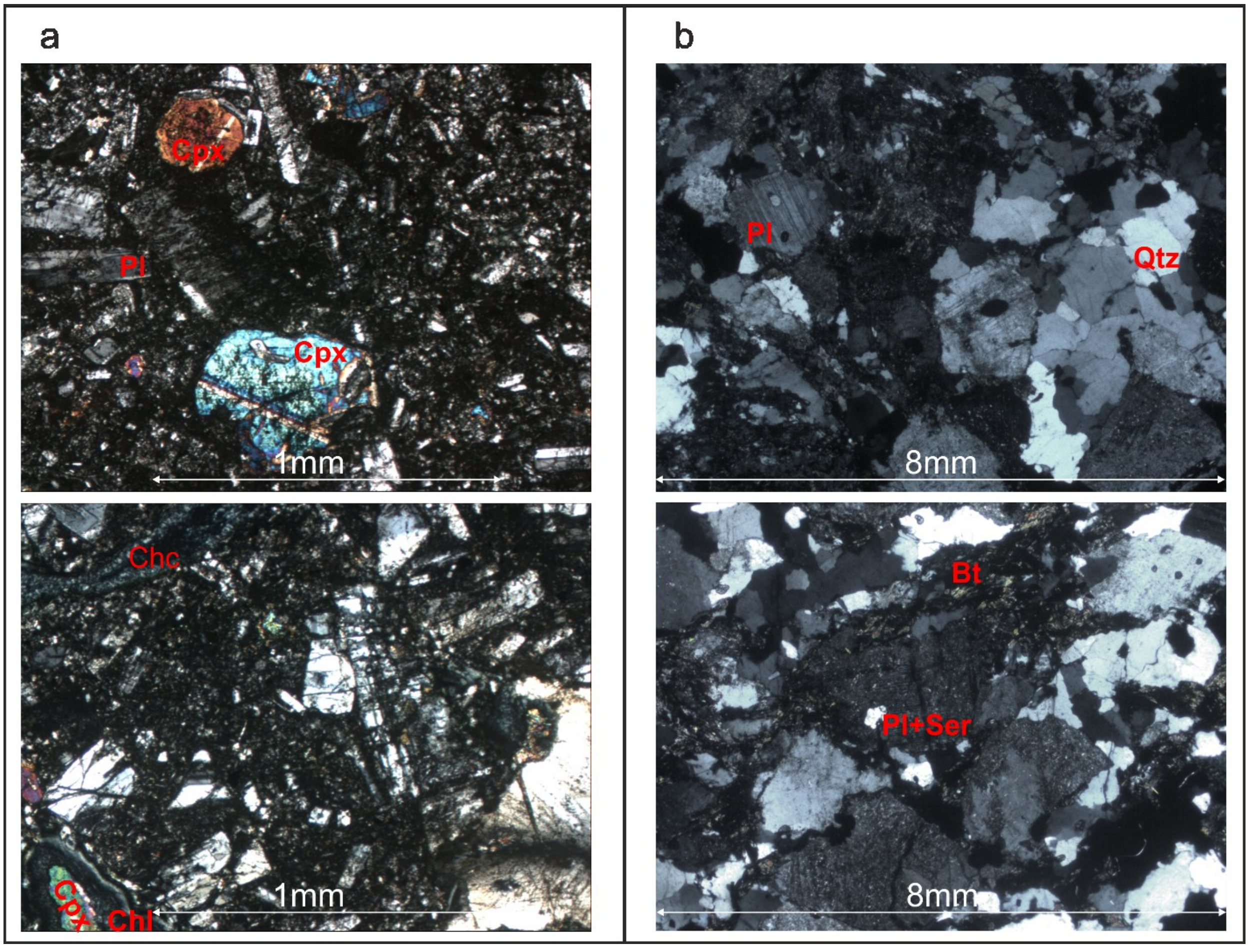

Figure 1: Thin section analysis of a) andesite sample showing a porphyritic structure with clinopyroxene and plagioclase phenocrysts and b) quartz and plagioclase rich tonalite sample.

For the experiments, the rock samples were ground with an agate disc mill to a grain size <63 µm. BET measurements reveal reactive surface area of both samples to be in the same order of magnitude (tonalite: 2.1 m^2/g, andesite: 3.6 m^2/g). 40 g of rock powder was transferred to a hermetic 150 ml stainless-steel reactor. The remaining volume was completely filled up with pure H_2O to avoid any headspace. The resulting rock-water ratio was ~0.3. According to estimations in previous works for the most-likely mean reservoir temperature, the reaction temperature for the experiments was chosen to be 140 °C. To keep track of the chemical development of the fluids over time and to enable the identification of steady state conditions, experiments were sampled and analyzed as a time series after

1, 2, 4, 6, 10, 20, 30, 45, 60, 90, 120, and 180 days. Each time step represents an autonomous experiment and therefore ensures the reproducibility of results. After termination of each experiment, the fluid was diluted immediately (pure H_2O) to stabilize the solution. Fluid composition was measured using inductively coupled plasma mass spectrometry (ICP-MS) for the cations and ion chromatography (IC) for the anions. Silicon concentrations were determined by spectrophotometry.

Table 1: Mineralogical composition of reservoir rock analogues used for laboratory experiments.

	Tonalite [%]	***Andesite [%]***
Quartz	*50*	-
Chalcedony	-	*5*
K-feldspar	-	*5*
Plagioclase	*25*	*40*
Pyroxene	-	*30*
Serizite	*10*	-
Muscovite	*< 5*	-
Chlorite	*< 5*	*< 5*
Biotite	*10*	-
Clays	-	*10*
Magnetite	-	*10*

The evolution of the major constituents of the experimental fluids are depicted in Fig. (2). Comparing both experiments, a significant difference of fluid compositions is obvious. After 180 days the fluid in contact with tonalite shows a higher mineralization with a TDS of about 700 mg/L, whereas the TDS of the fluid from the andesite experiment is only about 500 mg/L. The tonalite fluid is a Na-SO_4 fluid of near neutral pH (6.7), while the andesite fluid is classified as a Na-Cl fluid with a higher pH of 8.5. Sodium concentrations are very similar (5-6 mmol/L) in both fluids at the end of the reaction time, with a nearly continuous increase over time. The tonalite fluid is found to have high concentrations of potassium and calcium at early stages, but decreasing over the course of the experiment. The andesite fluid is showing relatively constant concentrations for both cations, but remaining on a significantly lower level compared to the tonalite fluid. Aqueous SiO_2 concentrations also differ strongly, where the andesite fluid reaches calculated quartz saturation for the reaction temperature of 140 °C, the concentration of the tonalite fluid is significantly higher reaching chalcedony saturation.

Applying solute geothermometers to these fluids, the consequences for SiO_2 geothermometers are quite obvious (Fig. 3). If the SiO_2 geothermometer based on the inappropriate polymorph is selected calculated temperatures will result in an over- or under estimations of about 20 K (for the given reaction temperature of 140 °C). This deviation of saturation temperatures will even increase with increasing fluid temperatures. However, in previous works the equilibrated SiO_2 polymorph is considered to depend upon the expected temperature niveau, the here presented results rather reveal a dependence upon reservoir rock composition. Surprisingly, the tonalite fluid is saturated with respect to chalcedony, although the SiO_2 polymorph contained in the rock is quartz. For the andesite it is vice versa, despite the SiO_2 occurs only as chalcedony, the fluid is saturated with respect to quartz. An explanation for that unexpected equilibration behavior cannot be provided at the current stage of investigation.

Furthermore, it is shown that the application of Na/K geothermometers lead to even significantly greater discrepancies, when being applied to both fluids. Na/K geothermometers (especially the relations of Arnórsson (1983) or Fournier and Truesdell (1973)) work very well for the andesite fluids approaching the reaction temperature of 140 °C towards the end of the experiments, whereas the temperature of the tonalite fluids is strongly overestimated with calculated temperatures of >300 °C. This failure may easily be explained by the absence of K-feldspar in the tonalite and therefore a control of the Na/K equilibrium by other potassium phases than K-feldspar (e.g. muscovite), leading to a relative potassium enrichment, which results in that significant temperature overestimation.

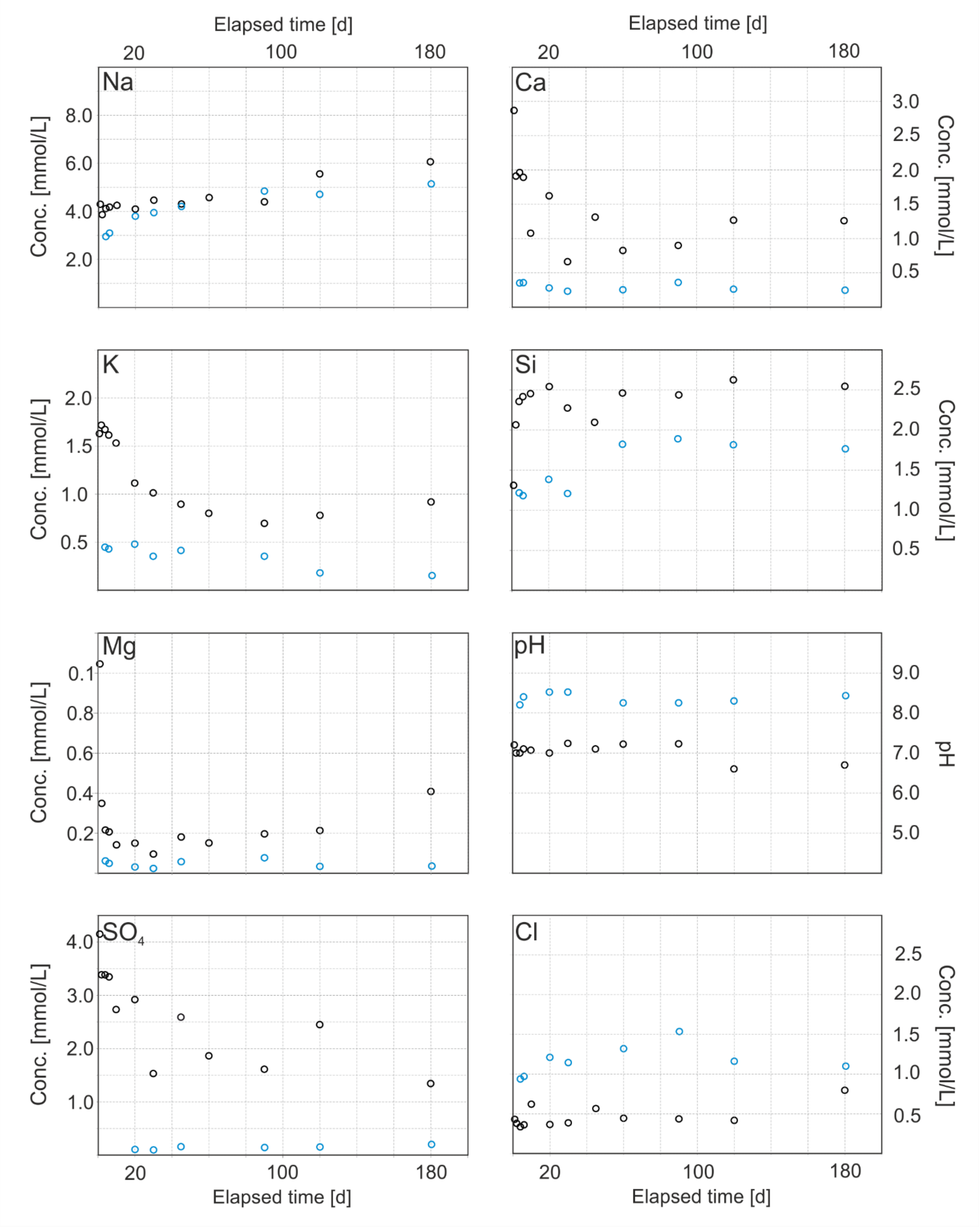

Figure 2: Development of concentrations of major constituents of the experimental fluids versus elapsed reaction time (tonalite experiments: black symbols, andesite experiments: blue symbols).

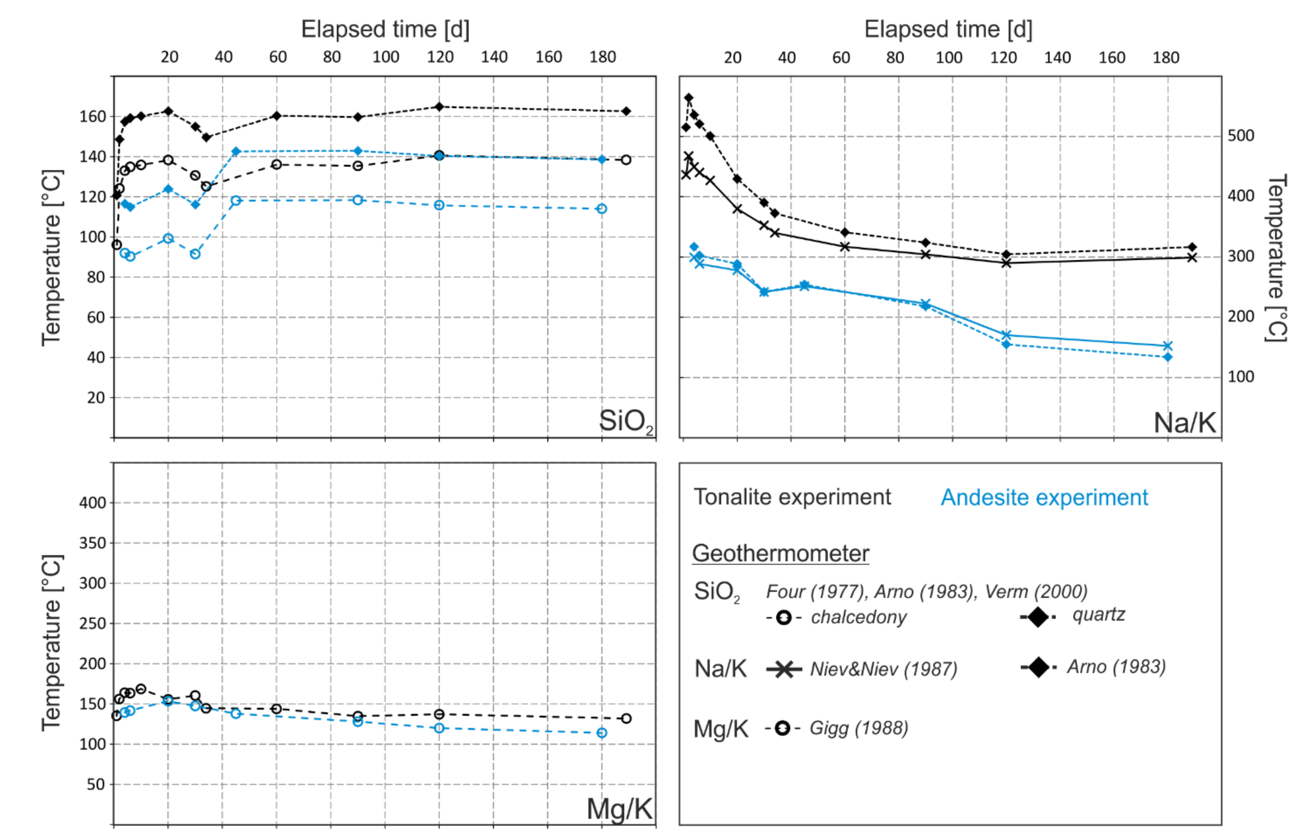

Figure 3: Calculated solute geothermometer temperatures calculated for the fluids derived from laboratory experiments plotted versus reaction time (tonalite experiments: black symbols, andesite experiments: blue symbols). Temperatures were calculated according to formulations from Arnórsson (1983), Fournier (1977), Giggenbach (1988), Nieva and Nieva (1987) and Verma (2000).

Applying the Mg/K geothermometer of Giggenbach (1988), calculated temperatures reflect reaction conditions for both experiments. Especially for the tonalite fluids the calculated temperature of 137 °C matches nearly perfectly the reaction conditions. For the andesite fluids calculated temperatures approaches reaction temperature over the course of the experiments, but being slightly too low towards the end (120 °C).

If the application of one geothermometer is appropriate, inaccurate or failing cannot be explained in every case (like it is for the Na/K geothermometer). Since all curves depicted in Fig. (3), are all more or less levelling off towards a steady state, major changes in fluid composition are not to be expected. Therefore it is plausible to assume, that reaction time was sufficient. As laboratory procedures are identical for both experiments, we conclude that the differences comparing both experimental series can only be put back to the differences in rock composition, which consequently lead to different chemical equilibria and calculated temperatures. Even if one geothermometer would yield a correct estimation of the reservoir temperature, exploring a geothermal system the geologist has no indication for the selection of that appropriate one.

2.2 Multicomponent Geothermometry

Conducting an exploration campaign reliable information about the reservoir lithology are usually rare. It would be preferable to calculate the subsurface temperature on basis of geothermometric methods being independent from reservoir rock composition. The more statistical approach of multicomponent geothermometry may fulfill these requirements and may therefore be more applicable for the evaluation of systems with unknown reservoir mineralogy. For in-situ temperature determination by multicomponent geothermometry, saturation indices ($SI = \log(Q/K)$) are calculated for a suite of possible (reservoir) rock minerals over a large temperature interval (containing the expected range of reservoir temperature). This procedure yields an equilibrium temperature (temperature for which $SI = 0$) for each considered mineral. In this way a temperature range is determined, in which the fluid has equilibrated with the host rock.

The approach which is applied here, is inspired by the method originally suggested by Reed and Spycher (1984). Since usually (as it is also the case in this study) only standard fluid analysis with limitations concerning pH relevant species (e.g. no gas analysis, carbon species titrated as alkalinity, no detection of organics, total sulfur measured as SO_4^{2-}, only total iron and total silica, etc.) are available, we adapt and simplified the original method. Equilibration temperatures are calculated for feldspars (K-feldspar and albite), SiO_2 polymorphs (quartz and chalcedony), phyllosilicates (muscovite, paragonite and kaolinite), zeolites, and epidotes based on concentrations of the major constituents Na, K, Ca, Si, Al, Fe, Cl, alkalinity and sulfate. Magnesium phases are omitted since mixing with surficial waters (with typically very high associated magnesium input) would cause a dramatic overestimation of temperatures for Mg-phases. Numerical calculations were conducted using PhreeqC version 3.1.4 (Parkhurst and Appelo, 2013) and thermodynamic data of (Delany and Lundeen, 1991**).** According to this, in-situ temperatures were calculated for the wells Caranco (Car), Chihuio (Chi), Liquine (Liq), Liucura (Liu), Los Pozones (Poz), Menetue (Men), Panqui (Pan), Rincon (Rin), Rinconada (Rin), San Luis (SL) and Trancura (Tra), all located in the vicinity of the Villarrica volcano. Fluid compositions were taken from analysis of Held et al. (in preparation).

Previous results of temperatures derived from multicomponent geothermometry are compared to results calculated by a suite of classical solute geothermometers (Fig. 4). The spread of calculated temperatures, which can in a way been considered as the uncertainty of that method, is small compared to the ranges of temperatures obtained from classical solute geothermometers. This is true for the springs in the Villarrica area as well as for the fluids derived from the experiments. It is shown that classical geothermometers generally lead to a very broad spread of temperatures of in some cases >>100 K, whereas multicomponent geothermometry lead to a variation of 50 K or less. But at the same time, the calculated mean (median) temperatures are significantly lower using multicomponent geothermometry. Although negative deviation of calculated temperatures from actual reaction temperature for the experimental fluids is quite small (124 °C for the andesite experiment and 133 °C for the tonalite experiment), estimations for some springs lead to implausible low values, ranging below the discharge temperature (e.g. discharge temperature/calc. temperature for Car = 82/77 °C or Chi = 85/69 °C). At least in those cases calculated temperatures are interfered by processes or parameters which were obviously not taken into account in our chemical model. But also for the other springs calculated temperatures appear to be too low, as in any case being significantly cooler compared to classical geothermometer temperatures. The deviation of measured pH compared to in-situ pH (due to degassing and as a function of temperature), dilution with surficial water during ascent of fluids as well as the uncertainties of in-situ aluminum concentrations (due to precipitations and measurement errors) are anticipated to be the most important processes for this systematical underestimation. It is part of our ongoing work to develop strategies how these affects can numerically be taken into account and how the results can be corrected accordingly.

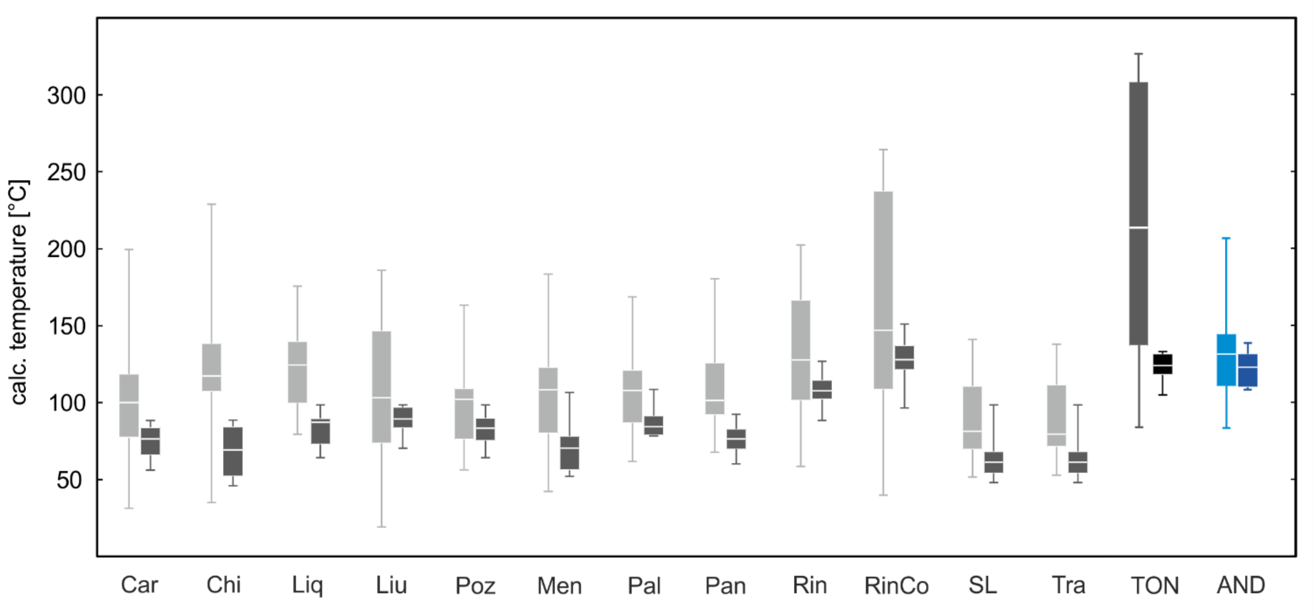

Figure 4: Distribution of temperatures calculated for the Villarrica springs and the laboratory experiments (TON: tonalite experiment, AND: andesite experiment) using classical solute geothermometers (light colors) compared to temperature distribution derived from multicomponent geothermometry (dark colors). Classical solute geothermometer temperatures (SiO_2, Na/K, Na/K/Ca, K/Mg, Li/Mg and Na/Li) were calculated using formulations of Arnórsson (1983), Can (2002), Diaz-Gonzalez et al. (2008) Fouillac and Michard (1981), Fournier (1977), Fournier (1979), Fournier and Potter (1982), Fournier and Truesdell (1973), Giggenbach (1988), Kharaka and Mariner (1989), Michard (1990), Nieva and Nieva (1987), Tonani (1980), and Verma and Santoyo (1997).

3. CONCLUSION

The results of long-term batch experiments equilibrating an andesite and a tonalite sample, two reservoir rock analogues from the Villarrica area, clearly show that reservoir rock composition has a major impact on classical solute geothermometry. Obviously it depends upon the reservoir rock composition (among other reasons), if a geothermometers is applicable or not and therefore if the deduced in-situ temperatures are reliable or not. Consequently, as usually little distinct information about reservoir mineralogy is available exploring an unknown geothermal system, application of different solute geothermometers lead to strongly differing reservoir temperatures. A fact which was also observed in this study, for the fluids derived from the laboratory experiments as well as for the natural geothermal fluids, with deviations of calculated temperatures of >200 K. It is part of our ongoing research to develop and establish a modified multicomponent geothemometry method, which can easily be used also on basis of standard fluid analysis. Due to its statistical nature, this approach should be more detached from reservoir rock composition. First results indeed reveal a significant smaller range of calculated temperatures (max. $\Delta T = 50$ K). Nevertheless, the calculated mean temperatures are apparently too low. First advances in correcting these results has already been made, but still further research is required to adapt this method.

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