Geochemical characterization of the Villarrica geothermal system, Southern Chile, part II: Site-specific re-evaluation of SiO$_2$ and Na-K solute geothermometers

Fabian Nitschke[*], Sebastian Held, Thomas Neumann, Thomas Kohl

Institute of Applied Geoscience (AGW) at Karlsruhe Institute of Technology (KIT), Adenauerring 20b, 76131, Karlsruhe, Germany

ABSTRACT

Solute geothermometry often leads to a broad range and often inconsistent calculated reservoir temperatures, in particular when exploring geothermal systems, where only limited information (geology, borehole data etc.) is available. The application of different Na-K and SiO$_2$ geothermometer, the most widely used methods, not uncommonly lead to deviations of results by up to 200 K for one sample.

In this study, the most effective interfering factors for these geothermometer applications are identified. A multi-step approach is proposed, combining experimental and numerical methods with specific fluid characterization to quantify these factors and to transfer these findings to the natural system enabling the correction of temperatures to realistic in-situ values.

Taking into account dilution with surface water, a chlorofluorocarbon concentration based mixing model was set up to correct analysed SiO$_2$ concentrations to original in-situ concentrations. A numerical model was used to determine the in-situ pH, which is highly sensitive to silica solubility. Results from long-term laboratory equilibration experiments were evaluated to identify the reservoir type dependent equilibrated SiO$_2$ polymorph.

In the case of the Na-K geothermometer, it is shown that the Na$^+$/K$^+$ concentration ratio in fluids is obviously not unequivocally controlled by temperature but is also dependent upon reservoir rock composition. Thus, different reservoir lithologies lead to different equilibration states in terms of Na$^+$/K$^+$. This is obviously one reason for the existence of the large number of different Na-K geothermometers. By modelling the stability of the Na$^+$/K$^+$ ratio governing feldspars, albite and orthoclase, we suggest a method that reveals the Na$^+$/K$^+$ equilibration state for each fluid supporting the allocation of the appropriate geothermometer equation.

The improvement procedure is demonstrated in a case study evaluating fluid data of geothermal springs from the Villarrica geothermal system, Southern Chile. It is shown that initially highly scattered results strongly converge after corrections, leading to a substantial improvement in in-situ temperature estimations with small deviations of ≤ 10 K between SiO$_2$ and Na-K geothermometers. Also absolute temperature calculated for each spring in the study area, ranging from 84 to 184 °C agree well (within $\Delta T < 20$ K) with results of multi-component geothermometry temperatures reported in a previous work.

1. Introduction

The determination of reservoir temperatures is of outstanding importance for geothermal exploration as subsurface temperature is a key parameter for the assessment of the economic potential of a future reservoir. Deducing subsurface temperatures from the fluid composition of natural emerging geothermal springs by using solute geothermometers, has been a common practice for decades. Already in the late 1960ies methods were established using the silica concentration as a measure of the equilibration temperature of a fluid (Bödvarsson, 1960;

Fournier and Rowe, 1966). Later empirical and semi-empirical approaches, like the Na-K, for which later also thermodynamic calibration approaches have been presented (Arnórsson, 2000a; Giggenbach, 1988) and the Na-K-Ca geothermometers came up, linking cation ratios to in-situ temperatures (Ellis, 1970; Fournier and Truesdell, 1973). In order to improve the reliability of temperature estimations, the development of new interrelations of fluid composition and temperature as well as the revision of existing geothermometers and their thermodynamic calibration are subject of ongoing research until today (e.g. Arnórsson (2000a), Pérez-Zárate et al. (2015), Verma (2015), Sanjuan et al.

Table 1
Reservoir temperature estimations from previous works on the Villarrica geothermal system based on classical solute geothermometers (Nitschke et al., 2017a;), oxygen isotope fractionation (Held et al., 2015) and multicomponent geothermometry (Nitschke et al., 2017b).

	Sánchez et al. (2013) classical solute [°C]	Nitschke et al. (2017a) classical solute [°C]	Held et al., (this issue) oxygen isotope [°C]	Nitschke et al. (2017b) multicomponent [°C]
Carranco	–	31–200	84–88	102 (−5/+5)
Chihuío	100–150	35–229	91–94	108 (−10/+6)
Liquiñe	100–150	79–176	83–87	112 (−4/+8)
Liucura	–	20–186	99–101	117 (−10/+12)
Los Pozones	–	56–163	123	100 (−11/+7)
Menetúe	–	42–184	110–112	119 (−11/+12)
Palguín	140–180	62–169	110–112	113 (−12/+9)
Panqui	–	68–180	138–139	96 (−13/+5)
Rincón	140–180	59–203	116–117	138 (−11/+13)
Rinconada	–	40–265	98–101	179 (−8/+14)
San Luis	100–150	52–141	126	117 (−17/+7)
Trancura	–	53–138	125	108 (−14/+10)

(2014)). However, uncertainties in solute geothermometry are still very large (Santoyo and Díaz-González, 2010; Verma and Santoyo, 1997). Applying different geothermometers to a single fluid sample, the scattering of resulting temperatures is often > > 100 K (Aquilina et al., 2002; Mutlu, 1998; Nitschke et al., 2016; Pepin et al., 2015). Facing such large uncertainties reliable reservoir temperature estimations are hardly possible.

The geothermal system of the Villarrica area in Southern Chile has been investigated in a number of recent surveys using different geothermometry methods. The studies yield widely differing estimations for the in-situ temperatures (Table 1). In this regard, the only valid conclusion, is that the subsurface temperatures are apparently rather cool for a geothermal system situated close to an active volcano. Reservoir temperatures > 200 °C are indicated only in a few exceptional cases but mostly in a significantly cooler range (100–180 °C). Of particular note are the very large discrepancies of up to 200 K for some samples obtained from the calculations of a suite of classical, commonly applied solute geothermometers (Nitschke et al., 2017a).

In order to reduce this range of uncertainties, it is obviously still a state-of-the-art procedure to calculate a large number of geothermometers (Powell and Cumming, 2010) and then just "select the most appropriate temperature" (Harvey et al., 2016). However, exploring a geothermal system, reliable indications for a reasonable selection or rejection of individual temperatures are typically rare or lacking at all.

Nevertheless, with shallow dilution (mixing), re-equilibration during ascent, immaturity (degree of dis-equilibrium), steam loss due to subsurface boiling (Arnórsson, 2000a; Giggenbach, 1988; Pérez-Zárate et al., 2015) and effects from different reservoir rock compositions (Meller et al., 2016; Nitschke et al., 2017b), parameters interfering with the results of calculations of well constrained subsurface temperatures are widely known. However, the handling of these parameters in the literature usually remains descriptive and their impact on calculated temperatures is only qualitatively discussed.

In this study, we suggest an approach to identify the most sensitive parameters and quantify their effect on in-situ temperature calculations of classical solute geothermometers and to correct results in order to obtain realistic in-situ conditions. Reflecting ongoing research, this work focusses on SiO_2 and Na-K geothermometers, which are, due to their widespread use, certainly the most important applications among the solute geothermometers. The proposed refining approach is demonstrated by applying it to data for natural fluids from hot springs from the Villarrica geothermal system in Southern Chile (Held et al., 2017) and to fluids obtained from batch-type equilibration experiments of reservoir rock analogues from that area (Nitschke et al., 2017b). For

the convenience of the reader, theses fluid compositions (main constituents) are again presented in this study (*appendix*). Being thoroughly investigated and well characterized previously, this study area was selected due to the occurrence of a large number of hot springs and the availability of particularly good data from a number of recently conducted geological and chemical surveys. A detailed description of the study area, its geology and the geothermal system in particular, is given in Part I by Held et al. (this issue). They specifically focus on the quantification of dilution, by establishing a chlorofluorocarbon concentration based mixing model, which is used in this study to determine realistic reservoir fluid composition. Additional background information is taken from strontium isotope measurements enabling the identification of the reservoir rock for each spring. Data on stable water isotopes (Held et al., 2017) is used for the quantification of boiling related loss of solvent.

2. SiO_2 geothermometry

The basic concept of standard SiO_2 geothermometry is the temperature-only control of SiO_2 solubility. For natural systems this is a strongly simplified first-order approximation. Effectively, the analysed SiO_2 concentrations of fluids, are not only a function of the reservoir temperature but also of a number of other processes interfering with the temperature signal from the deep reservoir: 1) Changes in the amount of solvent as a consequence of mixing and boiling processes are considered to cause the greatest interference to SiO_2 geothermometers (Arnórsson, 2000a). 2) Due to the more defective crystalline structure of chalcedony, its solubility is significantly higher than that of quartz (Gislason et al., 1993), which leads to different equilibration temperatures calculated for the two most commonly applied polymorphs in geothermometry (Fig. 1). 3) The pH of a fluid is a key parameter controlling SiO_2 solubility and very sensitive for the obtained SiO_2 temperature (e.g. Arnórsson et al., 1982). A correction of SiO_2 solubility was proposed by Arnórsson (2000b) for fluids with a pH value in excess of pH 9. Since the original pH at depth can significantly differ from the pH of the cooled fluid at discharge, it is also necessary to determine the in-situ pH.

To illustrate the sensitivity of the SiO_2 polymorph and the pH on SiO_2 geothermometry, we set up a geochemical equilibrium model. Theoretical equilibration temperatures for quartz and chalcedony are modeled by equilibrium dissolution of the polymorphs for the pH bandwidth measured at discharges in the study area (pH 6.1–9.3). Reaction temperature is increased stepwise. Geochemical modeling in this study is conducted using PhreeqC version 3.1.4 (Parkhurst and Appelo, 2013) and thermodynamic data of Delany and Lundeen (1991).

The results clearly reveal an impact of pH on calculated equilibration temperature already at pH > 8.0. In combination with the impact regarding the relevant polymorphs, large deviations in resulting SiO_2 temperature estimations are possible. As an example, for the SiO_2 concentrations determined for sample Chi this deviation could be up to 59 K and for RinCo 63 K (Fig. 1). This spread of temperatures demonstrates the necessity of a precise in-situ pH determination as well as for the specification of the equilibrated SiO_2 polymorph. In the following sections, a stepwise methodology is suggested, to numerically determine the in-situ pH, to identify the equilibrated polymorph and to correct the data for effects of mixing and boiling.

2.1. In-situ pH determination

The pH values for the spring fluids at discharge conditions vary strongly across the study area (*appendix*), being slightly acidic (RinCo) to moderately alkaline for the majority of hot springs (e.g. Men, Car, Liq, Chi). However, for geothermometry the dissolution conditions at depth are of interest. The measured pH at discharge, however, can significantly deviate from the in-situ pH being a function of temperature dependent speciation. Therefore it has to be corrected with respect