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Sulphur deposits in Leirhnjúkur, Krafla area, NE-Iceland

Daniel Gustavo Villarroel Camacho

THE GEOCHEMISTRY OF SILICA IN ICELANDIC GEOTHERMAL SYSTEMS

Report 5
December 2017

UNITED NATIONS
UNIVERSITY
UNU-GTP
Geothermal Training Programme

Orkustofnun, Grensasvegur 9,
IS-108 Reykjavik, Iceland

Reports 2017
Number 5

THE GEOCHEMISTRY OF SILICA IN ICELANDIC GEOTHERMAL SYSTEMS

MSc thesis
School of Engineering and Natural Sciences
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United Nations University
Geothermal Training Programme
Reykjavík, Iceland
Published in December 2017

ISBN 978-9979-68-465-7 (PRINT)
ISBN 978-9979-68-466-4 (PDF)
ISSN 1670-7427

This MSc thesis has also been published in October 2017 by the
School of Engineering and Natural Sciences, Faculty of Earth Sciences
University of Iceland

INTRODUCTION

The Geothermal Training Programme of the United Nations University (UNU) has operated in Iceland since 1979 with six-month annual courses for professionals from developing countries. The aim is to assist developing countries with significant geothermal potential to build up groups of specialists that cover most aspects of geothermal exploration and development. During 1979-2017, 670 scientists and engineers from 60 developing countries have completed the six month courses, or similar. They have come from Africa (39%), Asia (35%), Latin America (14%), Europe (11%), and Oceania (1%). There is a steady flow of requests from all over the world for the six-month training and we can only meet a portion of the requests. Most of the trainees are awarded UNU Fellowships financed by the Government of Iceland.

Candidates for the six-month specialized training must have at least a BSc degree and a minimum of one-year practical experience in geothermal work in their home countries prior to the training. Many of our trainees have already completed their MSc or PhD degrees when they come to Iceland, but many excellent students with only BSc degrees have made requests to come again to Iceland for a higher academic degree. From 1999, UNU Fellows have also been given the chance to continue their studies and study for MSc degrees in geothermal science or engineering in co-operation with the University of Iceland. An agreement to this effect was signed with the University of Iceland. A similar agreement was also signed with Reykjavik University in 2013. The six-month studies at the UNU Geothermal Training Programme form a part of the graduate programme.

It is a pleasure to introduce the 56th UNU Fellow to complete the MSc studies under a UNU-GTP Fellowship. Daniel Gustavo Villarroel Camacho, BSc in Chemical Engineering from Empresa Nacional de Electricidad (ENDE) in Bolivia, completed the six-month specialized training in Chemistry of Thermal Fluids at UNU Geothermal Training Programme in October 2014. His research report was entitled: *Geochemical studies of geothermal fluid and evaluation of well test results from wells SM-01, SM-02 and SM-03, Sol de Mañana field, geothermal project, Laguna Colorada, Bolivia.* After one year of geothermal energy work in Bolivia, he came back to Iceland for MSc studies in chemistry of thermal fluids at the School of Engineering and Natural Sciences, Faculty of Earth Sciences, University of Iceland in September 2015. In September 2017, he defended his MSc thesis presented here, entitled: *The geochemistry of silica in Icelandic geothermal systems*. His studies in Iceland were financed by the Government of Iceland through a UNU-GTP Fellowship from the UNU Geothermal Training Programme. We congratulate Daniel on the achievements and wish him all the best for the future. We thank the School of Engineering and Natural Sciences, Faculty of Earth Sciences, University of Iceland for the co-operation, and his supervisors for the dedication.

Finally, I would like to mention that Daniel's MSc thesis with the figures in colour is available for downloading on our website www.unugtp.is, under publications.

With warmest greetings from Iceland,

Lúdvík S. Georgsson, Director
United Nations University
Geothermal Training Programme

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to the United Nations University Geothermal Training Programme for awarding the scholarship and especially to the director, Lúdvík Georgsson, for giving me the opportunity to enrol in this programme, for his support and for believing in me. Many thanks go to Ingimar Haraldsson, Thórhildur Ísberg, Málfrídur Ómarsdóttir and Markús A.G. Wilde for their priceless help during these two years; they are indeed an amazing staff.

I am very grateful for the support, teachings, and patience from my supervisor, Andri Stefánsson. He has the gift of explaining difficult things in easy ways. My special appreciation to Sigrún Nanna Karlsdóttir who introduce me into the world of the silica scales and to Jóhann Gunnarsson Robin for the WATCH scripts, without it, I would be still creating input files.

I do not know how to begin to thank Frída, for her invaluable friendship, keeping me on track and for always being there.

I would like also thank all the people who kept up with me and joined me in travelling, barbecuing, drinking beer, playing and watching football, riding a bike, and in all those small adventures that made me enjoy these two years.

Finally, I would like to thank my parents and my brother for their immense love and support.

DEDICATION

Dedicated to my parents and my brother,
who encouraged me to pursue my dreams

ABSTRACT

The geochemistry of silica in Icelandic geothermal fluids was studied. The data considered span over 60 years of a sample collection of both sub-boiling liquid water and two-phase well discharges, in total ~1650 samples from >30 geothermal areas. The measured concentration of silica in the samples ranged from >10 to ~1000 ppm. It was observed to increase with increasing temperature, typically <200 ppm at <75°C whereas for boiling and close to boiling water (90-100°C) concentrations up to 700 ppm were observed. Silica concentrations in two-phase well discharges of high-temperature areas were much greater than for the low-temperature areas, typically ~400-1000 ppm with highest values observed at Krafla, Hellisheidi and Nesjavellir. Aqueous speciation calculations revealed that the dominant Si species in all cases were H_4SiO_4(aq) and $HSiO_3^-$ at acid to neutral and alkaline pH values, respectively, with $NaHSiO_3$(aq) also being important at elevated Na concentration. pH was observed to be the major factor controlling aqueous silica species distribution with temperature and salinity being less important. Geothermal fluids with neutral to alkaline pH values and temperatures >20°C were generally observed to be close to saturation with respect to common silica containing geothermal minerals. In contrast, acid fluids were observed to be undersaturated. At low temperatures, these are typically clays and zeolites whereas, at temperatures >230°C feldspars, prehnite and epidote together with quartz are often most important. Geothermal geothermometry relies on the assumption of such fluid-mineral equilibria, that are in turn primarily dependent on the temperature at geothermal conditions. It follows, that equilibrium of the fluids with many silica containing geothermal minerals may be used to predict reservoir temperatures. The simplest is only involving silica like quartz and chalcedony, but more complex reactions involving two or more minerals and many components may also be applied. It is further demonstrated that the silica concentrations in geothermal fluids may be used to predict indirectly spatial reservoir temperature variations, here demonstrated for the low-temperature systems at the southern lowlands and at the high-temperature system at Krafla.

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1. INTRODUCTION

Silica is the second most abundant element in the Earth's crust after oxygen. It is present in most crustal materials: melts, rock-forming minerals and fluids. Silicate minerals constitute approximately 90% of the minerals in the Earth crust and dominate virtually every water-rock system. At least ten different pure silica oxides (SiO_2) phases are known in natural and engineered systems: quartz, cristobalite, tridymite, moganite, coesite, stishovite, lechatelierite, chalcedony, amorphous and opaline silica. Of those, quartz is the most common (e.g., Dove and Rimstidt, 1994).

Silica is one of the major elements in all geothermal systems. It is present in the primary rocks and minerals, in secondary minerals and various aluminium silicates, in the liquid phase and also present in trace amounts in the vapour phase (e.g., Arnórsson et al., 1978; Rodgers et al., 2002). The major silica oxides in geothermal systems are quartz, chalcedony and amorphous silica. Other silica containing secondary minerals are also common. At temperatures below 150°C silica containing minerals include various clays and zeolites whereas at temperatures of ~200-400°C various clays, zeolites, prehnite, epidote, feldspars, amphiboles, garnets and oxides are observed (e.g., Browne, 1978). Silica minerals are also common geothermal scales that is one of the major problems associated with geothermal fluid utilization. Such scaling formation occurs when the geothermal fluids become supersaturated with respect to the solid upon changes in physical conditions of the fluids during utilization, like depressurization and cooling (e.g. Corsi, 1986). Many methods have been applied to minimise silica scalings like hot fluid re-injection, silica removal by ageing or pond retention. Silica mineralization is also common at the surface of geothermal systems, often forming silica sinters. Such silicification and subsequent fossilization is generally closely linked to microorganisms, that play an important role in their structures and textures (e.g. Tobler et al., 2008).

Silica concentrations in geothermal liquid solutions range from a few to >1000 ppm whereas concentrations in the vapour phase are generally on the ppb to lower ppm scale (e.g., Arnórsson et al., 2007). It is generally assumed that the concentrations in the waters are controlled by equilibrium with secondary silicate minerals, for example, quartz and chalcedony (e.g., Arnórsson et al., 1978; Arnórsson et al., 1983; Stefánsson and Arnórsson, 2000) according to the reactions,

$$SiO_2(s) + 2H_2O \leftrightarrow H_4SiO_{4(aq)} \tag{1}$$

where $SiO_2(s)$ stands for quartz and chalcedony. The respective equilibrium constant is defined as,

$$K = \frac{a_{H_4SiO_4(aq)}}{a_{SiO_2} \cdot a_{H_2O}^2} \approx m_{H_4SiO_4}\gamma_{H_4SiO_4} \tag{2}$$

assuming activity of the solid and water to be unity.

It follows that the silica concentration in geothermal liquid water, in equilibrium with quartz or chalcedony, are controlled by temperature and pressure, with pressure being usually unimportant relative to temperature (Arnórsson et al., 1983) as well as ionic strength (I) as the activity coefficient (γ) depends on I. The observed fluid-mineral equilibria involving quartz and chalcedony has been applied to calculate sub-surface temperatures of geothermal fluids from surface water composition data, i.e. using reaction (1) and the respective equilibrium constant to make the theoretical background for the silica geothermometers (e.g., Arnórsson, 2000).

Over the past six decades, a large dataset of the chemical composition of geothermal fluids in Iceland has been collected. Some of these data have been published whereas others have not. The fluids span variable chemical composition ranging in pH (~2-11), temperature (~10-450°C) and chloride concentration (Cl <10 to >20,000 ppm). However, since the 1970's and early 1980's the distribution of silica in Icelandic geothermal fluids has not been systematically studied including the effects of ionic strength, pH and temperature on silica (Arnórsson et al., 1978; Arnórsson, 2000). Recently, the composition of sampled geothermal fluid composition in Iceland was gathered into a single dataset named GeoFluids (Stefánsson et al., 2016). In this thesis, the silica concentrations in geothermal fluids in Iceland was studies using this newly gathered dataset, including fluid-rock interaction, aqueous silica speciation and the application of silica geothermometry to understand underground temperatures.

2. GEOTHERMAL ACTIVITY IN ICELAND

Iceland is a mountainous, volcanic and geologically young country located in the North Atlantic on the boundary between the Eurasian and the North American plate. The regional geology of Iceland is the result of both extension and migration of the Mid-Atlantic divergent plate boundary relative to the Iceland mantle plume (Figure 1). The plate boundary is migrating westwards relative to the mantle plume, causing the volcanic zones in Iceland to shift eastwards (e.g., Bjarnason, 2008). Recent volcanic activity is most intensive where these extensional zones cut across the plate boundary.

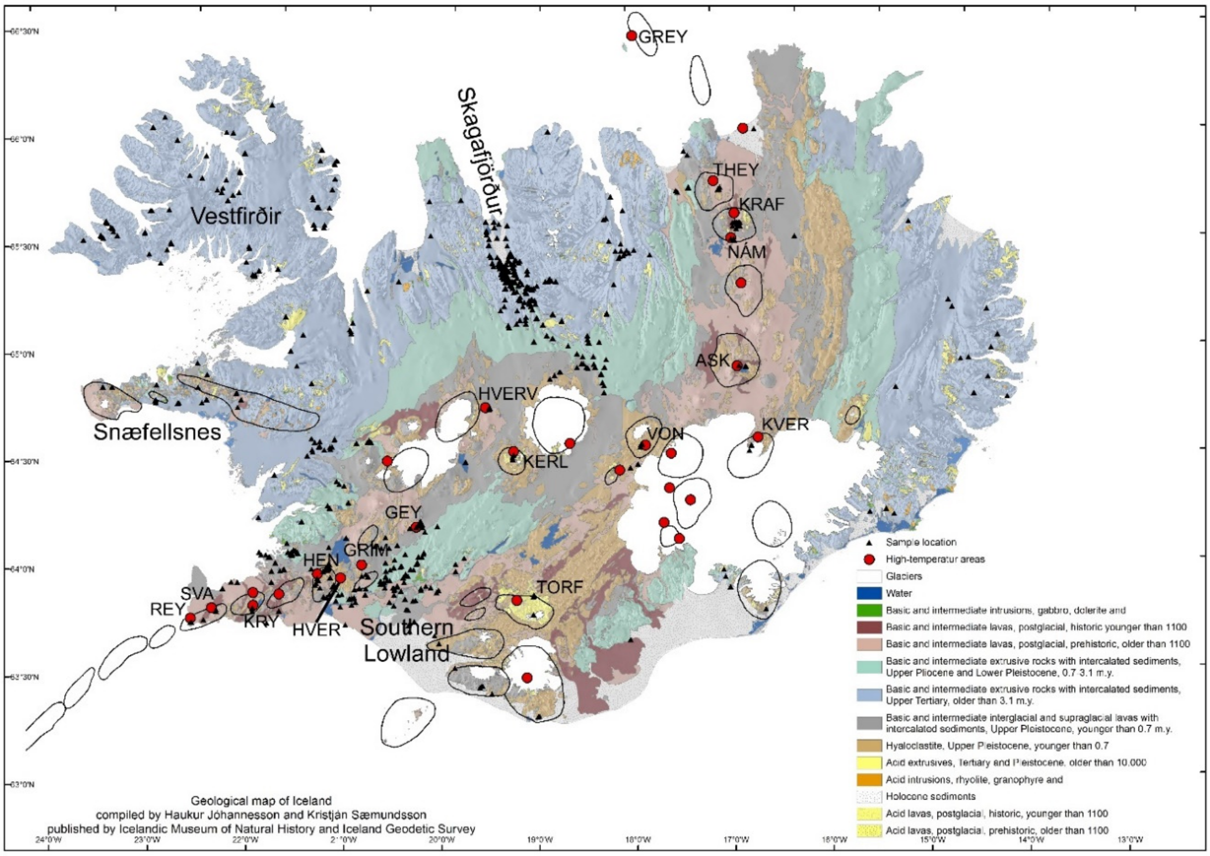

FIGURE 1. Geology and geothermal activity in Iceland and location of fluids considered in this study. The names on the map correspond to Table 1 (Stefánsson et al., 2017 modified from Jóhannesson and Saemundsson, 1999)

Subsurface temperatures, heat output and surface manifestations, among others, have been the base to classify the geothermal activity in Iceland into low- and high-temperature systems (Bödvarsson, 1961; Fridleifsson, 1979). Most of the high-temperature geothermal systems are located in central parts of the belts of active volcanism and rifting. In the Eastern and Northern Volcanic Zones, the high-temperature geothermal systems are typically associated with the volcanic complexes. In the Western Zone, between Langjökull and Lake Thingvallavatn, no high-temperature systems are present, whereas, between Lake Thingvallavatn and the Reykjanes Peninsula, there are several high-temperature systems. Low-temperature geothermal activity is widespread in the Quaternary and Tertiary formations of Iceland with the main activity mostly confined within the North American Plate and the southern lowlands. The low-temperature activity is frequently associated with active fractures and faults. Some systems are located within the active fissure swarms that run into older formations, whereas others are placed in the crust where the build-up of stress by plate movements leads to deformation and fracturing (e.g., Arnórsson, 1995).

A summary of the main geothermal areas in Iceland is shown in Table 1. The high-temperature systems have been developed in order to produce electricity (~660 MW_e) mainly, although, in combination with the fluid from the low-temperature areas, the hot water is used for space heating, swimming pools, greenhouses, industry, among others. Iceland is well known to be a world leader in the use of geothermal district heating with about 9/10 households heated with geothermal energy. Space heating is the largest component in the direct use of geothermal energy in Iceland (Orkustofnun, 2017)

TABLE 1. A summary of high- and low-temperature geothermal activity in Iceland
(after Stefánsson et al., 2017)

Area	**Temp (°C)**[a]	**Cl (ppm)**[b]	**Status**
High-Temperature areas[a]			
Askja (ASK)	180-350		Surface activity
Bárdarbunga			Subglacial
Brennisteinsfjöll	240		Surface activity
Fremrinámur	270		Surface activity
Geysir (GEY)	260	~100	Surface activity
Gjástykki	280		Surface activity
Grímsey (GREY)	240	~19,500	Submarine
Grímsnes (GRÍM)	100-230		Wells and surface activity
Grímsvötn (GRÍM)	235		Subglacial
Hágöngur	280-310	~200	Well and surface activity
Hengill (HEN)	200-380	~100	744 MWe power plants and surface activity
Hofsjökull			Probably subglacial
Hrúthâls			Surface activity
Hveragerdi (HVER)	170-230	~150	20 MWt space heating and surface activity
Hveravellir (HVERV)	280	~60	Surface activity
Kerlingarfjöll (KERL)	260-310		Surface activity
Kolbeinsey (KOLB)	180	~19,500	Submarine
Krafla (KRA)	200-440	~50	60 MWe power plant and surface activity
Krýsuvík og Trölladyngja (KRÝ)	220-320	~700	Wells and surface activity
Kverkfjöll (KVE)	290-350	>150	Surface activity
Mýrdalsjökull			Subglacial
Námafjall (NAM)	220-320	~30	3 MWe power plant and surface activity
Öxarfjördur (ÖXF)	100-200		Wells and surface activity
Reykjanes (REY)	260-345	~19,500	100 MWe power plant and surface activity
Skaftárkatlar	310		Subglacial
Steinhóll	130-250	~19,500	Submarine
Svartsengi-Eldvörp (SVA)	220-260	~12,000	60 MWe power plant
Theistareykir (THEI)	230-310	~100	Wells and surface activity
Thórdarhyna (TORF)			Subglacial
Tindfjallajökull			Probably subglacial
Torfajökull (TORF)	260-300	~300	Surface activity
Vonarskard (VON)	280-325		Surface activity
Low-temperature areas[a,c]			
East and Southeast (E&SE)	90	<10-400	Wells and surface activity
Skagafjördur (SKAG) and North (N)	100	<10-400	Wells and surface activity
Snaefellsnes (SNAE) and Northwest (NW)	150	<10-4000	Wells and surface activity
Southeast (SW)	125	10-1900	Wells and surface activity
Southern lowlands (SLL) and South (S)	150	<10-1100	Wells and surface activity
West (W)	150	<10-110	Wells and surface activity
Westfirdir (VES)	120	<10-2500	Wells and surface activity

[a] Reservoir temperature range based on down-hole measurements, solute and gas geothermometry.

[b] Typical reservoir Cl concentrations for high-temperature fluids and range of Cl observed at the surface for low-temperature areas. The high-temperature reservoir Cl concentrations were based on surface well and hot-spring discharge data and were obtained using the WATCH program (Bjarnason, 2010) for high-temperature.

[C] The low-temperature geothermal activity in Iceland is widespread in the Tertiary and Quaternary formations to the west and east of the active belt of volcanism. Here the locations have been grouped based on geographical location.

3. GEOFLUIDS DATABASE

The current study relies on the newly published dataset on geothermal liquid water and steam composition of Icelandic geothermal fluids. The database is named GeoFluids. The full dataset is published in Stefánsson et al. (2016) and is available upon request to Ríkey Kjartansdóttir (rikey@hi.is). Here the dataset will be briefly described, i.e. the source of data and construction of the database.

The GeoFluids database reports the composition of geothermal liquid water and steam from high- and low-temperature geothermal areas in Iceland. The data are divided into three parts (spreadsheets): (1) fumarole samples (GeoGas), (2) two-phase well samples (Two-Phase Wells) and (3) single-phase liquid samples (ThermalWater).

The sources of data are various and include reports, MSc and PhD thesis and published scientific journal articles. In many cases, there are multiple sources for a given sample. A large part of the dataset has not previously been published nor systematically applied to understand geothermal fluid chemistry.

The data span over 60 years of sample collection and include both published and unpublished data, i.e. the detection limits between samples can vary due to different analytical methods. The list of reported major elements in the liquid phase included: SiO_2, B, Na, K, Ca, Mg, Al, Fe_{tot}, Cl, F, CO_2, SO_4, H_2S whereas for selected samples, trace elements have also been included, some or all of: Ag, As, Au, Ba, Be, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, DOC (dissolved organic carbon), Dy, Er, Eu, Fe^{II}, Fe^{III}, Ga, Gd, Ge, Hf, Hg, Ho, I, Ir, La, Li, Lu, Mn, Mo, Nb, Nd, NH_4, NH_3, NO_3, NO_2, O_2, Os, PO_4, Ptot, Pb, Pd, Pr, Pt, Rb, Re, Rn, Ru, Sb, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr. Major elements analysed in the gas phase were: H_2O, CO_2, H_2S, H_2, N_2, O_2 and Ar. Other gases have not been routinely analysed. A separate dataset has been compiled for isotope ratios, IsoFluid (Stefánsson et al., 2017).

The samples have been divided into seven subgroups depending on the type of sample and fluid: g: gas and fumaroles; w: well fluids, both single liquid and two-phase liquid and vapour discharges; sp: springs; s: soil water; rs: rivers and stream. The dataset comprises approximately n = ~1650 samples; ~1350 single-phase liquid samples and ~300 two-phase wells discharges. In addition, the GeoFluids dataset contains ~800 fumarole samples not further considered here.

4. METHODS

4.1 Calculations of reservoir fluid composition

The reservoir fluid composition was calculated from data on two-phase well discharges and liquid water of boiling hot springs. The WATCH speciation program version 2.4 was used for the calculations (Arnórsson et al., 1982; Bjarnason, 2010) and the reservoir fluid temperature was calculated based on the quartz (Fournier and Potter, 1982) and chalcedony (Fournier, 1977) geothermometry above and below 180°C, respectively. For two-phase well discharges, the calculated and measured enthalpy (h) was used for the calculations, and equilibrium degassing was assumed. For the boiling hot springs, the model given by Arnórsson et al. (2007) was applied and studied by Stefánsson et al. (2005), where degassing was assumed to be 0.3. In the case of sub-boiling springs, wells and surface water, the measured chemical composition and temperature was used for the calculations.

4.2 Calculations of aqueous speciation and mineral saturation indices

The calculated activities of the dissolved components (or species) for homogeneous equilibrium at the reference temperature, can be used to calculate the degree of super- or undersaturation of the aqueous phase with the secondary minerals at each temperature. This is expressed for the mineral *n* in terms of $\log(Q/K)_n$:

$$log\left(\frac{Q}{K}\right)_n = log\prod^{i} a_{i,k}^{v_{i,k}} - \log K_n \tag{3}$$

where Q is the ion activity product and K is the equilibrium constant for the mineral n, α is the activity and $v_{i,k}$ is the stoichiometric coefficient of component species i in the equilibrium mass action equation for the mineral n. The numerical value of this index is less than zero for undersaturated minerals and greater than zero for supersaturated minerals, and zero for equilibrium between the mineral and dissolved species.

The aqueous species distribution and mineral saturation indices of the calculated reservoir fluids and sub-boiling fluids were calculated using the PHREEQC 3.3.8 program (Parkhurst and Apello, 1999) and the llnl.dat database. The activity distribution of the species was calculated using the sulphate-sulphide redox couple (S^{+VI}/S^{-II}). The temperature used for these calculations were quartz or chalcedony geothermometry in the case of two-phase well discharges and boiling hot springs but measured temperatures for other waters. The output files contain the activity of more than 90 chemical species of 17 different elements (Table 2). For these calculations, the reservoir pH was selected from the WATCH program. WATCH calculates the pH based on conservation of alkalinity (i.e., “temperature pH sliding”) whereas PHREEQC applies charge balance, the latter sometimes resulting in erroneous calculated pH values. The mineral saturation indices were further calculated from the calculated aqueous species activities at the selected temperatures. The solubilities of the minerals (K_n) were taken from the llnl.dat database.

4.3 Geothermometry calculations

The temperatures selected for the calculations of reservoir fluid composition, aqueous speciation and mineral saturation were quartz and chalcedony geothermometry for two-phase well discharges and boiling hot springs. For sub-boiling water, the measured temperature was used as the reference temperature. The temperatures functions for the quartz and chalcedony geothermometers were selected from Fournier and Potter (1982) and Fournier (1977), respectively, and were calculated with the aid of the WATCH program. These geothermometer temperatures were further compared with another solute (Na-K) geothermometry temperature in order to assess and compare various methods of calculating sub-surface temperatures. The quartz and chalcedony geothermometry temperatures were further compared for selected fluids with the multiple geothermometry approaches. A summary of the geothermometry temperature functions is given in Table 3.

TABLE 2. Aqueous species used in the geochemical calculations

H_2O	**Al**		**B**	**C(-4)**	**C(+IV)**	**Ca**	**Cl**	**F**	**H(0)**
OH^- H^+ H_2O	AlO_2^- $NaAlO_2$ $HAlO_2$ $Al(OH)_2^+$ AlF_2^+ AlF_3	AlF^{+2} AlF_4^- Al^{+3} $AlSO_4^+$ $Al(SO_4)_2^-$	BH_4^- $B(OH)_3$ BO_2^- $NaB(OH)_4$ $CaB(OH)_4^+$ $BF_2(OH)_2^-$ $B_2O(OH)_5^-$ BF_4^- BF_3OH^-	CH_4	CO_2 HCO_3^- $CaHCO_3^+$ $CaCO_3$ CO_3^{-2} $NaHCO_3$ $NaCO_3^-$	Ca^{+2} $CaSO_4$ $CaCl^+$ CaF^+ $CaCl_2$ $CaOH^+$	Cl^- $NaCl$ KCl HCl	F^- HF NaF HF_2^-	H_2
K	**N**	**Na**	**S(-II)**	**S(+VI)**	**Si**	**Mg**	**Fe**		
K^+ KSO_4^- $KHSO_4$ KOH	N_2	Na^+ $NaHSiO_3$ $NaOH$	H_2S S^{-2} HS^-	SO_4^{-2} HSO_4^- H_2SO_4 $NaSO_4^-$	SiO_2 $HSiO_3^-$ $H_2SiO_4^{-2}$ $Na\ HSiO_3$	$MgSO_4$ $MgHCO_3^+$ Mg^{+2} $MgCl^+$ MgF^+ $MgCO_3$	Fe^{+2} $FeHCO_3^+$ $FeCl^+$ $FeCO_3$ $FeSO_4$ $FeOH^+$ FeF^+ $FeCl_2$	$FeCl_4^{-2}$ $Fe(OH)_2$ $Fe(OH)_3^-$ $Fe(OH)_2^+$ $Fe(OH)_3$ FeF^{+2} $FeOH^{+2}$ $FeSO_4^+$	FeF^{+2} $FeCl^{+2}$ Fe^{+3} $FeCl_2+$ $FeCl_2^+$ $FeCl_2^+$ $Fe(OH)_4^-$

TABLE 3. Temperature equations for silica and cations geothermometers (Arnórsson, 2000)

Geothermometer [°C]	**Equation**	**Source**
Quartz[a]	$-53.5 + 0.11236S - 0.5559 \cdot 10^{-4}S^2 + 0.1772 \cdot 10^{-7}S^3 + 88.390 \log S$	Fournier and Potter (1982)
Chalcedony[a]	$-\frac{1032}{4.69 - \log S} - 273.15$	Fournier (1977)
Na-K[b]	$\frac{933}{0.993 + \log Na/K} - 273.15$	Arnórsson et al. (1983)

[a] S represents the SiO_2 concentration in ppm

[b] Cations concentrations are expressed in ppm.

4.4 Graphical presentation of data

Distribution maps of silica concentrations for selected geothermal areas in Iceland were done. The source of data for the maps came from the GeoFluids database.

The data was classified into 8 breaks. Manual breaks were used since the aim was to show how the silica concentration changes with location.

The Natural Neighbour method was used for interpolation, considering the silica concentrations in the reservoir fluid. Interpolation is a method or a mathematical function that estimates the values of cells at locations that lack sampled points. In addition, interpolation is based on spatial dependence, which measures the degree of dependence between objects. The two types of interpolation techniques are deterministic and geostatistical. Deterministic techniques create surfaces based on measured points or mathematical formulas. Geostatistical techniques are based on statistics and are used for more advanced surface modelling. Here, the Spatial Analyst extension was used to make the interpolation maps. The Spatial Analyst extension provides tools for spatial data analysis that apply statistical theory and techniques to the modelling of spatially referenced data (Childs, 2004).

5. GEOTHERMAL FLUID COMPOSITION AND THE GEOFLUIDS DATABASE

5.1 Fluid composition

The chemical composition of selected geothermal fluids is given in Tables 4 and 5 for single phase liquid water and two-phase well discharges, respectively. It is based on the data given in the GeoFluids database (Stefánsson et al., 2016). The chemical composition of thermal fluids in Iceland is dominated by H_2O, which generally accounts for >97 mol% of the total fluid. Fluids of meteoric origin are relatively low in chloride (Cl) compared to geothermal fluids worldwide (e.g., Ellis and Mahon, 1977). Low-temperature waters typically have Cl concentrations <50 ppm and high-temperature waters typically have Cl concentrations <200 ppm (e.g., Ármannsson et al., 2015; Stefánsson et al., 2016). The reason for the low Cl concentration of many Icelandic thermal fluids is related to the generally low Cl content of basaltic rocks which make up the bulk of the Icelandic crust (Sigvaldason and Óskarsson, 1976; Arnórsson and Andrésdóttir, 1995). Thermal water associated with silicic rocks (rhyolites) are generally higher in Cl and other volatiles, for example, fluids from the Torfajökull and Geysir areas (Arnórsson 1985). Geothermal systems that have a seawater component, such as Reykjanes and Svartsengi on the Reykjanes Peninsula and some on the southern lowlands, display much higher Cl concentration, up to ~20,000 ppm, similar to seawater salinity values (Arnórsson and Andrésdóttir, 1995; Ármannsson et al., 2015).

The geothermal fluids in Iceland have divided into two groups based on their source and formation nature: primary and secondary fluids. Primary fluids are considered to reflect reservoir fluid at depth that may have undergone

TABLE 4: Selected chemical composition of liquid samples only (from GeoFluids, Stefánsson et al., 2016). The concentrations are given in ppm

Sample #	Area	Source	Temp °C	pH	/	°C	SiO_2	B	Na	K	Ca	Mg	SO_4	Cl	F	CO_2	H_2S
07-HK13	Krafla	sp	76	6.60	/	21	40.0	<0.005	17.9	0.77	197	65.3	627	3.35			4.55
07-SC-12	Námafjall	s	100	2.48	/	21	132	0.006	0.42	0.22	2.48	3.76	252	<1			
82-3011	Geysir	rs	5	8.01	/	20	30.6	0.10	11.8	0.96	3.22	0.461	0.50	7.40	0.070	59	
W233	Southern lowlands	sp	98	9.10	/	98	194	0.530	123	5.70	2.60	0.030	71.8	89.5	2.20	15.7	1.20
W275	Torfajökull	sp	95	9.20	/	95	300	1.94	372	23.9	0.900	0.050	71.7	386	27.0	89.8	24.9
W263	Flúdir	sp	100	8.40	/	100	156	0.620	76.2	2.20	2.00	0.040	61.3	15.6	1.60	43.1	1.30
05-024	Hengill/Hveragerdi	rs	11	7.52	/	21	20.7	0.004	7.69	1.12	12.5	5.63		9.9			
14-KERL-21	Kerlingajöll	sp	91	4.12	/	20	178	8.96	11.2	4.78	25.5	10.9	361	<5	0.296	22.8	0.084
W356	Krýsuvik	sp	12	5.80	/	12	76.0	0.060	17.5	0.900	18.7	11.2	127	17.8	0.400	5.800	<0.1
79-3021	Borgafjördur	sp	75	8.92	/	20	156	0.200	68.3	2.55	2.38	0.034	59.8	18.6	1.19	40.8	0.660
11-VON-1	Vonarskard	sp	62	6.86	/	16	178	0.065	68.6	6.43	42.3	6.81	87.0	4.45	0.780	170	<0.1
W324	Hveravellir	sp	90	8.60	/	25	599	0.800	161	16.4	3.00	0.190	137	66.8	3.30	81.7	1.00
96-04	Skagafjördur	s	6	6.69	/	26	27.3	0.012	13.2	0.263	11.2	4.70	3.44	14.6	0.096	60.6	3.44
03-101	Vestfirdir	g	66	9.81	/	22	70.1	0.011	66.0	1	6.56	<0.002	56.6	37.9	0.610	8.50	0.221
79-3050	Austfirdir	w	59	9.99	/	23	59.2	0.170	63.4	0.850	4.92	0.008	47.5	42.2	0.600	18.1	0.060
79-3056	Vesturland	w	61	9.78	/	11	63.5	0.030	48.7	0.93	3.24	0.002	53.5	10.6	0.630	17.4	0.34
79-3036	Nordvesturland	w	66	9.46	/	23	116	0.040	61.9	2.14	2.56	0.056	58.0	7.60	5.69	28.7	1.16
W317	Reykjanes	sp	99	5.10	/		531	12.4	16440	1,900	2370	129	214	31300	0.300	<5.0	<0.1
04-040	South and Southeast	w	66	8.07	/	23	107	0.978	188	2.84	8.40	0.307	204	33.1	2.52	158	0.007
02-001	Reykjavík	w	108	8.37	/	27	95.0	0.234	593	13.0	582	0.502	291	1820	0.720	5.40	0.091

TABLE 5: Chemical composition of selected samples from high-temperature systems (from GeoFluids, Stefánsson et al., 2016)

					Liquid phase (ppm)													***Steam phase (mmol/kg)***		
Sample #	**Area**	**Enthalpy kJ**	**p^{sample} bar**	**t^{sample} °C**	**pH**	**/**	**°C**	**SiO_2**	**B**	**Na**	**K**	**Ca**	**Mg**	**Cl**	**CO_2**	**SO_4**	**H_2S**	**CO_2**	**H_2S**	**H_2**
04-3010	Krafla	1941	15.5	200	8.34	/	18.1	432	0.90	244	26.60	4.473	0.0017	31.8	67.9	304	72.6	158	11.9	47.0
79-3049	Krafla	1601	5.5	155	8.52	/	20.0	767	1.50	193	36.00	1.900	0.0670	57.2	187	143	22.2	334	11.2	8.7
97-3108	Námafjall	1712	24.8	223	7.63	/	20.6	447	4.85	112	16.81	0.401	0.0024	41.5	13.2	14.4	110	142	51.4	89.5
04-3007	Námafjall	1060	14	195	8.67	/	18.6	457	0.72	151	19.40	2.581	0.0016	35.6	38.6	43.9	62.1	65	24.1	106
04-3040	Nesjavellir	1800	15.5	200	8.41	/	22.6	713	1.59	164	31.40	0.334	0.0011	117	58.5	8.1	59.6	143	40.8	34.0
04-3002	Nesjavellir	1711	6	159	7.13	/	21.7	861	3.32	147	32.90	0.087	0.0007	148	25.7	1.9	85.3	30	37.9	30.1
10-5082	Hellisheidi	1597	9.8	179	8.79	/	20.0	684	1.13	182	30.00	0.490	0.0019	167	16.4	9.6	55.5	83	24.2	9.3
08-3009	Hellisheidi	1385	9.4	177	8.97	/	19.0	682	0.84	165	27.60	0.310	0.0010	144	18.9	8.8	57.9	65	18.1	12.1
04-3005	Svartsengi	1028	15.5	200	6.24	/	20.2	468	7.07	7263	1050	1167	0.428	13831	24.8	26.0	2.2	168	4.8	2.2
92-0124	Svartsengi		15.5	200	6.61	/	25.1	483	8.10	7110	1080	1190	0.450	13818	36.8	28.3	0.6	57	2.0	0.1
05-3004	Reykjanes	1316	42	253	4.88	/	21.9	679	6.79	10166	1434	1680	0.796	19288	104	15.8	11.5	447	14.7	0.9
3009	Reykjanes	1150	19	210	6.38	/	20.0	631	8.72	11150	1720	1705	1.440	22835	63.1	28.4	2.2	117	5.1	0.2
79-0136	Hveragerdi		4.5	148	9.29	/	19.0	259		168	13.80	2.180	0.000	142	44.2	40.1	18.4	19	0.9	0.6
79-3032	Hveragerdi		6.8	164	8.82	/	20.0	281	0.62	153	13.40	1.730	0.0020	110	74.2	43.7	19.2	37	1.3	1.2
79-3030	Sudurland		4	144	9.28	/	20.0	253	0.65	102.2	6.21	1.280	0.0480	41.6	54.3	70.7	4.1	52	0.9	0.6
15-AS-15	Sudurland		6.9	164	6.55	/	23.0	258	0.88	647	34.94	1.582	1.950	1.4	1047	139	0.5	16719	4.4	0.5
88-3254	Hveravellir		1	100	9.39	/	24.0	199	0.09	59.9	2.72	1.250	0.0050	10.7	25.1	32.0	1.1	83	0.02	0.03

depressurization boiling. These fluids are originated from meteoric water, seawater, magmatic volatiles or a combination thereof. Based on their major chemical composition primary fluids have been subdivided into NaCl-, sulphate- and saline fluids (Arnórsson et al., 2007).

In NaCl fluids, Na is commonly the major cation and Cl and CO_2 the major anion. For sulphate fluids, Na is also usually the major cation whereas SO_4 and CO_2 are the major anions. NaCl and sulphate fluids are, however, usually characterized by relatively low salt (NaCl) concentration (<500 ppm Cl) and mildly acid to neutral pH. Saline fluids are, in contrast, characterized by elevated salt content, typically NaCl, often reaching concentrations >20,000 ppm Cl. Most Icelandic primary fluids of meteoric origin are NaCl-fluids, but some sulphate fluids are observed at Krafla and Námafjall. Geothermal fluid of seawater origin or a mixture of seawater and meteoric water, for example at Reykjanes and Svartsengi, are classified as saline fluids (Arnórsson et al., 2007).

Upon ascent to surface processes like depressurization boiling, conductive cooling and mixing with shallow non-thermal surface water can occur, these leading to the formation of secondary geothermal fluids. Typical examples are alkaline boiling hot springs that represent the boiled liquid fraction of primary geothermal fluids and steam vents that represent the steam fraction of the boiled fluid. The boiled liquid and/or steam may also mix and condense into non-thermal fluids at surface leading to the formation of various types of secondary fluids like carbonate waters and acid-sulphate water. Upon these processes, the fluids may also interact with the surrounding rocks further changing their composition. Three major types of secondary geothermal fluids can be recognized: (1) boiled and sub-boiling alkaline waters, that represent the reservoir fluids sometimes mixed to various degree with non-thermal waters, typically characterized with neutral to alkaline pH and dominated by Na, Cl and CO_2, (2) acid-sulphate waters that are formed upon steam condensation into non-thermal waters, characterized by acid pH values, high concentration of SO_4 and often metals like Ca, Mg, Fe and Al, and (3) carbonate waters that have midly acid pH values, are enriched in CO_2 and have relatively high Ca and Mg concentration relative to Na. As a result, secondary fluids have a variety of chemical composition, ranging from Cl- to SO_4 to CO_2-rich (Figure 3). However, all secondary fluids are usually dominated by Na and/or Ca-Mg cations with K usually being unimportant.

Here we have not made an attempt to classify individual fluids into primary- and secondary fluids and sub-divisions of each type. Instead, the chemical variations relative to major elements are shown in Figures 2 and 3 for various geothermal area together with typical characteristics of various fluid types. In summary, for most high-temperature geothermal systems, both primary- and secondary fluids are observed, whereas, for low-temperature areas, primary fluids mixed to a various degree with non-thermal fluids is most common.

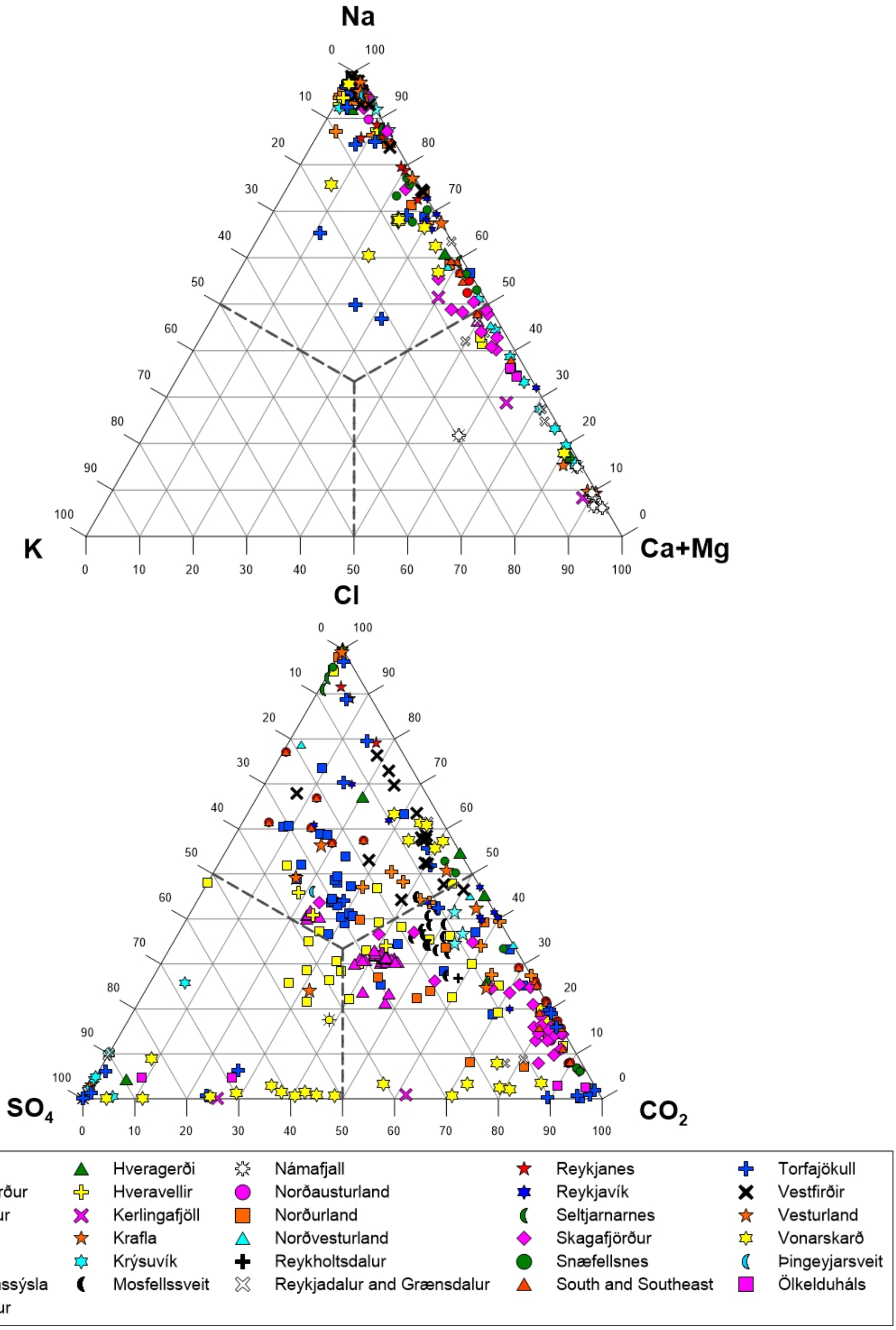

FIGURE 2: Ternary diagrams of Na-K-Ca+Mg (above) and Cl-SO4-CO2 (below) for single-phase liquid samples

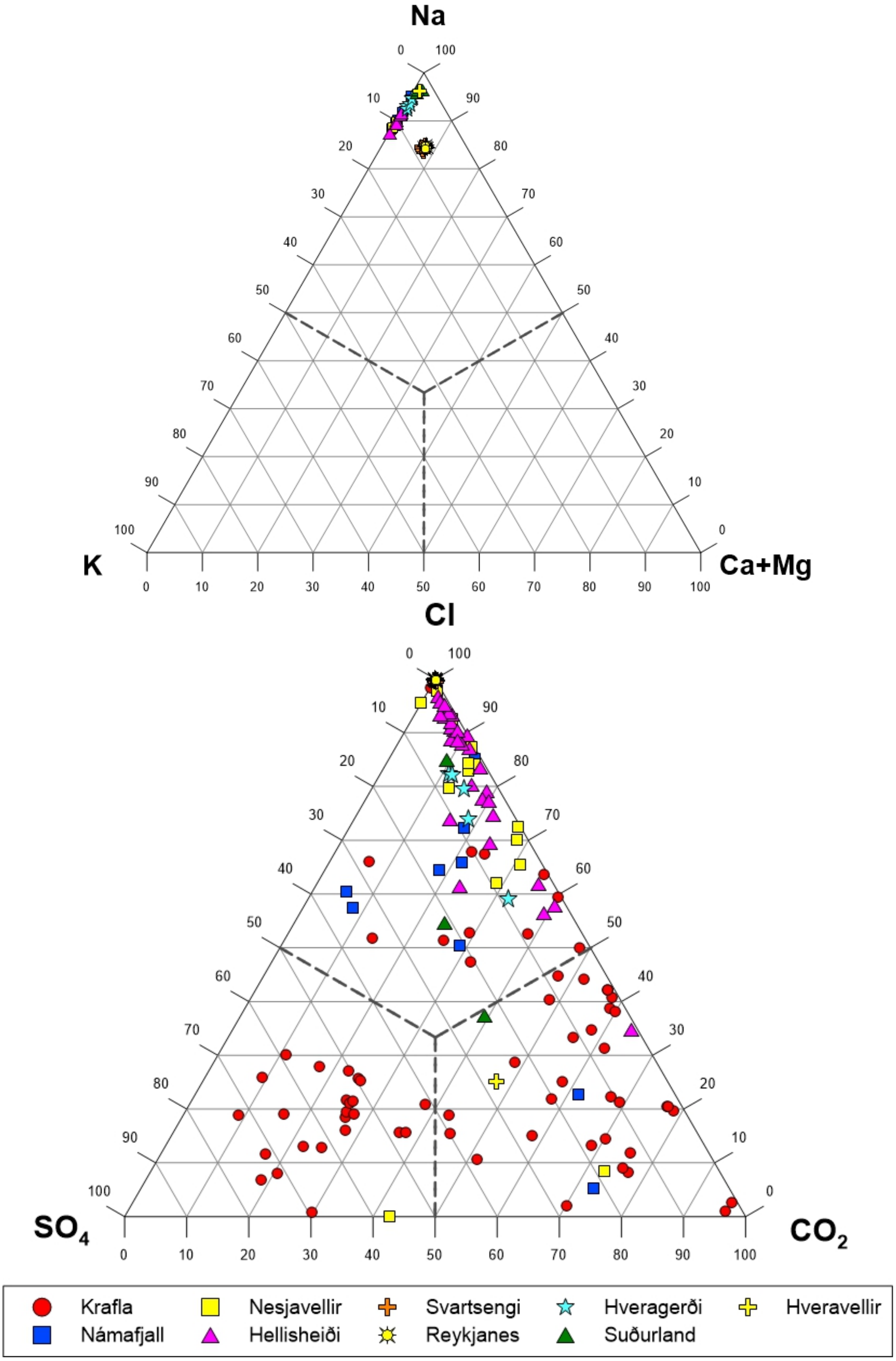

FIGURE 3: Ternary diagrams of Na-K-Ca+Mg (above) and Cl-SO4-CO2 (below) for two-phase well samples

5.2 Silica concentration

The measured concentration of silica ranged from >10 to ~1000 ppm in single-phase non-thermal and thermal liquid water and in the liquid phase of two-phase well discharges (Figure 4). The concentration was generally observed to increase with increasing temperature, typically <200 ppm at <75°C. For boiling and close to boiling water (90-100°C), much greater Si concentration range was observed, ~50-700 ppm, this considered to reflect different origin of the fluids, for example, boiled high-temperature reservoir fluids and steam heated water.

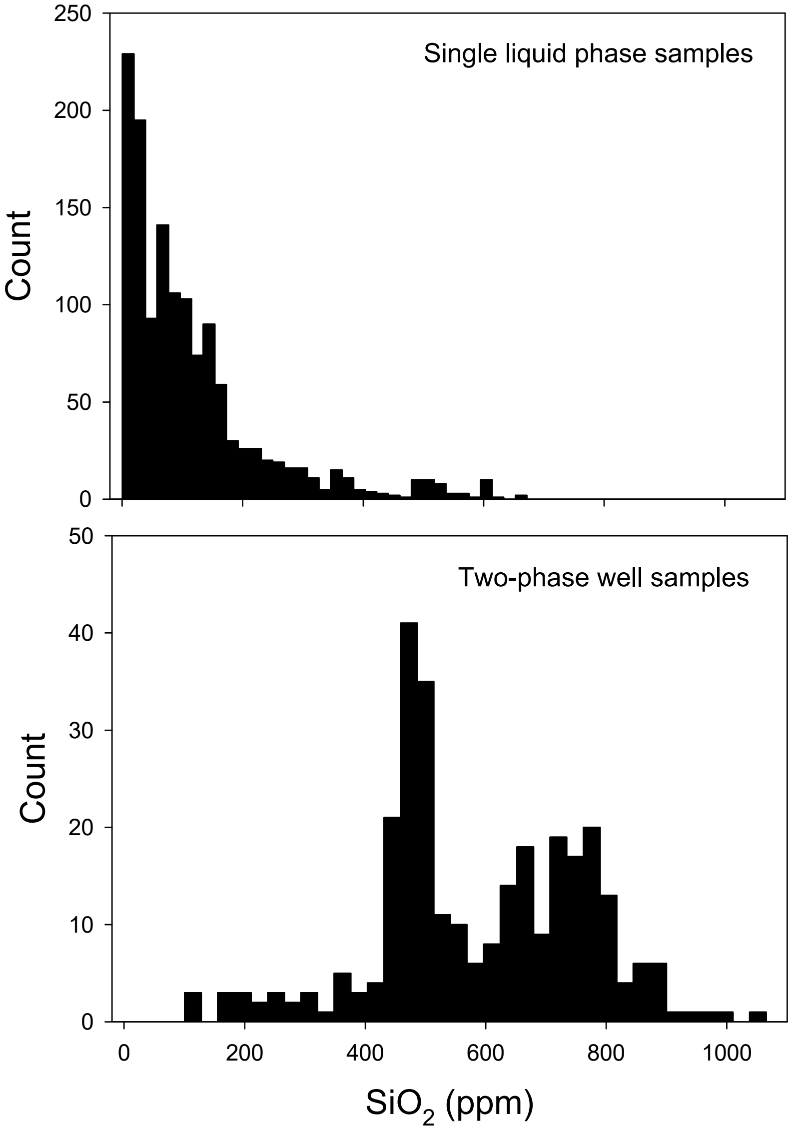

FIGURE 4: Silica concentration in single liquid phase and two-phase well samples

The concentrations of Si in single-phase non-thermal and thermal liquid water and in the liquid phase of two-phase well discharges for different locations in Iceland is further shown in Figures 5 and 6. Most areas represented by single-phase fluids have Si concentrations <200 ppm, these being in all cases low-temperature geothermal areas. Exceptions are the high-temperature geothermal areas at Geysir, Hveravellir, Hveragerdi and Reykjadalir that have Si concentrations of boiling hot springs of up to ~500, ~600, ~300 and ~400 ppm, respectively. Concentrations of Si in two-phase well discharges of high-temperature areas was much greater than for the low-temperature areas, typically ~400-1000 ppm. Highest values are observed at Krafla, Hellisheidi and Nesjavellir. This may be considered to be reacted to high reservoir temperatures, but also caused by the mechanism of boiling, with Si in the boiled liquid phase becoming enriched in Si upon open system boiling in some cases (e.g., Scott et al., 2014).

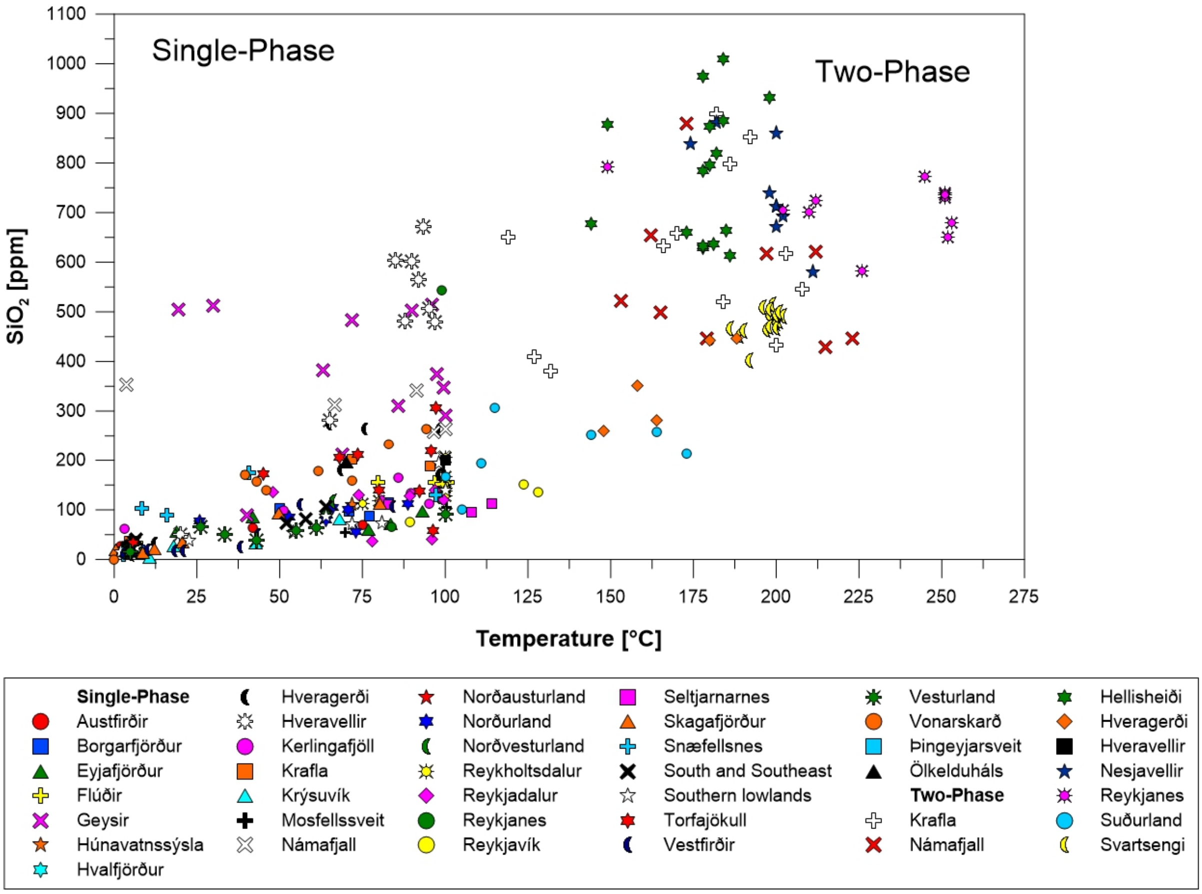

FIGURE 5: The measured concentration of silica as a function of sampling temperature for single liquid phase and two-phase well samples

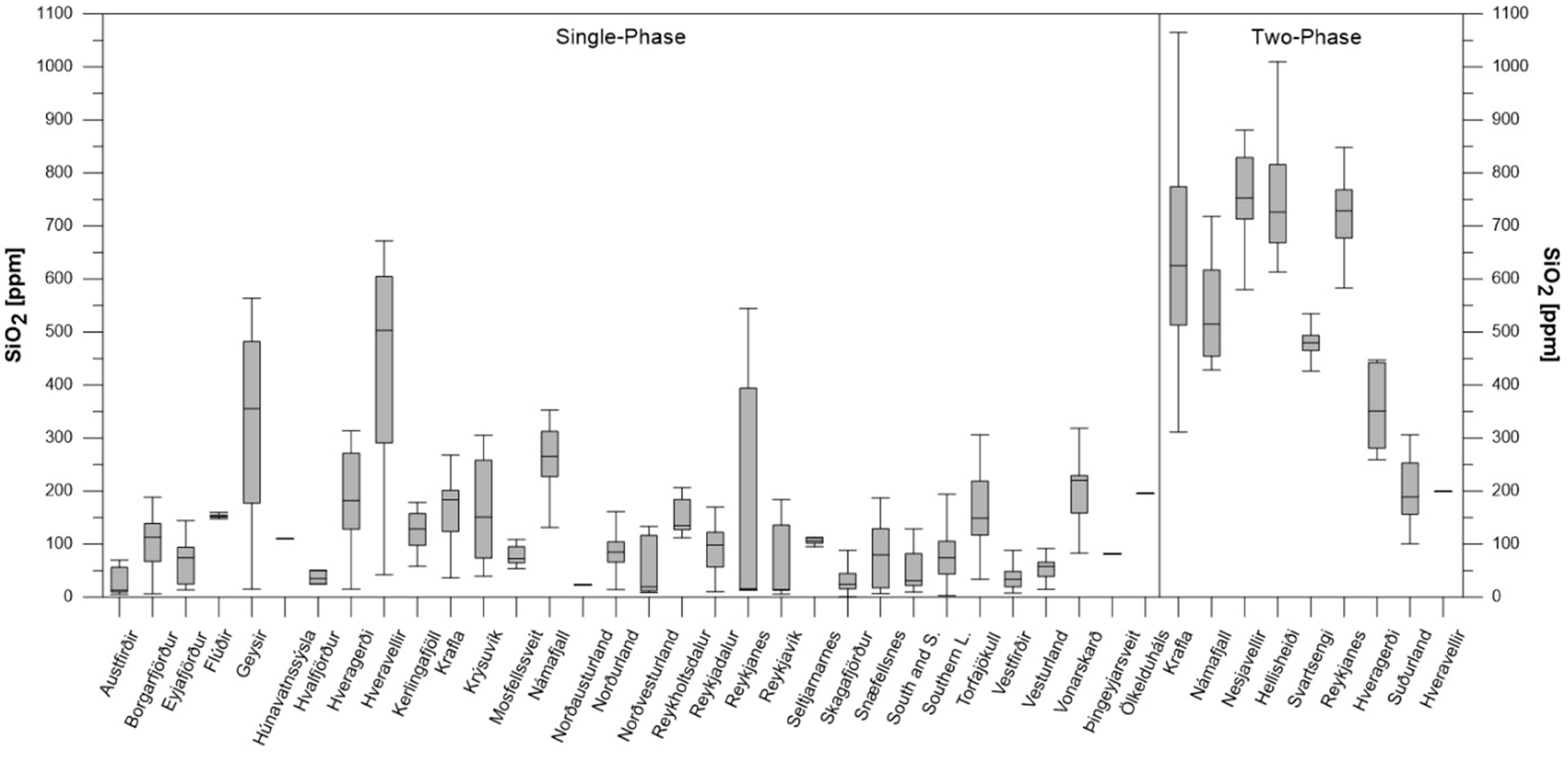

FIGURE 6: Range of silica concentrations for different locations

6. DISCUSSION

6.1 Geothermal reservoir fluid composition

Geothermal reservoir fluid composition was calculated from data of two-phase well discharges and boiling hot springs. The reservoir temperature was calculated using the quartz and chalcedony geothermometry. For sub-boiling water, the measured composition was taken as the reservoir composition and the calculations were done at the measured temperature. The calculations were carried out with the aid of the WATCH program. Example of selected results is given of primary and secondary fluids are given in Table 6 and Table 7, respectively.

TABLE 6: Chemical composition of selected primary fluids calculated with the aid of the WATCH program (Bjarnason, 2010). The concentrations are given in ppm

Sample #	Area	Source	Type	Temp °C	pH	SiO_2	B	Na	K	Mg	Ca	F	Cl	SO_4	CO_2	H_2S
97-3105	Krafla	tpw	Na-Cl	333	7.66	926	3.24	168	41.1	0	0.97	1.447	59.99	54.58	1252	251.5
78-1082	Námafjall	tpw	Na-Cl	248.7	6.80	463	0	130	21.6	0.008	1.86	0.456	31.33	15.2	739	344.9
02-073	Flúdir	sp	Na-Cl	134.1	6.84	155	0.322	78.2	2.32	0.001	1.27	1.38	24.4	55.5	41.48	1.68
10-5081	Hellisheidi	tpw	Na-Cl	307.2	7.44	706	1.05	118	26.1	0.001	0.25	0.767	146.7	7.02	146.5	90.37
79-0140	Svartsengi	tpw	Brines	226.3	6.63	370	0	7123	1155	0.559	990	0.113	13422	22.15	23.36	0.03
79-3009	Reykjanes	tpw	Brines	268	5.55	545	7.54	9636	1486	1.245	1474	0.182	19736	0	674.5	16.38
W313	Vesturland	w	Brines	83.7	7.54	66	0.96	1152	17.3	0.18	587	0	2750	41.9	8.3	0
W359	Reykjanes	w	Brines	212.4	5.87	394	12.8	11400	1600	5.9	1780	0.2	22600	84.7	0	0
76-0176	Krafla	tpw	Sulphates	193.8	7.95	283	0	170	20.4	0.027	2.09	0.855	21.73	175.5	69.35	34.01
09-ÁKS-03	Geysir	sp	Sulphates	165	3.73	247	0.076	18.3	1.73	1.917	4.63	0.353	8.74	64.58	34	0.01
14-KERL-28	Kerlingafjöll	sp	Sulphates	133.5	4.28	152	0.229	6.53	6.27	51.3	193	0.426	0	824	21.95	0.04
02-033	Eyjafjördur	w	Sulphates	68.5	9.01	75.5	0.217	45.9	0.66	0	2.45	0.6	11.3	33	0	0.05

The variation of the pH and Cl in function of the quartz and chalcedony temperature is presented in Figure 7. The temperature of the non-thermal and geothermal fluids in Iceland range from ~10 to 310°C. The pH varies from ~2-11. It is lowest for steam-heated waters whereas sub-boiling and two-phase geothermal ground waters of meteoric origin (low salinity) have pH typically of ~7-10, decreasing with increasing temperature. Saline reservoir fluids like at Reykjanes and Svartsengi have lower pH values, or ~5. The concentrations of Cl in non-thermal.

Non-thermal and geothermal fluids of meteoric origin are typically <200 ppm. This is somewhat lower compared to many other geothermal fluids in the world. The reason is considered to be low Cl concentrations in basaltic melts and rocks interacting with the geothermal fluids in Iceland (e.g., Stefánsson et al., 2017). For geothermal systems fed by seawater or partially seawater, like at Reykjanes and Svartsengi, much higher Cl concentrations are observed, up to ~20,000 ppm.

The concentrations of Si in sub-boiling non-thermal and thermal liquid water was typically <200 ppm, with expectations of some locations like Geysir and Hveravellir where Si concentrations to ~500 and ~600 were observed, respectively. For boiling hot springs and two-phase well discharges, the reservoir Si concentrations were calculated to be somewhat lower than measured in the discharge liquid water. The reason for this is the removal of H_2O to the steam phase upon boiling and subsequent concentration of Si in the boiled liquid water (Figure 8).

6.2 Aqueous silica speciation

Aqueous silica species distribution was calculated for the reservoir fluid composition with the aid of the PHREEQC program and the llnl.dat database. The silica species include were: H_4SiO_4(aq) (or SiO_2(aq)), $HSiO_3^-$, $H_2SiO_4^{-2}$ and $NaHSiO_3$(aq). The results are shown in Figure 9. H_4SiO_4(aq) and $HSiO_3^-$ were observed to predominate in all cases at acid to neutral and alkaline pH, respectively. $NaHSiO_3$(aq) was also observed to be important at elevated Na concentration. The results of the calculations demonstrate that the major factor controlling aqueous silica speciation is pH with temperature and salinity being less important.

6.3 Mineral saturation

Mineral saturation indices of common Si-containing secondary minerals is shown in Figure 10 as a function of pH and measured temperature for sub-boiling water and calculated reservoir temperatures for boiling hot springs and two-phase well discharges. The minerals considered were albite, analcime, epidote, prehnite and clinochlore. The calculations were carried out with the aid of the PHREEQC program.

Geothermal fluids with mildly to strongly acid pH values are generally observed to be undersaturated with respect to Si-containing minerals. Exception to this is saturation with respect to amorphous SiO_2 associated with surface argillic (acid) alteration, for example at Krýsuvík and Torfajökull (Markússon and Stefánsson, 2011; Björke et al., 2015). With progressive fluid-rock interaction, the pH of the waters increases from neutral to alkaline values (e.g., Gysi and Stefánsson, 2011, and Gysi and Stefánsson, 2012). As a result, the geothermal fluids become saturated with secondary minerals, the most common being Si-containing minerals. At low temperatures, these are typically clays and zeolites whereas, at temperatures >230°C feldspars, prehnite and epidote together with quartz are often most important. This is indeed what is observed (Figure 10). Geothermal fluids are close to saturation with respect to analcime and chlorite at low-temperatures whereas epidote, albite and prehnite become saturated at elevated temperatures.

TABLE 7: Chemical composition of selected secondary fluids calculated with the aid of the WATCH program (Bjarnason, 2010). The concentrations are given in ppm

Sample #	Area	Source	Type	Temp °C	pH	SiO_2	B	Na	K	Mg	Ca	F	Cl	SO_4	CO_2	H_2S
07-SC-06	Námafjall	s	Acid-Sulphate	152.8	2.58	217	0.021	1.26	0.38	4.63	5.73	0	0.35	620	0	0
06-3818	Torfajökull	sp	Acid-Sulphate	125.7	2.91	133	0.050	2.84	3.76	1.94	2.71	0.094	0.39	312.42	4.87	0
15-HEN-16	Reykjadalur	sp	Acid-Sulphate	109.8	2.87	101	0.378	8.75	2.02	8.49	4.28	0.018	10.89	577.88	0.23	0.38
09-ÁKS-12	Ölkelduháls	sp	Carbonate	149.7	4.69	196	0.01	19.79	2.61	10.2	42.2	0.021	5.2	35.62	203.7	0.01
03-107	Borgarfjördur	sp	Carbonate	-9.9	8.20	5.90	0.0052	7.41	0	2.11	21.6	0.04	9.65	16.6	44.6	0
79-3070	Snaefellsnes	sp	Carbonate	101.1	7.37	88.1	0.04	65.2	1.2	27.5	54.3	0.36	0	22.8	342	0
03-093	Reykjanes	sp	Boiled-Alkaline	18.8	7.66	14.3	0.0161	33.77	1.44	7.52	8.4	0.07	70.6	9.65	18.6	0
79-3043	Eyjafjördur	sp	Boiled-Alkaline	44.6	9.45	50.2	0.03	28	0.16	0.032	2.32	0.18	6.4	5.9	15.9	0.07
09-007	Snaefellsnes	sp	Boiled-Alkaline	125.5	7.55	134	0.1009	157.67	2.3	1.07	22.01	0.503	117.97	60.77	149	0
85-3024	Vestfirdir	sp	Mixing	61	9.22	73.7	0.098	53.88	0.78	0.06	6.52	3.18	29.7	34.72	11.3	0.15
97-21	Skagafjördur	sp	Mixing	54.8	9.52	83.2	0.268	51.86	0.45	0.003	1.51	0.952	12.89	16.58	19.5	0.05
82-3133	Hveravellir	sp	Mixing	71.9	7.21	50.61	0.1	45.9	1.76	1.05	7.77	0.4	26.4	51.8	40	0

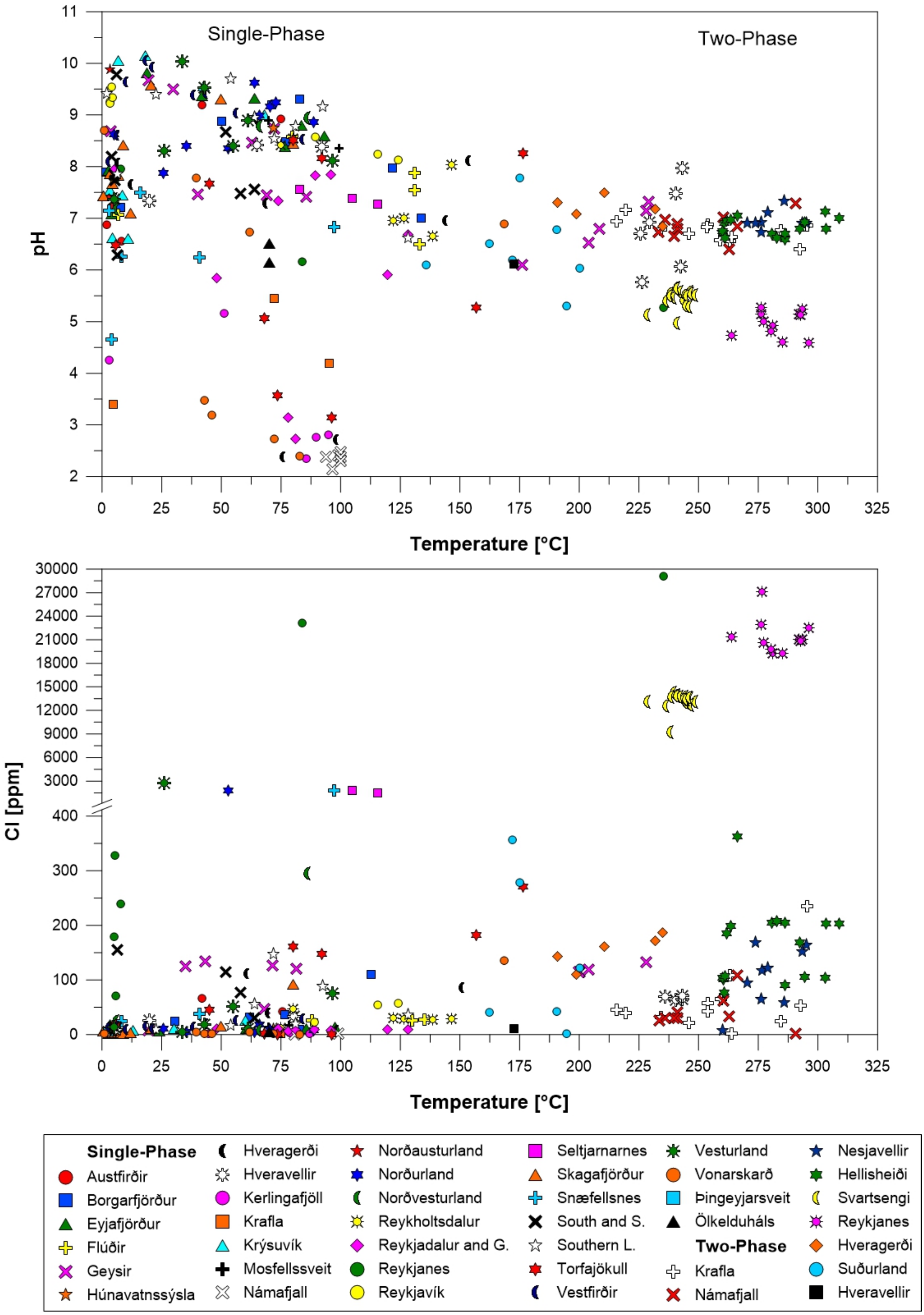

FIGURE 7: The pH and Cl of reservoir fluids as a function of quartz or chalcedony temperature

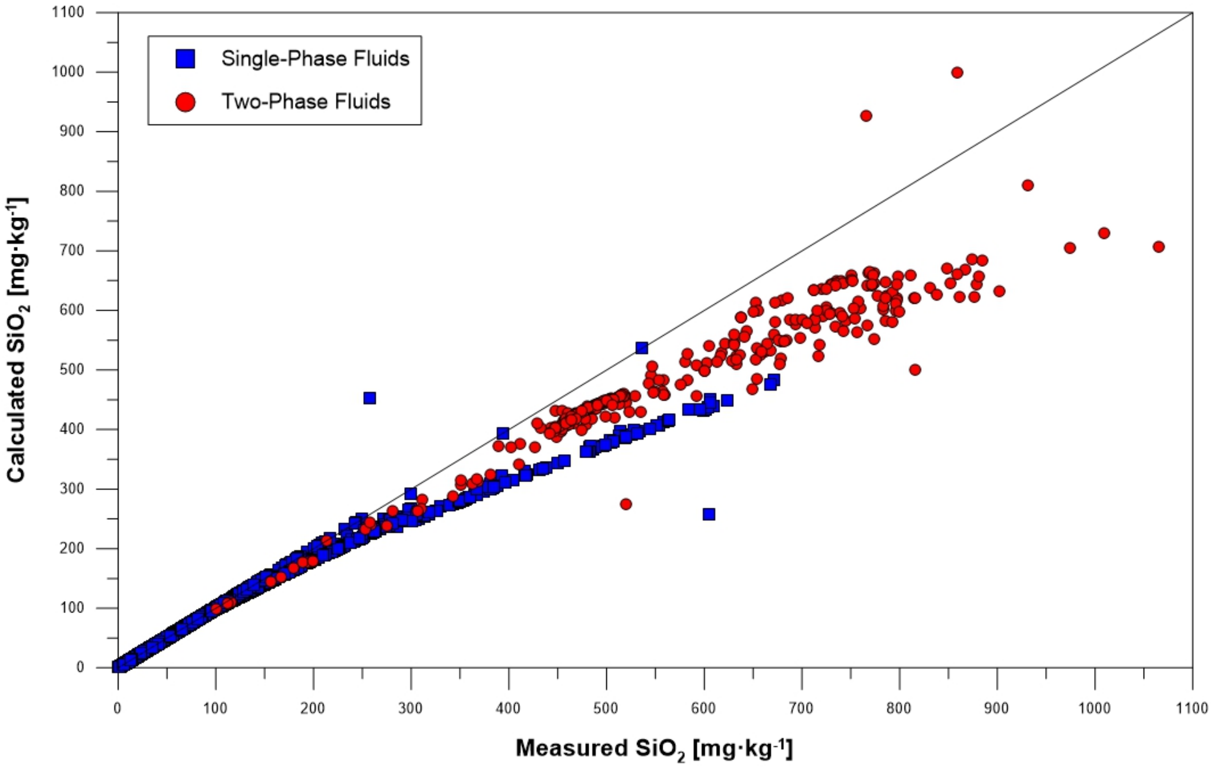

FIGURE 8: Comparison between the measured and the calculated silica concentration in single and two-phase samples

6.4 Silica concentrations and geothermometry

It is generally recognized that geothermal fluids are in close to equilibrium with common secondary minerals (e.g., Giggenbach, 1981; Arnórsson et al., 1983). With respect to Si-containing minerals, this is what is indeed observed (Figure 10). Most geothermal geothermometry relies on the assumption of such fluid-mineral equilibria, that are in turn primarily dependent on temperature at geothermal conditions (Arnórsson et al., 1983). In addition, geothermal geothermometry relies on the assumption that non-chemical reactions occur upon fluid ascent from the reservoir to surface, i.e. the system is assumed to be thermodynamically closed.

The simplest case of geothermal geothermometry is one that involves one mineral and one component, for example, quartz or chalcedony and aqueous silica according to the reaction:

$$SiO_2(s) + 2H_2O \leftrightarrow H_4SiO_{4(aq)} \tag{4}$$

The silica solubility is further described by the respective equilibrium constant:

$$K = \frac{a_{H_4SiO_4(aq)}}{a_{SiO_2} \cdot a_{H_2O}^2} \approx m_{H_4SiO_4}\gamma_{H_4SiO_4} \tag{5}$$

where K is the equilibrium constant, and m and γ stand for concentrations and activity coefficients, respectively.

More complex reactions can also be considered, for example involving feldspars according to the reaction:

$$albite + K^+ = K\text{-}feldspar + Na^+ \tag{6}$$

where the equilibrium constant is defined as:

$$K = \frac{a_{Na^+}a_{K-feldspar}}{a_{K^+}a_{albite}} = \frac{m_{Na^+}\gamma_{Na^+}}{m_{K^+}\gamma_{K^+}} \tag{7}$$

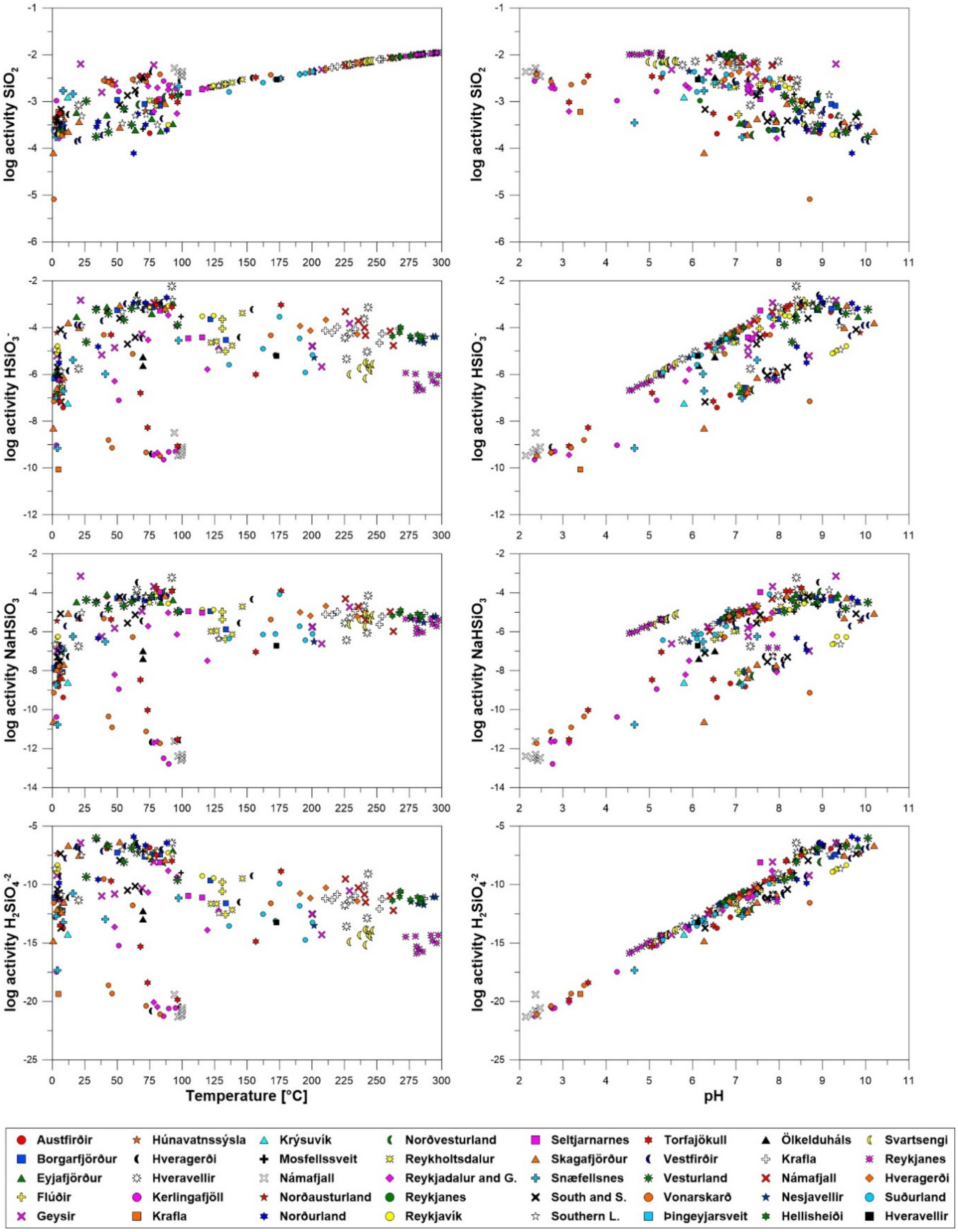

FIGURE 9: Aqueous silica speciation as a function of temperature and pH

The equilibrium constants (K) depends on temperature and pressure, the latter being unimportant under geothermal conditions relative to temperature. Assuming the minerals to be pure ($a_{\text{mineral}} = 1$) it follows that there is a direct relation to temperature through K and fluid composition in terms of aqueous species concentrations (m) and their respective activity coefficients (γ). More complex reactions can also be considered that includes more minerals and more components, like Ca, Mg, CO_2, H_2S and H_2. In this case, all the respective secondary minerals have to be in equilibrium with the geothermal fluids at the same time and conditions in order for the general assumptions to be valid. This may not always be the case.

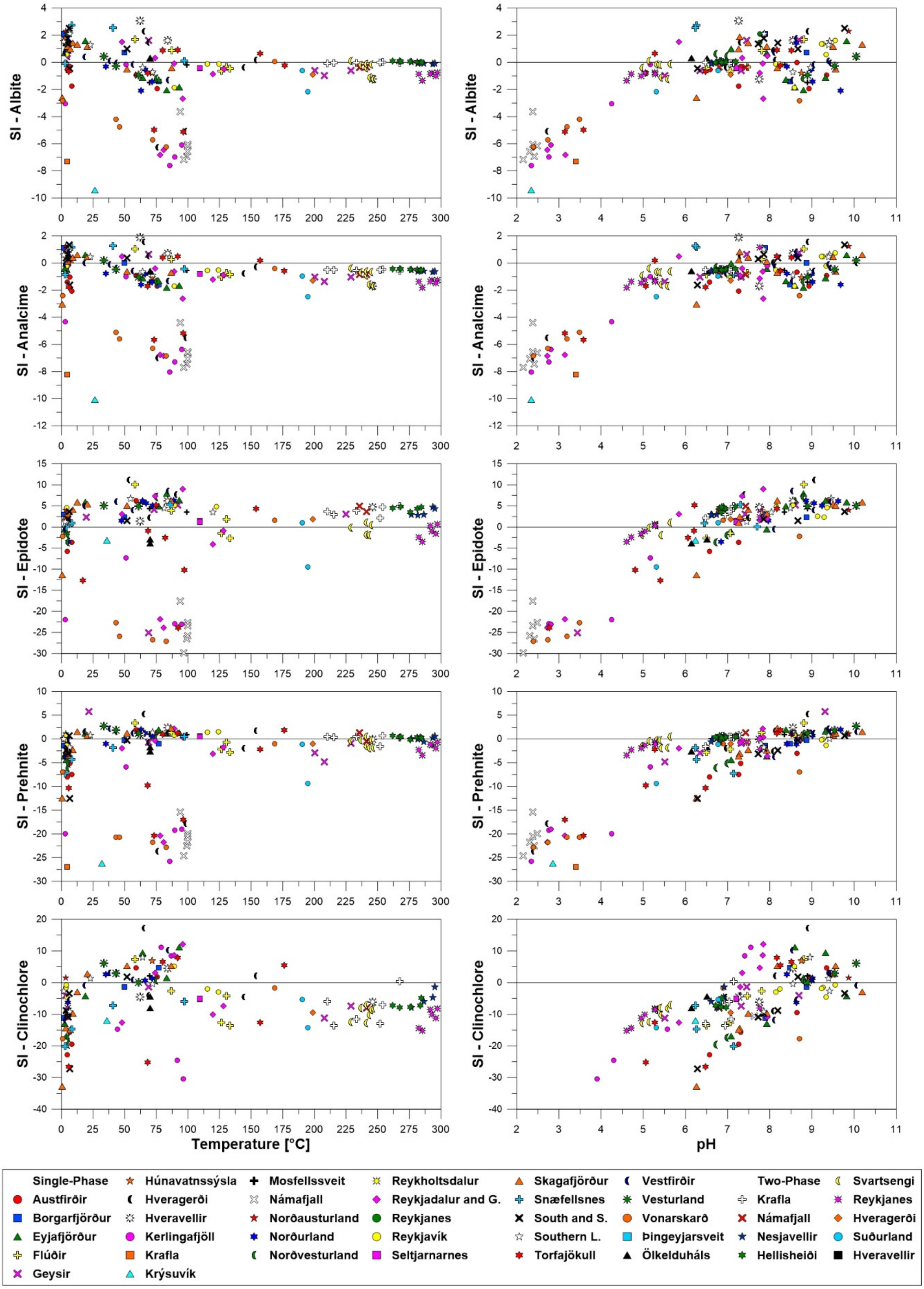

FIGURE 10: Mineral saturation indices as a function of temperature and pH

Among the basic assumptions for the application of geothermometry to predict reservoir temperatures is that no reactions occur upon fluid ascent from the reservoir to surface. In many cases, this assumption may not hold. Alternatively, to minimize these effects of later stage reactions on the calculated geothermometry temperatures, these changes in fluid component concentration upon ascent have to be minimum. This may hold in the case of many of the more concentrated major elements, like Si and Na, whereas minor elements like Mg may be more sensitive to late-stage reactions. For example, let us assume reservoir Si concentration to be 600 ppm, and upon fluid ascent, Si-containing minerals form lowering the Si concentration to 550 ppm, or by ~10%. Such mineralization is considerable but has minor effects on the calculated silica geothermometry temperatures. In contrast, K$^+$ concentrations are commonly in the range of ~1-40 ppm, for low- and high-temperature geothermal waters in Iceland of meteoric origin. Similar mass movement or mass of secondary minerals formed as in the case of silica would lead to>99% loss of K from the fluid upon ascent and resulting in major effects on the calculated geothermometry temperatures. The same may be true for Ca and Mg. For this reason, it is considered more reliable to apply geothermometers based on the main components of the geothermal fluids, for example, Si, rather than trace elements like Mg, even though the latter is commonly applied.

Here, the quartz and chalcedony geothermometry were used to calculate the reservoir temperatures. These have been compared with the Na-K geothermometry temperatures in Figure 11. Reasonable good agreement between these geothermometers is generally observed at >200°C. Inspection also reveals often systematically lower Na-K temperatures compared with quartz or chalcedony temperatures, this is considered to be related to changes in K$^+$ concentrations of the geothermal fluids upon ascent, but the T_{Na-K} are sensitive to such changes. Similar concentrations changes with respect to Na$^+$ and H_4SiO_4(aq) are expected to have minor effects on the calculated geothermal geothermometry temperatures.

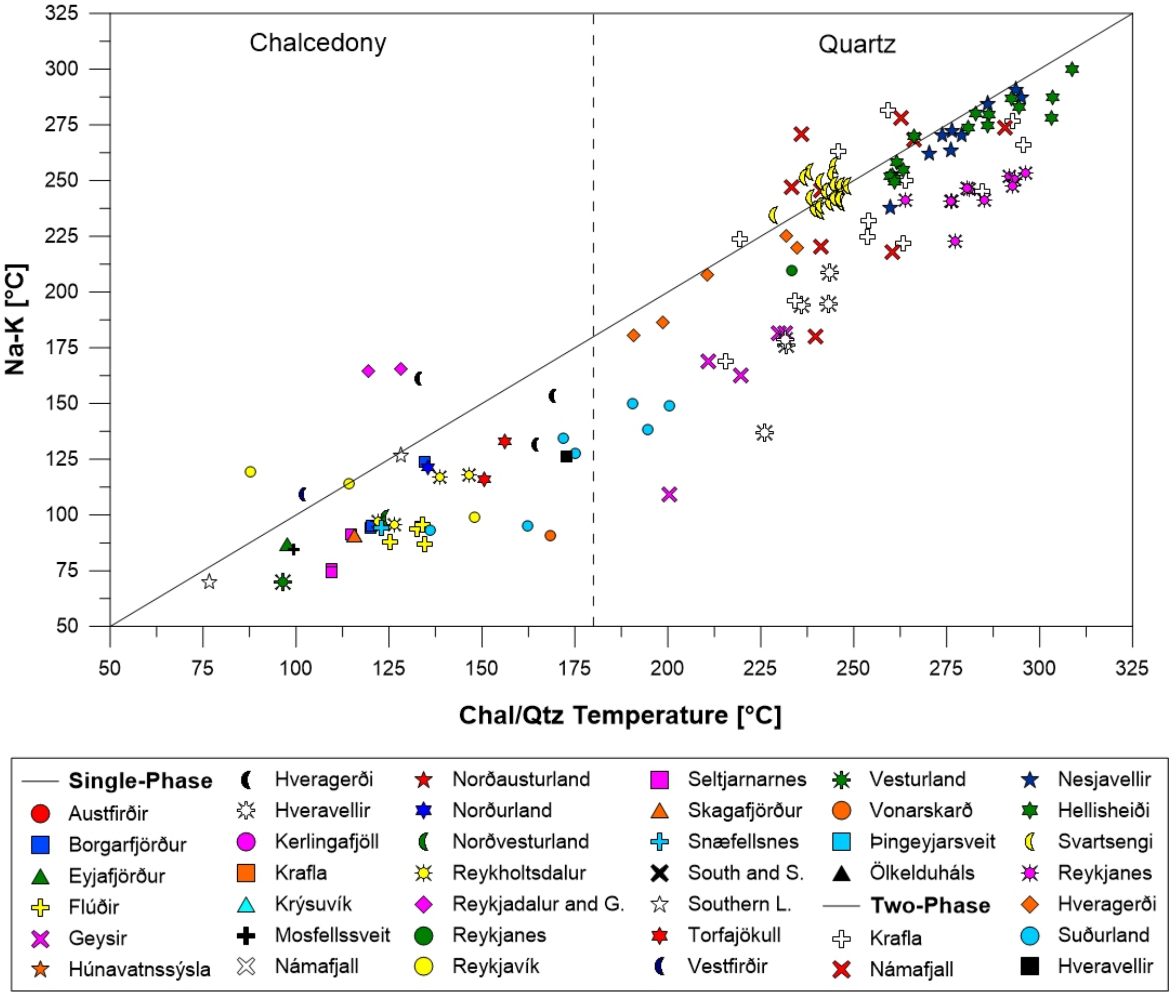

FIGURE 11: Comparison of the calculated SiO2 temperatures (quartz and chalcedony temperatures above and below 180°C, respectively) and the Na-K geothermometry temperatures

The Si concentrations in geothermal fluids are therefore often considered to closely reflect the reservoir temperatures of the geothermal systems. It follows that Si concentrations in geothermal waters may be used to indirectly map temperature variations of both low- and high-temperature systems. Two examples are shown in Figures 12 and 13, for the southern lowlands and Krafla geothermal system, respectively.

Southern lowlands, are a typical low-temperature geothermal area. A large part of the area is characterized by silica concentrations <100 ppm corresponding to geothermal temperatures of up to 70-100°C (Figure 12). Exceptions of this are mainly three locations, Grímsnes, Hrunamannahreppur including Flúdir and Biskupstungur including Geysir. At these locations, significantly higher silica concentrations were observed, >150 ppm, demonstrating considerably higher reservoir temperatures of up to ~250°C. Such large-scale mapping of geothermal waters over an extensive area can, therefore, be used to get a general overview of the distribution of reservoir temperatures.

The distribution of silica in reservoir fluids at Krafla is shown in Figure 13. Considerable variations are observed in silica concentrations considered to reflect the temperatures of the main feeding aquifers of the well discharges. At Hvíthólar and around Leirbotnar, considerably lower Si concentrations are observed whereas, in Sudurhlídar and Vesturhlídar, higher Si concentrations are observed, indicating more elevated reservoir temperatures. These observations indicate that Si concentrations of high-temperature geothermal areas can on its own be a useful tool to predict temperature distributions within a geothermal system.

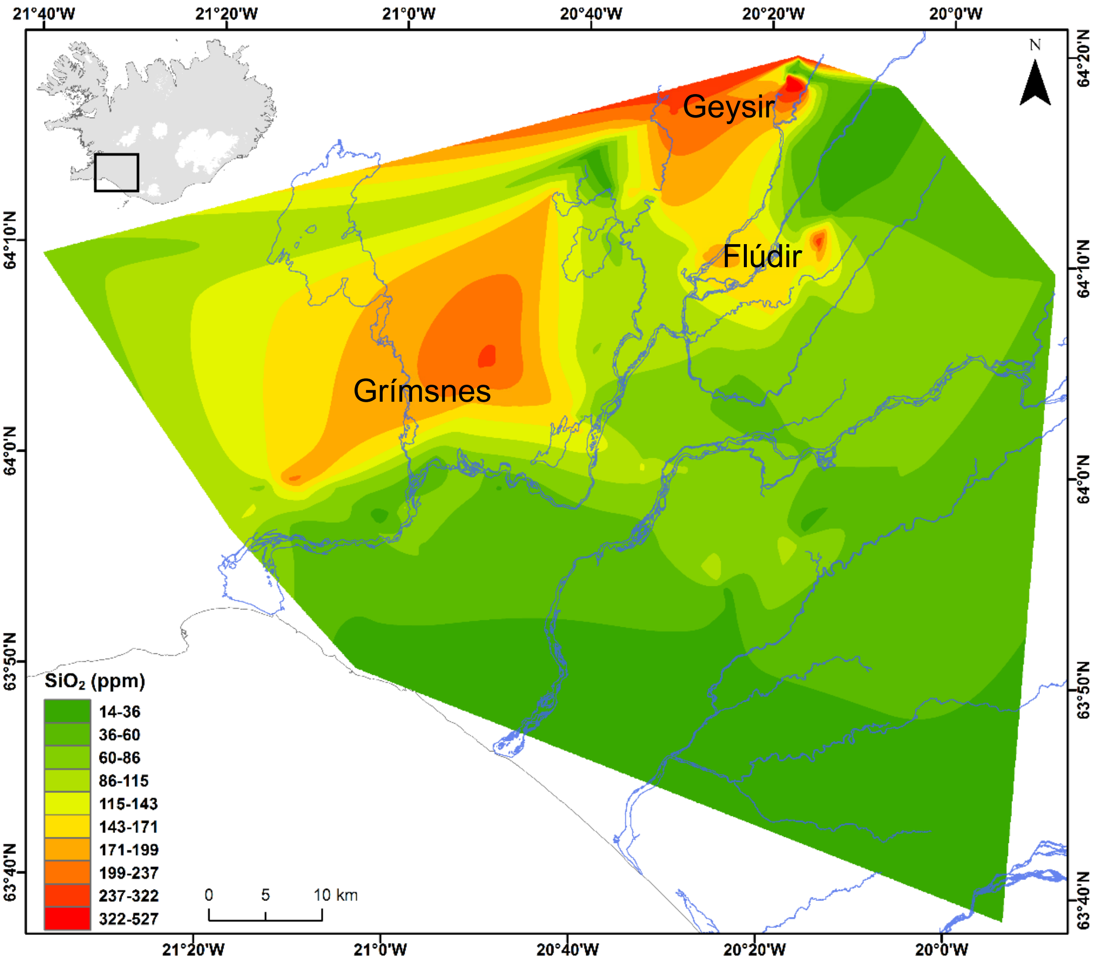

FIGURE 12 Distribution of silica concentration in geothermal fluids on the Southern lowlands

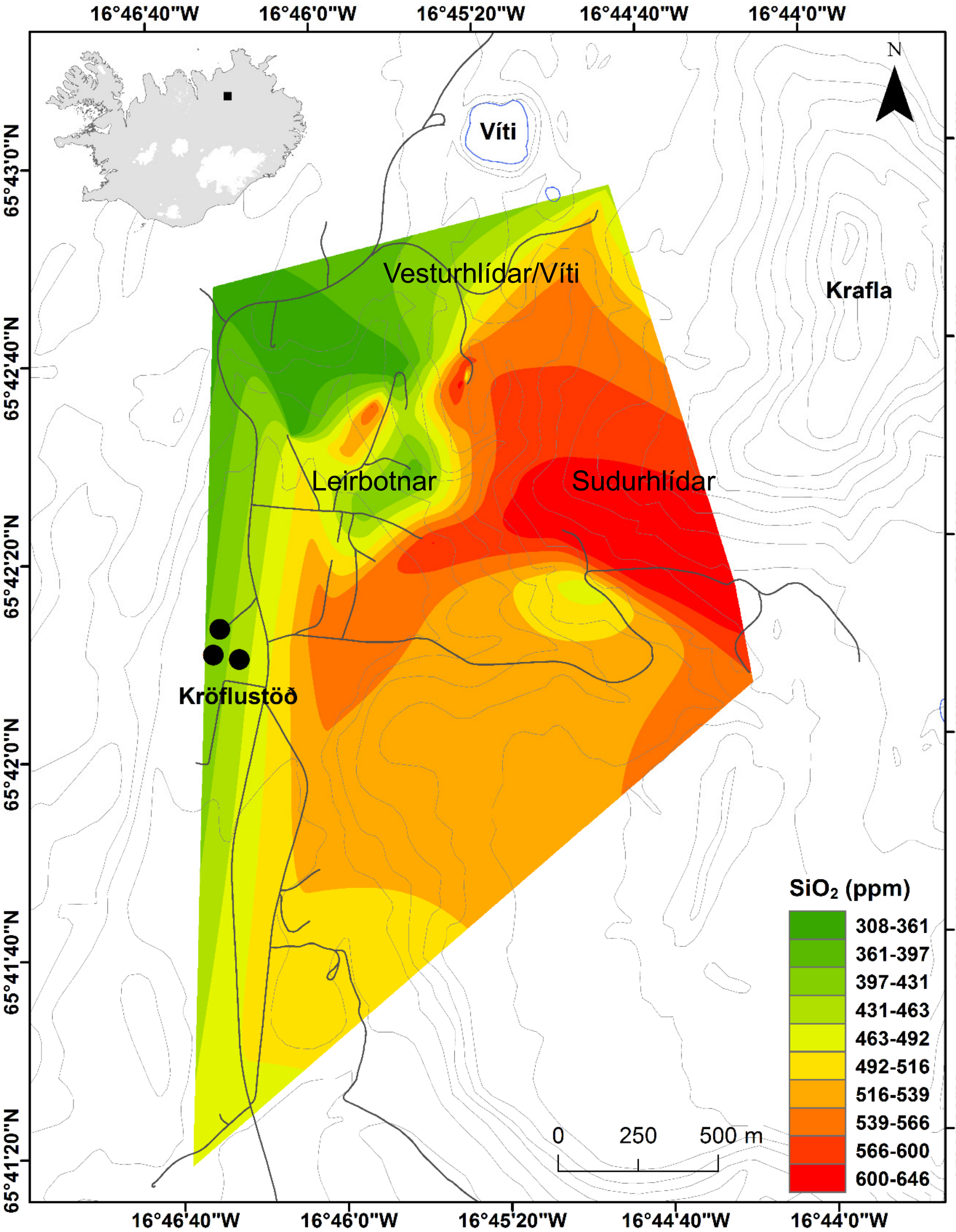

FIGURE 13: Distribution of silica concentration in geothermal fluids at Krafla, NE Iceland

7. CONCLUSIONS

The geochemistry of silica in Icelandic geothermal fluids was studied using a dataset spanning over 60 years of sample collection, in total ~1650 samples from >30 geothermal areas. The samples include various types of geothermal fluids, including sub-boiling liquid water and two-phase well discharges. The measured concentration of silica in the samples ranged from >10 to ~1000 ppm and was observed to increase with increasing temperature, typically <200 ppm at <75°C whereas for boiling and close to boiling water (90-100°C) concentrations up to 700 ppm were observed. Silica concentrations in two-phase well discharges of high-temperature areas were much greater than for the low-temperature areas, typically ~400-1000 ppm with highest values are observed at Krafla, Hellisheidi and Nesjavellir.

Aqueous speciation and mineral saturation indices were calculated using the PHREEQC program. The results revealed that the dominant silica species in all cases were $H_4SiO_4(aq)$ and $HSiO_3^-$ at acid to neutral and alkaline pH values, respectively. $NaHSiO_3(aq)$ was also observed to be important in geothermal fluids characterized by elevated Na concentrations.

Geothermal fluids with neutral to alkaline pH values and temperatures >20°C were generally observed to be close to saturation with respect to common silica containing geothermal minerals. In contrast, acid fluids were observed to be undersaturated, indicating that most silica containing minerals are unstable in contact with such fluids. At low temperatures, the typically secondary minerals in equilibrium with neutral to alkaline fluids were clays and zeolites whereas, at temperatures of >230°C feldspars, prehnite and epidote together with quartz are most important.

Geothermal geothermometry relies on the assumption of such fluid-mineral equilibria is approached. In turn, such equilibrium depends primarily on the temperature at geothermal reservoir conditions. It follows, that equilibrium of the fluids with many silica containing geothermal minerals may be used to predict reservoir temperatures. The simplest case involves only silica, like quartz and chalcedony, but more complex reactions involving two or more minerals and many components may also be applied. It was further demonstrated that the silica concentrations in geothermal fluids may be used to indirectly predict spatial reservoir temperature variations, here demonstrated for the low-temperature systems at the southern lowlands and at the high-temperature system at Krafla.

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