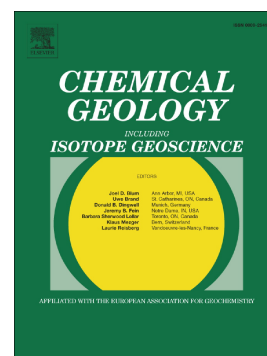


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Extreme alteration in an acid-sulphate geothermal field: Sulphur Springs, Saint

Lucia

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Abstract

Sulphur Springs is a vigorous geothermal field associated with the Soufrière Volcanic Centre in southern Saint Lucia. Intensely altered rocks occur over an area of at least 200 x 400 m, together with bubbling hot pools and fumaroles. The pools are sodium-calcium-sulphate type, with pHs of 3–7 and temperatures of 41–97°C. Fumaroles have temperatures up to, and at times above 100°C. Gases collected from both fumaroles and bubbling pools have high contents of CO₂ (601–993 mmol/mol) and commonly high H₂S (3–190 mmol/mol).

Least-altered host rocks surrounding Sulphur Springs comprise calc-alkaline, feldspar-quartz-porphyritic dacites of near-uniform chemical composition. These rocks, which form massive domes and volcaniclastic units, were emplaced 13–30 Ka ago (Lindsay et al. 2013). Within the geothermal field, the dacites have been moderately to highly altered to acid-sulphate assemblages of kaolinite, illite, smectite, alunite, natroalunite, cristobalite, opaline silica, native sulphur, jarosite and amorphous compounds. Muddy sediments from grey to blackish thermal pools additionally contain iron sulphides.

Despite intense alteration of the volcanic rocks (and derived volcaniclastic sediments), Zr and Ti have remained essentially immobile, which allows identification of the precursors (dacites) and calculation of mass changes. Many of the altered rocks and sediments show major depletions of Fe, Mg, Ca, Na. Extremely altered samples additionally show notable losses of Al, P, K, REE and Y, implying leaching by highly acidic waters. A few of the highly altered rocks, however, have

gained Al, together with P, presumably due to neutralization or evaporation of acidic thermal waters. Also present within the geothermal field are metre-scale zones with very high contents of silica and native sulphur, <1 % Al_2O_3 . Based on mass change results, the silica in the silica-sulphur zones, although recrystallized, was mainly inherited from the precursor dacites, rather than added as new hydrothermal precipitates.

Surface thermal waters define a linear trend in a plot of $\delta^{18}\text{O}$ vs. δD , and reach high levels of isotopic enrichment. This trend is ascribed to progressive evaporation of meteoric water. The low slope of the trend (1.4) can be accounted for by surficial mixing between meteoric waters and steam condensates derived at about 230°C from the deep brine that underlies the geothermal field. The whole-rock O-H-isotopic composition of four highly altered samples (kaolinite-smectite-opal-sulphates) can be accounted for if it is assumed that the alteration fluid was a 50:50 mixture of steam and meteoric water, and alteration occurred at 50-125°C. Whole-rock $\delta^{34}\text{S}$ values of samples containing variable amounts of sulphates, sulphides and native S are all notably negative (-5 to -16 ‰), consistent with derivation of sulphur from volcanic gases such as SO_2 and H_2S . Altered rocks and thermal pool sediments in the geothermal field are commonly enriched in Hg and Se (up to 50 mg/kg).

At Sulphur Springs, primary dacitic rocks have been chemically and mineralogically transformed by reaction with acidic fluids that formed when uprising volcanic gases condensed into neutral

meteoric waters. In extreme cases, this has led to losses or gains in Al, P and REEs. Regardless of the degree of alteration, however, the precursor rocks can still be identified using Ti-Zr relations.

Key words: rock alteration, immobile elements, mineralogy, stable isotopes, geothermal waters, Sulphur Springs

Introduction

The island of St Lucia, located in the southern portion of the Lesser Antilles volcanic arc, has an area of 617 km² and rises up to 950 metres above sea-level. The volcanic rocks that make up almost the entire island are mainly andesites, but include basalts and dacites. A large collapsed caldera structure known as the Soufrière Volcanic Centre (SVC) is present in southwestern St Lucia (Fig. 1). This 8 x 6 km arcuate depression, which opens onto the west coast, formed 100-250 ka ago (Lindsay et al., 2013). In the SVC area, dacites are the most abundant rock type and include block and ash pyroclastic flows and massive domes. The famous Gros Piton and Petit Piton volcanic domes on the western side of the SVC were intruded about 75 ka and 100 ka ago, respectively (Samper et al, 2008; Schmitt et al., 2010). The youngest dates obtained so far for large pyroclastic flows in southwestern St Lucia that were derived from the SVC are in the 20-30 ka range, although several lava domes and explosion craters within the SVC formed subsequently to this, e.g. the Belfond dome at 13.6 ± 0.4 ka, and the Terre Blanche dome at 15.3 ± 0.4 ka (see summary of dating methods and ages in Lindsay et al., 2013). The Terre Blanche dacitic dome flanks the Sulphur Springs geothermal area to the northeast, while the Belfond dacitic dome lies to the south, and the andesitic Rabot Ridge to the west. Massive dacites of the Terre Blanche and Belfond domes are rich in phenocrysts, including quartz, plagioclase and alkali feldspar, hornblende and biotite.

The Sulphur Springs geothermal field, which crops out over at least 400 x 200 m, lies partly within dacitic volcanoclastic rocks and partly within massive dacites of the Terre Blanche dome. Thermal manifestations include boiling springs, pools and fumaroles with hot ground, and extensive rock alteration to assemblages of kaolinite, illite, smectite, silica phases, alunite and native sulphur. Fumaroles have strong steam flows in the range of $5.2\text{--}74 \times 10^4$ cal/sec (Robson and Willmore, 1955) and temperatures of $89\text{--}138^\circ\text{C}$ (Joseph et al., 2013). Previous studies of the thermal waters have been made by Goff and Vuataz (1984), Greenwood et al. (2004), Stout et al. (2009) and Joseph et al. (2013). The thermal waters are of acid-sulphate type, with high SO_4 but low Cl contents; divalent and trivalent cations (Ca, Mg, Al, Fe) dominate over Na and K. Boron contents are commonly very high, up to 3500 mg/kg (Greenwood et al., 2004; Stout et al., 2009). The microbial composition of the thermal waters has been determined by Stout et al. (2009). Chemical and isotopic data for deep brines and condensates recovered from a geothermal well at Sulphur Springs are given in Bath (1976), while data for three condensates from steam vents are given in Ander et al. (1984). A subsurface reservoir temperature of 280°C was estimated by Ander et al. (1984) based on their gas samples and the empirical gas geothermometer of D'Amore and Panichi (1980). Low-temperature thermal springs, generally higher in bicarbonate but lower in sulphate than the hot pools at Sulphur Springs, are present at Diamond and Cresslands to the north of the Terre Blanche dome (Fig. 1) (Wohletz et al., 1986; Joseph et al., 2013).

In 1986 a geothermal feasibility study of the SVC was jointly conducted by the United Nations Revolving Fund for Natural Resources Exploration (UNRFNRE) and the United States Agency for International Development (USAID). Based on analysis of geothermal fluids collected from exploratory drill wells, UNRFNRE (1989) reported that the geothermal reservoir was a vapour-dominated system with an estimated temperature of 292°C. A boiling brine was inferred to be present in the deep reservoir (Geotermica Italiana, 1991). Gas-rich steam produced from the deep brine is present within fractured levels in the volcanic rocks (Battaglia et al., 1991). Vent condensates have high B/Cl ratios, suggesting that the steam is derived from deep boiling of a high-temperature brine (Aguater, 1982). Ander et al. (1984) report high sulphate and low Cl contents in two fumarole condensate samples. These latter authors also infer that the Sulphur Springs geothermal field lies entirely within a vapour-discharge zone.

The heat source for the Sulphur Springs geothermal system was speculated to be the cooling magma body responsible for the young volcanism of the SVC (Wohletz and Heiken, 1984). Although further studies (Battaglia et al., 1991; Geotermica Italiana, 1991; GENZL, 1992) have found the Sulphur Springs area to have significant geothermal potential, no successful exploitation has taken place to date. Recently, however, the Government of St Lucia has been examining the possibility of new geothermal exploration in areas a few kilometres east and southeast of Sulphur Springs (Panorama Environmental, Inc., 2018).

Objectives

The main objective of the present study was to assess the chemical changes that have occurred during severe rock alteration at Sulphur Springs by using immobile-element methods to quantify mass gains or losses of each element on a sample-by-sample basis. However, in order to correctly identify the precursors of the altered rocks and calculate mass changes, at least one pair of immobile elements is required. At first glance, the mineralogical evidence of acid leaching, combined with large variations in the absolute contents of normally immobile elements such as Al, Ti, Zr and the REEs, raises the possibility that these elements have been mobilized to varying degrees. It was therefore first necessary to determine which, if any, of these elements remained essentially immobile. The approach used in this study should help in the assessment of lithogeochemical data from acid-sulphate altered terranes in general. A second objective was to obtain data on the chemistry and O-H-isotopic composition of the thermal pools and meteoric waters at Sulphur Springs (adding to a database on waters that have been collected since the 1970s by various workers). A third objective was to document the mineralogy and O-H-S isotopic composition of the altered rocks in order to help interpret reactions between thermal waters and rocks at surface.

Samples

Detailed lithogeochemical analysis was carried out on 25 variably altered rocks from outcrops within the geothermal field, 10 sediments (mixtures of volcaniclastic sand and chemical precipitates) from hot pools and creeks, and 15 samples of volcanic rocks up to 2 km away from the field. A subset of 7 altered samples was also analysed for bulk O-H-S isotope compositions. All of these samples were collected in 2017. Seventeen samples of waters were also taken for chemical and O-H-isotopic analysis (9 samples in 2014 and 8 in 2017).

Sample locations outside the Sulphur Springs geothermal field are shown in Figure 2, which also illustrates the strong degree of topographic variation within the main depression of the SVC area, with post-collapse dacite domes rising from the floor (at Terre Blanche, Belfond and Petite Piton). The sample classifications shown in this figure are based on lithogeochemical data presented later in the paper. Most of the rocks in the sampled area consist of dacites, although a few andesites are also present. Almost all of the samples outside the Sulphur Springs geothermal field (small box in Figure 2) are chemically unaltered or only weakly altered.

Figure 3 shows the Sulphur Springs geothermal field from an aerial perspective, together with the locations of most of the whole-rock samples, including sediments from the thermal pools.

Altered rocks in the geothermal field are clearly visible as white to greyish zones that are free of vegetation as a result of chemically aggressive gas and steam that waft across the area.

A sketch map of the main geothermal pools and streams at Sulphur Springs is given in Figure 4. All of the hot pools and fumarolic activity are currently in the southern part of the geothermal field. One feature of interest is the conjunction between a clear “rainforest” creek that enters the active geothermal area from the southeast, and a blackish warm creek that drains Witches Pool from the southwest. The clear creek contains fresh meteoric water, whereas the blackish creek carries highly modified meteoric water containing condensed steam and gases and amorphous precipitated compounds including sulphides and silica. From the point of confluence, a single dark creek flows north-westwards, passing through the tourist baths near the park entrance. This creek then winds downslope through dense vegetation over several kilometres to the coastal town of Soufrière, where it enters the sea. It has not yet been established how far downstream the dark grey colouration of the creek is maintained, but by Diamond Falls, about halfway to the sea, the creek has become clear.

Analytical Methods

Rocks

Whole-rock samples were chemically analysed by Bureau Veritas in Vancouver using their complete characterisation package LF200 with AQ200 add-on. In the LF200 package, rock powders are fused with lithium borate prior to acid dissolution and analysis by ICP-ES (major elements) and ICP-MS (refractory trace elements). The AQ200 add-on provides analyses of 12 metals by ICP-ES and ICP-MS following dissolution by aqua regia only. Total C and total S were analysed by Leco furnace.

X-ray diffraction (XRD) analysis was performed on a Panalytical X'Pert Pro diffractometer equipped with Cu X-ray source and an X'Celerator detector and operating at the following conditions: 40 kV and 40 mA; range 5-70 deg 2θ and 3.5-30 deg 2θ ; step size 0.017 deg 2θ ; time per step 50.165 sec; fixed divergence slit, angle 0.5°; sample rotation 1 rev/sec. The X'Pert HighScore Plus software along with the PDF4/Minerals ICDD database were used for mineral identification. Corundum was added as an internal standard to determine the X-ray amorphous content. The quantities of the crystalline phases were determined using the Rietveld method, which is based on the calculation of the full diffraction pattern from crystal structure data. Clay speciation analysis was additionally carried out on 3 samples. The <25 μm size fraction was separated by wet sieving and a portion of the suspension was placed on a glass slide, which was analysed both air dried, and after treatment with ethylene glycol.

Mineral Liberation Analysis (MLA) was carried out at Activation Laboratories, Ancaster, Ontario, on an FEI Quanta600F scanning electron microscope (SEM). Results are based on a combination back-scattered electron (BSE) signal intensity and Energy Dispersive X-ray Spectrometry (EDS) using two Bruker 5010 SDD detectors. The mineral matter was identified and quantified using XBSE and XMOD measurement modes. The XBSE measurement was applied to collect reference spectra. Mineral phases were discriminated based on their BSE grey value; a point X-ray analysis was then performed in the centre of each phase with a defined grey level. The XMOD measurement (point counting) was used for quantification of mineral abundances. X-ray spectra were taken along lines that intersected particles. The step size along the x direction was 2 μm ; traverse lines were separated in the y direction by 32 μm . Each collected X-ray spectrum was compared to the spectra in the reference list by the MLA software.

O-H-isotope ratios of whole-rock silicates were measured at the Laboratory for Stable Isotope Science, University of Western Ontario. For oxygen, sample powders were reacted overnight at $\approx 580^\circ\text{C}$ with ClF_3 to release the silicate-bound oxygen (Borthwick and Harmon, 1982; following Clayton and Mayeda, 1963). The oxygen was converted to CO_2 over red-hot graphite for isotopic measurement using a Micromass Optima dual-inlet, stable-isotope-ratio mass-spectrometer. Hydroxyl-group hydrogen was extracted from silicate whole-rock samples using a method modified after Godfrey (1962), Kyser and O'Neil (1984) and Vennemann and O'Neil (1993). H_2 was analysed using a Thermo ScientificTM Delta^{Plus}XL or Delta V^{Plus} dual-inlet stable-

isotope-ratio mass-spectrometer. O-H-isotope results are reported using standard δ -notation relative to VSMOW, to which internal laboratory standards have been calibrated on the VSMOW-SLAP scale following the protocol of Coplen (1996). Reproducibility of $\delta^{18}\text{O}$ and δD measurements is typically $\pm 0.2\text{‰}$ and $\pm 3\text{‰}$, respectively (1σ). S-isotope ratios were determined (on splits of the same whole-rock samples) at the G.G. Hatch Stable Isotope Laboratory of the University of Ottawa. Samples were loaded into an Isotope Cube (Elementar, Germany) elemental analyser to be flash-combusted at 1150°C . Released gases are carried by helium through the analyser to be cleaned, then separated. SO_2 gas is carried into the Delta Plus XP isotope ratio mass spectrometer (ThermoFinnigan, Germany) via a ConFlo IV interface for ^{34}S determination. Reproducibility of S-isotope measurements is typically $\pm 0.2\text{‰}$.

Waters

Sampling of thermal waters at Sulphur Springs took place in 2014 and 2017, with 17 sets of water samples taken, each comprised of three aliquots. Samples were filtered ($0.45\text{ }\mu\text{m}$) and stored in polyethylene bottles. One bottle was acidified with suprapure HNO_3 for determination of cation analyses and another one was kept unacidified for anion analyses. Unfiltered water samples were stored in glass Quorpak bottles for stable isotope analyses. Major ion and trace element contents were determined using Atomic Absorption Spectrophotometry (AAS), Ion Chromatography (IC), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at the Department of Chemistry, University of the West Indies in Trinidad (2014 samples) and at the

Department of Geology, Union College, New York (2017 samples). The charge balance error for the analyses is $\leq 10\%$.

Deuterium isotopic composition of water samples was analysed on a Thermo TC/EA (High Temperature Conversion Elemental Analyser) at 1425°C connected via a ConFlo IV to a Thermo Delta Advantage mass spectrometer in continuous flow mode at Union College. The analytical uncertainty for δD is $\pm 0.4\text{‰}$ (VSMOW). Oxygen isotopic composition of water samples was measured via a Thermo Gas Bench II connected to a Thermo Delta Advantage mass spectrometer in continuous flow mode at Union College. The analytical uncertainty for $\delta^{18}\text{O}$ is $\pm 0.2\text{‰}$ (VSMOW).

Field Aspects of the Altered Rocks and Thermal Pools

Typical features of the Sulphur Springs geothermal area are shown in Figure 5. The zone of present and recent steam discharge (Figs. 5a,b) is clearly marked by the prevalence of whitish alteration products dominated by kaolinite, alunite, illite, smectite and amorphous silica, with local enrichments of native sulphur and sulphates such as gypsum and jarosite (Greenwood et al., 2005; McKeeby, 2017; this study). The geothermal pools and the main geothermal creek that drains them (Figs. 5c,d) are grey to black due to the presence of fine-grained to amorphous precipitates including iron sulphides and silica. In several areas, massive dacite host rock has

been converted to a pseudo breccia as the result of selective alteration that has expanded outwards from fracture networks, leaving islands of less altered dacite within a kaolinite-rich matrix (Fig. 5e). In other areas, the matrix of coarse volcanoclastic breccias (probably block and ash flows originally) has been selectively altered to kaolinite (Fig. 5f).

Figure 6 shows representative hand specimens ranging from fresh porphyritic dacite to altered equivalents containing variable amounts of kaolinite, alunite, smectite, amorphous silica and native sulphur. The illustrated samples have been analysed for whole-rock geochemistry, mineralogy and stable isotopic composition.

Primary volcanic textures are commonly obliterated on the cm-scale by strong alteration but are still evident in occasional remnant domains (dm-scale) within the main geothermal field, and in less altered samples taken from the margins of the geothermal system. The outlines of feldspar phenocrysts are commonly visible, although the phenocrysts have been replaced by mixtures of fine-grained silica, kaolinite and other clays, and alunite. Original quartz phenocrysts are generally preserved although some have been corroded, whereas phenocrysts of biotite and amphibole have been converted largely to smectite and fine Fe-Ti oxides.

Mineralogy

The results of quantitative X-ray diffraction (XRD) and mineral liberation analysis (MLA), are given in Tables 2a and 2b, respectively. Although both methods identified kaolinite, smectite, quartz, alunite-natroalunite, native sulphur, pyrite, feldspars, illite-muscovite, amphiboles, pyroxene, and various impure compounds, there are some notable differences in estimated abundances. These result mainly from a major component of amorphous to semi-crystalline material in many samples; such material is identified by MLA but generally not by XRD. Some of this material is reported in Table 2b as mixed phases such as “alunite-natroalunite with silica hydroxide” and “silica hydroxide with chlorite or amphibole”. This material probably consists of largely amorphous hydrous silica (opal) containing minute inclusions of crystalline phases that contribute peaks to the overall spectrum. Scanning electron microscopy did not reveal any obvious organic structures in the amorphous material. Minor Fe-bearing sulphate was detected by MLA in a couple of samples. Minor jarosite could also be present in a few samples based on spectra that include Fe-K-S-Al peaks.

Composition of Waters

Chemical composition

The chemical composition of the waters, including O-H-isotopic values for a subset of samples, are given in Table 3. Hot pools previously sampled at Sulphur Springs have pHs of 3-7 and temperatures of 41-97°C (Greenwood, 2004; Joseph et al., 2013). Samples taken in the present study have near-neutral pHs, with Na and Ca as their major cations. The content of total dissolved solids (TDS) is mainly moderate (402-2099 mg/kg). Most waters having low to moderate contents of Na (3-177 mg/kg), Ca (33-268 mg/l) and K (5-165 mg/kg). The waters generally have relatively high contents of SO_4 (<1313 mg/kg), low contents of HCO_3 (<221 mg/kg), and low contents of Cl (19–87 mg/kg, with the exception of Clear Water Pool). A significant bicarbonate component is present in samples from Black Water Pool and Clear Water Pool.

Classification of the thermal waters, based on their relative amounts of Cl- SO_4 - HCO_3 (by weight %), is shown in Fig. 7a. The waters are classified mainly as Na/Ca- SO_4 steam-heated type, resulting from the condensation of acidic hydrothermal gases (H_2S and lesser HCl) into near-surface oxygenated waters of meteoric origin (Joseph et al., 2013). The H_2S is probably derived from magmatic SO_2 gas by disproportionation reactions in the subsurface.

Positive correlations between temperature and dissolved sulphate (data in Table 1), and between sulphate and O-H-isotopic enrichment (next section) are consistent with mixing between meteoric waters and acid condensates derived from uprising steam, followed by concentration due to surficial evaporation. Modest enrichments in cations such as Na and Ca pools probably resulted from leaching of the host dacites by acid condensates. Evidence from geothermal wells drilled at Sulphur Springs indicates the presence of a zone of super-heated steam in moderately fractured rocks at 915–1018 m depth, at temperatures of about 292°C (AQUATER, 1982).

O-H-isotopic composition

Oxygen and hydrogen isotopic compositions of surface waters from the Sulphur Springs geothermal area and a rainforest creek that enters this area are shown in Figure 7b. The 2017 data define a linear trend of positive isotopic enrichment that intersects the meteoric water line (MLW) at $\delta^{18}\text{O} = -3\text{‰}$ and $\delta\text{D} = -12\text{‰}$. The heavy end-member is estimated to have an isotopic composition of about $\delta^{18}\text{O} = +14\text{‰}$ and $\delta\text{D} = +12\text{‰}$. The 2017 isotopic trend is parallel to, and partly overlies the trends obtained by earlier workers for surface thermal waters in 2000-2002 (data in Greenwood et al., 2005; Joseph et al., 2013). These trends all have slopes of about 1.4. The slight variation in vertical position of the trends may be due to seasonal

variations in the isotopic composition of local precipitation (cf. Majumdar et al., 2005; Price et al., 2008).

The isotopic enrichment trends in Figure 7b could result from processes such as: (1) mixing between meteoric water and a high-temperature, isotopically heavy (“enriched”) volcanically derived fluid; (2) water-rock reactions at depth in the high-temperature reservoir; (3) progressive enrichment in ^{18}O and D due to surface evaporation of meteoric water.

The first possibility is unlikely, as the isotopically enriched part of the Sulphur Springs trend has δD values that are higher than those of typical andesitic-magmatic waters (field A in Fig. 7b). Also, magmatic gases generally contain high contents of chloride (derived from HCl), whereas the thermal pools at Sulphur Springs mainly have low contents of Cl. The second possibility is also unlikely, as high-temperature water-rock reactions lead to brines that are ^{18}O -enriched, but not D-enriched. The low content of Cl in the thermal pools also suggests that any contribution of deep brine is small.

In regard to the third possibility -- that of progressive isotopic enrichment in both ^{18}O and D due to non-equilibrium surface evaporation – the resulting slopes should in theory lie in the 3-5 range, depending on air humidity (cf. Oppenheimer et al., 2014). Many thermal pools in geothermal systems do in fact show slopes between 3 and 5 (e.g., Delmelle et al., 2000; Tassi et

al., 2005; González-Partida et al., 2005; Rouwet et al., 2008), although processes other than evaporation, e.g., mixing with magmatic waters, have commonly been invoked. In other thermal pools, such as those at Wairakei, El Tatio and The Geysers, isotopic enrichment trends have much lower slopes of about 1.5, which has been attributed to the introduction of D-depleted steam derived from boiling of a deep, chloride-rich reservoir fluid at temperatures of about 230°C (Giggenbach and Stewart, 1982). The same process may well have operated at Sulphur Springs, where the deep reservoir reaches temperatures of 280°C and is overlain by a vapour zone several hundred metres thick (Ander et al., 1984). Isotopic trends with low slopes (notably less than 3) also characterise thermal pools in Dominica (Joseph et al., 2011) and brine pools in Costa Rica (Rowe, 1994).

Giggenbach and Stewart (1982) proposed an equation that relates the slope of an isotopic enrichment trend in thermal pools to the maximum observed $\delta^{18}\text{O}$ shift between meteoric water and deep reservoir brine; the equation is based on single-step separation of steam from deep fluid at 230°C. Using the Sulphur Springs $\delta^{18}\text{O}$ values of -3 ‰ for meteoric water and a maximum of +11 ‰ for deep brine (Bath, 1977), the equation yields an isotopic slope of 1.8, reasonably close to the observed slope of 1.4. Use of a somewhat different equation (Giggenbach, 1978) based on the initial isotopic compositions of meteoric water and fumarolic steam (rather than brine) yields a calculated slope of 1.6. For this latter equation, a fumarole average of $\delta^{18}\text{O} = 4.0$, $\delta\text{D} = -26$ (Ander et al., 1984) was used.

Whole-Rock Chemistry

Primary Composition of Host Rocks

The major and trace element compositions of unaltered to highly altered samples from Sulphur Springs are given in Table 1. Unaltered rocks lateral to the geothermal area have been classified as either dacite I, dacite II, dacite III or andesite based on their immobile-element ratios, in particular their $\text{Al}_2\text{O}_3/\text{TiO}_2$ and Zr/TiO_2 ratios (Fig. 8a). Most of the unaltered samples have dacite I or dacite II compositions. All unaltered rocks have a calc-alkaline island-arc affinity, based on their Zr/Y and $(\text{La}/\text{Yb})_n$ ratios (6.5-9.5 and 8.5-12.5, respectively) and low Nb contents (4-6 mg/kg) (Table 1).

Moderately altered dacites are compared with unaltered dacites in Figure 8b, which shows that the $\text{Al}_2\text{O}_3/\text{TiO}_2$ and Zr/TiO_2 ratios of the precursors have been either retained or only slightly modified.

Highly altered samples and mobility of Al

Intensely altered dacitic material is compared to the field of precursor dacites in Figure 9a.

Although a few of the intensely altered samples plot near the precursor field, most of them along opposing sublinear trends extending well away from this field. These opposing trends can be explained by mass additions or losses of Al during the alteration process, with Ti and Zr remaining essentially immobile. Mobility of Al is considered further in a later section, where the results of mass-change calculations are given.

Intensely altered dacites also show systematic changes in $(La/Yb)_n$ ratios as Al is lost or added (Fig. 9b). There is a general increase in $(La/Yb)_n$ with mass addition of Al, and a decrease in $(La/Yb)_n$ with mass loss of Al. Although the increase in $(La/Yb)_n$ could, in theory, be due to either addition of light REEs or removal of heavy REEs, mass change results discussed in the next section suggest that the former process is dominant.

Most of the intensely altered samples, regardless of whether they have lost or gained Al, have higher Zr/Y ratios than those of the precursors (Table 1). Mass change results show that this is due to losses of Y, rather than additions of Zr. Apart from Ti and Zr, the only other element that has remained largely immobile is Nb (as shown by consistency of Zr/Nb ratios).

The quantitative effects of losses or gains of Al on immobile-element ratios involving Al, Ti and Zr are shown in Figures 10a and 10b, respectively. Using these plots, one can estimate the amounts of Al (in weight %) that must be removed from, or added to, a rock in order to produce a particular set of ratios. This plot is specifically for use with altered samples that have been derived from a dacite precursor, and where Ti and Zr have remained essentially immobile during alteration.

Rare-Earth Elements

REE patterns of highly altered dacites with either Al mass loss or Al mass gain are shown in Figures 11a and 11b, respectively. Also shown is the average REE pattern of precursor dacite. Samples with Al mass loss all appear to have lost REEs, with somewhat greater loss of light to middle REEs compared to heavy REEs. These samples also show notably negative Eu anomalies. By contrast, samples with Al mass gain appear to have lost middle to heavy REE, and show little or no Eu anomaly.

In order to evaluate REE mobility quantitatively, it is necessary to carry out mass-change calculations, as visual comparison of patterns can be misleading. Entire patterns can be shifted up or down due, respectively, to the removal or addition of mobile components such as silica. Mass changes in the REEs are discussed further in the next section.

Mass Changes

Mass changes were calculated for all samples using the single-precursor method (Kranidiotis and MacLean, 1987; Barrett and MacLean, 1991, 1994; MacLean and Barrett, 1993) for each of the four main chemical groups mentioned above (three dacite groups and andesite). The precursor composition of each group was taken as the average of the least-altered samples in that group. In view of the small amount of primary variation that exists within each group, the use of an average value for the precursor of each element probably introduces errors of up to $\pm 15\%$ in the calculated mass changes. For each altered sample, a mass-change factor was then calculated for both $\text{TiO}_2(\text{pre})/\text{TiO}_2(\text{alt})$ and $\text{Zr}(\text{pre})/\text{Zr}(\text{alt})$, where 'pre' and 'alt' refer to precursor and altered sample contents respectively. For the calculations, the average of these two mass-change factors was used in order to minimize any small natural variations in either Ti or Zr that might be present in the precursor groups. The average mass-change factor (as used in the calculations) differs from the individual Ti and Zr mass factors by up to $\pm 10\%$. Studies of element mobility in kaolinite-alunite-silica deposits have shown that Ti, Zr and Nb are generally immobile (Ece et al., 2009; Scher et al., 2013).

Mass-change results for the major elements and the REEs are given in Table 5. Results for representative samples of highly altered dacite that have experienced either mass loss or mass gain of Al are shown in Figures 12a and 12b, respectively. In these highly altered rocks, all major

elements with the exception of Ti have been mobilized, as have most trace elements with the exception of Zr and Nb. Samples that have lost Al show significant loss of all major elements, apart from silica (modest loss). In samples that have gained Al, silica mass changes are generally minor, but two samples show large additions. One sample with Al mass gain also shows notable additions of Ca and Fe due to the presence of gypsum and iron sulphides/sulphates. In a study of acid-sulphate alteration associated with fumarolic activity in Indonesia, Scher et al. (2013) found that Al and all other major elements except silica were leached from andesite under extremely acidic conditions, whereas Al, Fe, K and P were deposited in alunite-pyrite zones when the pH increased.

Mass change results for the REEs are shown in Figure 13a for highly altered dacites with Al mass loss. Also shown is the REE pattern for precursor dacite expressed as original mg/kg contents (not mass changes). Although the light REEs have lost the most total mg/kg, this is because elements such as La, Ce and Nd are much more abundant on a mg/kg basis than the middle to heavy REEs. All samples with Al mass loss have lost 60-95 % of their original REEs, but generally they have lost a greater proportion of light REEs, leading to lower La/Yb ratios. By contrast, samples with Al mass gain have gained up to 200 % light REEs relative to precursor values, but lost up to 90 % of their heavy REEs (data in Table 5), leading to an increase in La/Yb ratios. These latter samples also show increased Th/Yb ratios (Table 1). Y has been lost from most of the strongly altered samples that show Al mobility (whether Al is gained or lost).

Strongly altered samples that have gained Al mass have gained both P_2O_5 and light REE (using Ce as an example) (Fig. 13b). These relations suggests that the main control on REE abundances in samples with Al mass gain is the precipitation of an Al-REE-bearing phosphate/sulphate phase (or phases). One candidate is florencite, a member of the crandallite series having the general formula: $(REE)Al_3(PO_4)_2(OH)_6$, where the REE are dominated by La-Ce-Pr-Nd (Dill, 2001). Another possible phase is REE-bearing woodhouseite, which has the general formula: $CaAl_3(PO_4/SO_4)(OH)_6$. The precipitation of Al-bearing sulphates such as alunite and jarosite, which are enriched in the light REE, would similarly serve to increase La/Yb ratios (cf. Inguaggiato et al., 2015; Varekamp, 2015).

Interestingly, several altered dacites that show no evidence of Al mobility have lost both Y and Yb (samples SS01, SS13, SS23, SS28 and SS46 in Table 1). As result, they have notably higher Zr/Y and La/Yb ratios than the precursor dacite. These samples generally have been leached of most of their Fe, Mg, Ca and Na (but not Al). Similar effects have been noted at several VMS deposits in northern Sweden where aluminosilicate-rich 'acidic' alteration assemblages are present (Barrett et al., 2005; Barrett and Zetterqvist, 2007). These studies and the data in Table 1 suggest that once the acidity of the alteration fluid increases to the point where Fe-Mg-Ca-Na are largely leached from the rock, Y and the REEs become mobile. With a further increase in acidity, Al and K can also become mobile. In a study of crater lake waters in Columbia, Inguaggiato et al. (2015) found that dissolved Al (and total REEs) increased with decreasing pH, such that Al exceeded 10 mg/kg for pH values of <2.

Mercury and Selenium

Trace metal contents of whole-rock surface samples are given in Table 1. The most anomalous of these metals are Hg and Se, which in the highly altered dacites can reach values of up to 50 mg/kg. Ten of the altered dacites show anomalous values of Zn (40-80 mg/kg), three of which also contain anomalous Cu (30-60 mg/kg). As and Pb contents of almost all samples are low (<15 mg/kg). Surface values of Hg and Se within the geothermal field are shown in Figure 14. Although the highest values are from sublimate-rich encrustations on the flanks of Sulphur Hill, high values (10-30 mg/kg) are also found in some of the intensely altered dacites, and in dark muds from the thermal pools. Interestingly, Hg and Se values are mostly much lower in the northern part of the geothermal field, where fumaroles and thermal pools are now absent. Given that the dacites in this latter area are also highly altered, it is conceivable that fumaroles, pools and surficial accumulations of Hg and Se were once present, but the Hg and Se were then largely removed by erosion (due to abundant rainfall combined with steep slopes and lack of vegetation). It is worth noting that rock and sediment samples from the main rainforest creek entering the geothermal area (shown in blue in Figure 14) have very low contents of Hg and Se. By contrast, the creek draining the thermal pools (e.g., Witches Pool) contains high levels of both. Two samples 80-120 m downstream from the main recreational bathing pool, where the stream is still dark, also contain high levels of Se and Hg (samples SS21 and SS23; Table 1). The

first of these is a dark mud (northwest corner of Figure 14), while the second is an altered dacite located another 40 m downstream.

Rocks and sediments with high contents of Hg (mg/kg to tens of mg/kg) are known from a number of geothermal systems, including several localities in the western USA (Varekamp and Buseck, 1983; Rytuba, 1993; Janik et al., 2000), Kamchatka in Russia (Rychagov et al., 2010, 2014) and Ngawha Springs in New Zealand (Davey, 1979). Data on the Se contents of geothermal deposits are limited. Dark mud containing pyrite and iron oxide from a thermal pool at Anderson Springs in California contains 23 mg/kg Se (Janik et al., 2000). In Japan, native sulphur deposited from fumarolic gases contains 15-500 mg/kg Se (Suzuoki, 1964).

Whole-Rock Stable Isotopic Compositions

O-H-Isotopes

The whole-rock O-H-isotopic compositions of four samples of highly altered rock (Table 4) are shown in Figure 15, together with calculated isotopic values for a typical alteration assemblage formed in equilibrium with an arbitrary 50:50 mixture of Sulphur Springs meteoric water (M) and fumarolic steam (F) at temperatures of 50° to 125°C. For the steam O-H-isotopic end-member, the average of three fumarolic samples (Goff and Vuataz, 1984) was used. For the

isotopic calculations, standard mineral-water fractionations as compiled in Kharaka and Thordsen (1992) were used, together with newer fractionation equations for kaolinite and smectite given by Gilg and Sheppard (1996) and Sheppard and Gilg (1996). The calculated line shown in Figure 15 is for an alteration assemblage consisting of kaolinite (40 %), precipitated silica (30 %), smectite-illite (20 %), and sulphates (10 %) (alunite-jarosite-gypsum). Using these mineral proportions, a calculated line results that agrees reasonably well with the whole-rock trend, although offset to slightly higher isotopic values. While further adjustments to the mineral proportions or the initial fluid isotopic composition could be made in order to improve the fit, they are unwarranted given the uncertainties involved, including the ratio of steam to meteoric water, and the possible effect of residual phenocryst quartz on whole-rock O-isotopic compositions. The effect of having a 20 % component of phenocryst quartz (with a magmatic $\delta^{18}\text{O}$ value of 8 ‰) within the alteration assemblage at temperatures of 50° and 100°C is shown by the small horizontal arrows in Figure 15.

Two sulphur-silica-rich encrustations from areas of recent fumarolic activity were also sampled at Sulphur Springs (Table 4). These samples, which have δD values of -99 and -104 ‰, consist mainly of native sulphur with lesser quartz and opaline silica (and a near-zero content of aluminous phases). If the opaline silica, which is likely the main site of the deuterium, precipitated from a steam condensate with a δD value of -26 ‰ (the average value of the three fumaroles), temperatures of deposition of about 75-80°C are obtained based on the opal-water D/H fractionation curve (Faure and Matsuhisa, 2000). The $\delta^{18}\text{O}$ values of these two samples are

13.7 and 20.8 ‰. Assuming the oxygen is located entirely in quartz and opal, and that these phases formed from a steam condensate with a $\delta^{18}\text{O}$ value of 4.4 ‰ (the average value of the three fumaroles), inferred temperatures for the two samples are 240° and 140°C based on the quartz-water fractionation (Clayton et al., 1972) and near-identical opal-water fractionation (Kita et al., 1985). The upper value of 240°C, which is unusually high compared to other estimates of surface temperatures, may be due to the common remnant quartz phenocrysts that are present in this sample (as identified by SEM). If for example 50 % of the silica is phenocrystic quartz with a typical magmatic $\delta^{18}\text{O}$ value of 8 ‰, and 50 % is opaline silica with a $\delta^{18}\text{O}$ value of 20 ‰, the resulting bulk-rock value would be 14 ‰.

S-Isotopes

The $\delta^{34}\text{S}$ values of three highly altered rocks are -5 to -6 ‰, while a dark mud from a hot pool has a value of -7.8 ‰, and two S-rich sublimates taken near fumaroles have $\delta^{34}\text{S}$ values of about -13 and -16 ‰ (Table 4) (Fig. 16a). In addition, two sulphur sublimates reported in Ander et al. (1984) have values of -9 and -11 ‰.

Although the entire suite of Sulphur Springs samples is notably depleted in ^{34}S relative to most sulphides in submarine hydrothermal systems in volcanic arcs and spreading ridge settings,

strong ^{34}S -depletion commonly occurs in on-land volcanic geothermal systems (see data summary in Fig. 16b). At Volcan Puracé in Colombia, native sulphur lining thermal spring outflow channels has $\delta^{34}\text{S}$ values of -13.1 and -16.6 ‰, while H_2S gas (1 sample) has a value of -14.4 ‰, and a deposit of native sulphur has a value of about -10 ‰ (3 samples) (Sturchio et al., 1993). At Volcan Copiapo in Chile, 3 samples of native sulphur have $\delta^{34}\text{S}$ values of -12.0 to -15.4 ‰ (1 value of -7.1 ‰) (Stark, 1991), while native sulphur from the desiccated crater lake at Volcán Poás in Costa Rica has $\delta^{34}\text{S}$ values of -9.4 to -12.3 ‰ (Oppenheimer, 1992; Rowe, 1994). On White Island in the Bay of Plenty, New Zealand, $\delta^{34}\text{S}$ values as low as -15 ‰ have been recorded for both native sulphur and H_2S gas (Giggenbach and Matsuo, 1991). Notably ^{34}S -depleted samples have also been recovered from deeply submerged seamounts, for example Desmos Caldera off Papua New Guinea (native sulphur = -6.5 to -9.3 ‰, H_2S gas = -4.3 to -9.9 ‰) (Gena et al., 2006). According to Oppenheimer (1992), native sulphur that is highly depleted in ^{34}S may be typical of low-temperature aqueous settings where SO_2 , the primary volcanic gas, is hydrolysed to sulphuric acid plus sulphur or H_2S .

Sulphate minerals at Sulphur Springs, including alunite, jarosite and gypsum, have negative $\delta^{34}\text{S}$ values of -6 to -10 ‰ (Greenwood et al., 2005). The three altered dacites analysed in the present study with $\delta^{34}\text{S}$ values of -5 to -6 ‰ contain 5-10 % sulphates, but lack native sulphur (based on XRD and MLA results). The $\delta^{34}\text{S}$ values of these various sulphates, although notably negative, are several per mil heavier than the values of -13 and -16 ‰ determined for native

sulphur sublimates (present study). However, if the sulphate minerals are formed by surface oxidation of native sulphur, they should retain its strongly negative $\delta^{34}\text{S}$ values. The observed shift to somewhat heavier values (-5 to -6 ‰) in these three altered dacites suggests that some of the sulphate minerals formed from sulphate dissolved in thermal waters. A similar but smaller shift is seen at Volcan Copiapo in Chile, where two samples of massive sulphate (alunite) have $\delta^{34}\text{S}$ values of about -10 ‰, a few per mil heavier than that of interbedded native sulphur (Stark, 1991).

Discussion and Conclusions

The application of immobile-element methods to the geothermally altered rocks at Sulphur Springs has allowed quantitative evaluation of the chemical changes that have occurred relative to the compositions of their precursors. All altered rocks have near-constant Zr/Ti ratios matching those of the near-homogeneous suite of unaltered dacites that flank the geothermal field. However, many of the highly altered (acid-leached) samples have either lost or gained significant amounts of Al, and also display mobility of P, Y and the REE

The first stage of dacite alteration produces moderate mass losses of Si, Fe, Mg, Ca and Na, corresponding to the partial conversion of glass and phenocrysts of alkali feldspar and amphibole to clay minerals such as illite, montmorillonite, kaolinite and alunite. There is little

change in K at this stage, as it is retained in new phases such as illite and alunite. Quartz phenocrysts are well preserved, thus the whole-rock mass losses of 5-10 wt % SiO_2 in such samples must be due to removal of Si from glass and feldspar phenocrysts. LOI values have increased from 1-2 % in the precursor dacites to 5-15 % in the altered rocks, due to addition of H_2O now contained in clays and alunite, and S now in native sulphur and alunite. Moderately altered dacites generally preserve primary immobile-element ratios such as $\text{Al}_2\text{O}_3 / \text{TiO}_2$, Zr / TiO_2 , Zr / Y and La / Yb . Some of these samples have high absolute contents of Al_2O_3 (reaching 20 wt %), due to the residual concentration of Al, which has remained immobile as other elements are being removed. Moderately altered dacites commonly show evidence for mobility of Y and the REE (anomalously high Zr / Y and La / Yb ratios), as well as strong losses in Fe, Mg, Ca and Na (excluding a few samples where Fe sulphides have been added)

The most intensely altered dacites show significant mass losses or gains in Al, P and the REEs, as well as strong losses of K (in addition to losses of Fe, Mg, Ca and Na). Even where almost all of the initial Al has been removed by leaching, the original Zr / TiO_2 ratio of the dacites is retained. In the case of altered rocks with high contents of silica (90 %), one might assume that silica has been added to the rocks, particularly if the content of Al is much lower than that of the precursor dacite, which gives the impression of dilution by “new” silica. However, the Ti-Zr-based mass changes show that silica was either not added relative to the precursor dacite, or slightly removed. This suggests that the silica in the low-Al samples was derived from dissolution of silicates and glass in the dacite and then precipitated more or less in situ (apart

from a minor amount of silica in undissolved quartz phenocrysts). It follows that much of the “free” silica in these samples was not introduced by uprising deep fluids. In fumarolic environments, where condensates have very low pH values (<2), extreme acid leaching can remove all major elements except silica (Africano and Bernard, 2000).

Although some highly altered samples have lost Al, others have gained it. This suggests that the Al that is leached from the dacites by warm surficial waters does not travel very far before it is precipitated, presumably due to either an increase in pH upon mixing with normal meteoric waters, or evaporation. The phases most likely to accommodate Al are members of alunite-natroalunite-jarosite series, and, in those cases where P and REE are also precipitated, florencite and woodhouseite (cf. Dill, 2001). It is worth noting that in geothermal systems in other area globally, the contents of dissolved Al in thermal pools with pHs <2 can reach a few hundred mg/kg. Such pools can act as “holding stations” for leached Al until they become neutralized or dry out and Al-bearing compounds are precipitated.

Surface thermal waters at Sulphur Springs show a linear trend of isotopic enrichment in ^{18}O and D that is likely due to prolonged evaporation effects. The low slope of the trend (1.4) probably results from mixing between meteoric waters and steam derived from a deep brine. The δD values of the most enriched thermal waters are higher than those of andesitic-magmatic waters in other island-arcs globally (Taran and Zalenski, 2014), thus making unlikely any major magmatic contribution to the geothermal waters. Similar “elevated” isotopic trends are also

found for geothermal waters in Costa Rica (Tassi et al., 2005) and Dominica (Joseph et al., 2011). Such trends may in fact be a common feature of low-latitude regions where meteoric waters have high δD values (-20 to +10 ‰) and therefore the evaporated end-member will have an even higher value. This raises the possibility that some of the isotopic trends shown by geothermal waters at mid-latitudes are not necessarily the result of mixing between meteoric and andesitic waters, as is commonly inferred, but could be the result of evaporative surface processes, a point also made by Oppenheimer et al. (2014).

At Sulphur Springs, native sulphur associated with fumaroles has highly negative $\delta^{34}S$ values (-13 to -16 ‰), indicating that the S was derived from magmatic gases. Altered rocks have moderately negative $\delta^{34}S$ values (-5 to -6 ‰), probably due to the additional presence of sulphates that precipitated from thermal waters. Significant amounts of Hg and Se (up to 50 mg/kg each) can be present in sulphide-bearing muds from the thermal pools, in highly altered dacites, and around fumaroles where native S is present. It would be of interest in future studies to determine the extent to which Hg and Se, which are potentially hazardous elements, have been distributed downstream towards populated areas such as Soufrière on the southwest coast.

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Figure Captions

Figure 1

Location map for Sulphur Springs geothermal field in southwestern St Lucia (southern Antilles). The dashed line marks the approximate margin of the collapsed caldera of the Soufrière volcanic complex. Dacitic domes and dacitic pyroclastic rocks are shown in red and light green, respectively. Andesitic centres are in grey.

Figure 2

Topographic map of the inner part of the Soufrière caldera, showing location of the Sulphur Springs geothermal field (black box) and regional lithochemical samples. Sample locations within the geothermal field are shown in Figure 4.

Figure 3

Aerial view looking north of Sulphur Springs geothermal field showing lithochemical sample locations. The whitish area corresponds to main zone of acid-sulphate alteration (kaolinite-alunite-illite-silica-rich). Thermal pools and creeks within the geothermal field are shown in Figure 4. The Terre Blanche massive dacite dome occupies the upper right of the image. For clarify, the prefix 'SS' is omitted from the sample numbers.

Figure 4

Lithochemical sample locations, thermal pools and drainage creeks within the Sulphur Springs geothermal field. The main geothermal area is shown in pale grey; the surrounding light green area is largely rainforest, apart from the grassy western flank of the Terre Blanche dacite dome. The creek shown in blue contains fresh meteoric water, whereas the blackish creek carries highly modified meteoric water derived from thermal pools that also contains condensed steam and amorphous compounds, including sulphides. For clarity, the prefix 'SS' has been omitted from the sample numbers.

Figure 5

Field photographs. a,b: overviews of Sulphur Springs geothermal field showing highly altered volcanic rocks and steam emissions, with a hot pool visible in (b); c: a bubbling, dark, hot pool, 5 x 3 m across; d: dark creek 100 m downstream from dark hot pools, flanked by altered volcanic rocks; e: dacitic pseudobreccia within main geothermal field; "boulders" are surrounded by kaolinite-rich zones spreading out from fractures; f: true volcanic breccia with preferential kaolinitic alteration of pebbly matrix.

Figure 6

Lithochemical and petrographic samples. a: SS-04: unaltered porphyritic dacite; b: SS-22: kaolinite-alunite-rich tuff-breccia; c: SS-36; native sulphur and amorphous silica; d: SS-17B: kaolinitic matrix of pseudobreccia; e: scanned thin section of unaltered dacite SS-03 with phenocrysts of quartz, feldspar and amphibole; f: scanned thin section of SS46 showing transition in a dacite block from altered feldspars and quartz phenocrysts to massive fine-grained kaolinite with remnant quartz phenocrysts; g: BSE-image of native sulphur-rich sample SS-36 showing sulphur (bright) and microcrystalline silica (dark) in contact with a remnant quartz phenocryst; h: detail of SS-36 showing native sulphur (upper right) with bleb of microcrystalline pyrite (lower left).

Figure 7

Compositional features of surface thermal waters at Sulphur Spring. a: Cl-SO₄-HCO₃ plot of waters from pools and creeks. Most waters are of acid-sulphate type. b: O-H-isotopic composition of waters from pools and creeks. The thermal waters show an isotopic enrichment trend with a slope of about 1.4. By contrast, thermal waters in other geothermal area commonly have slopes of about 3 (red arrow) or higher. Also shown are the fields of high-temperature volcanic gases and “volcanic arc andesitic waters” (box A), deep brines from a geothermal well at Sulphur Springs (box B), deep steam condensates from the geothermal well (box C), and fumarolic steam from Sulphur Springs (X symbols in box C) (comparative data from

Bath, 1977; Goff and Vuataz, 1984; Mizutani et al., 1986, Taran et al., 1997, 2002; Oppenheimer et al., 2014).

Figure 8

a: Immobile-element ratio plot for unaltered dacites and andesites up to 2 km beyond the Sulphur Springs geothermal field (locations in Figure 2). Most samples fall into two groups, termed dacites I and II. b: Immobile-element ratio plot for moderately altered dacites in the geothermal field, with unaltered samples from (a) shown for comparison. Circles = unaltered; triangles = moderately altered.

Figure 9

a and b: Immobile-element ratio plots for intensely altered dacites, together with fields showing the range of possible precursor compositions. In (a), mass losses or gains of Al produce a trend that passes through the field of precursor compositions. In (b), mass losses or gains in La relative to Y are evident; these show broad correlations with Al mass changes (which are the cause of the $\text{Al}_2\text{O}_3/\text{TiO}_2$ variations). Note log scale for both axes. Al mass loss: minus symbol; Al mass gain: plus symbol.

Figure 10

Calculated effects of Al mass losses (a) and Al mass gains (b) on the Zr/Al_2O_3 and Al_2O_3/TiO_2 ratios of altered dacites, compared to observed ratios. These diagrams provide a simple means of estimating mass changes in Al based on whole-rock data.

Figure 11

Chondrite-normalized REE patterns for highly altered dacites in the Sulphur Springs geothermal field. a: dacites with Al mass loss; b: dacites with Al mass gain. The REE pattern of precursor dacite (average of 6 near-identical samples) is shown by the bold solid line.

Figure 12

Calculated mass changes in major elements (in wt %) for representative highly altered dacites in the Sulphur Springs geothermal field. a: dacites with Al mass loss; b: dacites with Al mass gain. The sample set includes dacite subtypes I, II and II. Calculations were made using separate precursors for each of these three subtypes.

Figure 13

a: Calculated mass changes in individual REEs (in mg/kg) for highly altered dacites that have experienced Al mass loss. Also shown is the REE pattern for precursor dacite. b: Calculated mass

changes (in wt %) for P_2O_5 and Al_2O_3 for all highly altered dacites, together with La mass changes (in mg/kg).

Figure 14

Contents of Hg and Se (red numbers) in altered outcrops and muddy sediments from thermal pools and creeks at Sulphur Springs. The colour of the sample symbols reflects the degree of Al mass loss (pink = minor, dark red = major), or Al mass gain (light blue = moderate; dark blue = major). Unfilled symbols = no demonstrable Al mobility.

Figure 15

O-H-isotopic composition of four highly altered dacites, and calculated whole-rock isotopic values for a kaolinite-opal-smectite-sulphate assemblage in equilibrium with a 50:50 mixture of meteoric water and fumarolic steam at 50-125°C. M = average local meteoric water; F = local fumarolic water.

Figure 16

a: S-isotopic composition and total S content of altered dacitic rocks, muds from thermal pools and sublimates at Sulphur Springs. All samples show notable ^{34}S depletion, with the native sulphur sublimates having the most negative $\delta^{34}S$ values. b: S-isotopic composition of Sulphur

Springs samples compared to sulphides, sulphates and native sulphur from a variety of geothermal and hydrothermal volcanic settings (comparative data from Gemmell et al., 2004; and sources cited in text). Black = sulphides; white = native sulphur and sulphur gases; light grey = sulphates; dark grey = mixed.

Table Captions**Table 1**

Chemical composition of weakly altered to highly altered volcanic rocks and thermal pool sediments from the Sulphur Springs geothermal area.

Footnote: The first part of the table lists samples according to primary rock type; these samples are only weakly altered and do not show mobility of Al. The second part of the table lists highly altered samples that have either lost Al or gained Al; these samples are all derived from dacites I or II (based on their Zr/TiO₂ ratios).

Table 2

Mineralogy of 8 selected samples from the Sulphur Springs geothermal area. Part A gives the results determined by standard XRD analysis (Rietveld method), while Part B give the results obtained from Mineral Liberation Analysis (MLA).

Table 3

Chemical composition, including O-H-isotopic ratios, of waters from surface thermal pools and creeks in the Sulphur Springs geothermal area. Samples were collected in 2014 and 2017.

Table 4

O-H-S isotopic composition of rocks, sublimates and thermal pool sediments in the Sulphur Springs geothermal area.

Table 5

Calculated mass changes for major elements (wt %) and rare-earth elements (mg/kg) for weakly altered to highly altered volcanic rocks and thermal pool sediments from the Sulphur Springs geothermal area.

Table 1

Sample no.	Latitude	Longitude	Sample notes	Chemical type	Al mobility	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	MnO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Cr ₂ O ₃	Ba mg/kg
						%	%	%	%	%	%	%	%	%	%	%
						*										
						LF20	LF2	LF2	LF2	LF2	LF2	LF2	LF2	LF2	LF2	LF2
						0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
						**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
						0.01	1	1	4	1	1	1	1	1	0.02	1
Samples with no Al mobility																
		61°			None											
	13°50'33.3	2°57.84"		demonstrab		64.9	0.4	17.	3.6	1.0	0.0	4.7	2.8	1.5	0.0	0.0
SS12	6"N	W		Dacite I	le	3	1	24	3	9	6	4	4	7	9	03 485
		61°			None											
	13°50'24.1	2°17.50"	Massive porphyritic dacite; track leading	demonstrab		65.4	0.4	17.	4.5	1.6	0.1	5.4	3.0	1.6	0.1	<0.
SS49	5"N	W	west from Bois D'Inde Road	Dacite I	le	2	2	19	6	7	0	5	6	8	1	002 488
		61°			None											
	13°50'8.19	3°14.13"	Road leading to SS park entrance, sample	demonstrab		65.0	0.4	17.	4.5	1.6	0.0	5.8	3.0	1.6	0.1	0.0
SS20	"N	W	full of phenocrysts	Dacite I	le	2	2	17	0	1	9	1	9	5	0	04 463
		61°			None	65.2	0.4	16.	4.3	1.2	0.1	5.2	2.8	1.6	0.1	<0.
SS19	13°50'13.9	1°8.28"W	Migny road cut (10 m back from road)	Dacite I	demonstrab	6	1	71	4	9	0	2	3	3	1	002 449

	3"N				le												
		61°			None												
	13°49'35.0	2'46.96"			demonstrab	63.5	0.4	18.	4.5	1.6	0.1	5.3	2.9	1.4	0.0	<0.	
SS04	0"N	W	Next to house with shop at base of wall	Dacite I	le	9	5	04	0	3	1	2	6	4	8	002	512
		61°			None												
	13°49'14.0	2'25.38"			demonstrab	64.9	0.4	17.	4.2	1.5	0.1	5.6	3.0	1.6	0.1	0.0	
SS06	3"N	W	Quarry off main road to Belfond	Dacite I	le	5	3	21	3	7	0	0	2	7	0	02	474
		61°			None												
	13°49'40.0	2'21.39"			demonstrab	65.1	0.4	17.	4.1	1.5	0.0	5.0	3.0	1.6	0.0	<0.	
SS05	3"N	W	Hard "plug", phenocrysts seen	Dacite I	le	5	4	50	9	0	9	5	2	8	6	002	478
		61°			None												
	13°49'43.4	2'56.03"	Main road back to SS park (opposite grassy		demonstrab	65.3	0.4	17.	4.2	1.5	0.1	5.1	2.9	1.6	0.0	<0.	
SS08	5"N	W	field)	Dacite I	le	0	3	09	4	5	0	9	3	3	9	002	445
		61°			None												
	13°50'13.5	2'43.80"	Pinkish dacite along walkway to		demonstrab	63.6	0.4	17.	3.9	1.5	0.0	4.3	2.7	1.6	0.1	0.0	
SS27	6"N	W	Interpretation Centre	Dacite I	le	8	5	86	0	3	8	0	9	9	1	03	536
		61°			None												
	13°49'17.9	2'48.83"	10 m from Belfond turnoff, 20 m from bus		demonstrab	65.2	0.4	16.	4.2	1.6	0.1	5.4	2.9	1.6	0.1	0.0	
SS03	2"N	W	shed	Dacite I	le	0	4	94	3	0	0	7	6	6	1	02	490
		61°			None												
	13°50'10.6	2'37.50"	Along cart track, past Turning Point on SS		demonstrab	64.1	0.4	17.	4.3	1.6	0.0	4.8	2.9	1.5	0.0	0.0	
SS47	8"N	W	road	Dacite I	le	7	6	59	9	0	8	8	2	8	9	03	454
SS50		61°	Diamond Botanical Estate, bouldery flat area	Dacite I	None	63.3	0.4	17.	4.8	1.7	0.0	5.0	2.8	1.5	0.1	<0.	496

	13°51'1.40"	2°52.00"	in front of waterfall		demonstrable	9	6	58	5	6	9	7	9	8	0	002	
	"N	W			le												
		61°			None												
	13°50'34.8"	2°59.28"			demonstrable	63.3	0.4	17.	4.6	2.0	0.0	5.0	2.7	1.1	0.0	0.0	
SS11	0"N	W	On road entering SS park	Dacite I	le	5	5	17	3	7	9	7	5	8	8	07	447
		61°			None												
	13°50'25.3"	2°49.56"	Outcrop at small "waterfall" next to SS21,		demonstrable	60.6	0.4	18.	4.8	2.1	0.0	3.8	2.3	1.3	0.0	0.0	
SS24	0"N	W	not altered	Dacite I	le	9	9	26	4	4	9	0	9	6	9	06	386
		61°			None												
	13°50'20.9"	2°48.28"	Softer rock near sign along SS creek near		demonstrable	62.6	0.4	19.	1.0	0.2	<0.	0.2	0.6	1.8	0.3	<0.	
SS42	0"N	W	entrance to Bridge Pool	Dacite I	le	9	8	85	4	3	01	6	1	0	0	002	467
		61°			None												
	13°50'25.3"	2°49.56"	Mud sample 80 downstream from main		demonstrable	51.8	0.4	15.	4.8	0.4	0.0	0.6	0.6	0.7	0.1	0.0	
SS21	0"N	W	tourist pool in SS park	Dacite I	le	4	1	90	3	6	3	9	5	8	3	04	315
		61°			None												
	13°50'14.6"	2°43.80"	Top of ascending steps leading to Viewing		demonstrable	53.2	0.4	16.	0.4	0.0	<0.	0.1	1.2	2.9	0.1	0.0	
SS28	4"N	W	Platform	Dacite I	le	4	4	85	6	2	01	0	1	1	9	03	643
		61°			None												
	13°50'15.0"	2°42.95"	Volcaniclastic? from cliff above Clear Water		demonstrable	64.7	0.5	18.	1.9	0.6	0.0	0.8	0.8	1.0	0.0	0.0	
SS30	0"N	W	Pool	Dacite I	le	4	1	67	2	0	3	9	4	8	3	03	366
		61°			None												
	13°50'17.3"	2°46.00"	Sandy sediment at junction of clear water		demonstrable	69.2	0.4	13.	4.3	1.2	0.0	3.5	2.0	1.0	0.0	0.0	
SS37	7"N	W	and black water creeks	Dacite II	le	0	1	84	3	9	7	1	1	7	7	03	332

		61°			None												
	13°50'13.5	2'40.92"			demonstrab	67.4	0.4	15.	1.6	0.4	0.0	3.5	2.6	2.0	0.1	0.0	
SS02A	6"N	W	Block in pseudobreccia	Dacite II	le	2	5	08	7	3	3	1	3	2	3	02	573
		61°			None												
	13°50'15.2	2'43.50"			demonstrab	70.2	0.4	13.	4.6	1.4	0.1	3.8	2.2	1.1	0.0	0.0	
SS29	0"N	W	Sediment sample above Clear Water Pool	Dacite II	le	0	2	73	1	6	2	7	2	6	6	02	364
		61°			None												
	13°50'22.5	2'46.40"			demonstrab	56.9	0.4	15.	0.5	0.0	<0.	0.0	0.4	3.1	0.1	0.0	
SS45	6"N	W	Slope of Terre Blanche	Dacite II	le	3	5	34	4	2	01	8	8	1	0	11	408
		61°			None												
	13°50'13.5	2'40.92"			Dacite	demonstrab	50.1	0.2	9.1	0.6	0.1	0.0	0.3	1.1	1.0	0.1	0.0
SS02B	6"N	W	Finer soft matrix in pseudobreccia	II?	le	7	7	6	3	6	2	1	0	7	0	02	554
		61°			None												
	13°50'36.6	3'5.04"W	Side of road near SS park entrance; tuff of		demonstrab	65.7	0.5	16.	4.5	1.0	0.0	1.3	1.3	1.4	0.0	0.0	
SS09	0"N		small clasts and sand	Dacite II	le	2	0	29	9	3	4	3	2	8	2	03	395
		61°			None												
	13°50'26.4	2'50.45"	120 m downstream from tourist pool:		demonstrab	55.8	0.4	14.	1.7	0.0	<0.	0.0	0.7	2.8	0.1	0.0	
SS23	9"N	W	moderately altered	Dacite II	le	0	8	85	8	1	01	5	7	8	2	05	356
		61°			None												
	13°50'21.0	2'46.68"			demonstrab	58.5	0.5	14.	0.6	0.0	<0.	0.0	0.4	2.9	0.1	0.0	
SS13	0"N	W	Above old geothermal borehole	Dacite II	le	3	0	57	4	2	01	7	6	9	0	13	483
		61°			None	60.4	0.5	14.	0.9	0.0	<0.	0.1	0.8	2.0	0.1	0.0	
SS46	13°50'22.9	2'45.80"	Slope of Terre Blanche	Dacite II	demonstrab	8	0	10	9	9	01	7	3	3	2	07	401

	0"N	W			le												
		61°			None												
	13°50'15.8	2°41.94"			demonstrab	56.8	0.4	18.	1.0	0.0	<0.	0.1	0.8	1.7	0.4	0.0	
SS01	9"N	W	Sandy-pebbly tuff: altered	Dacite III	le	3	2	41	9	5	01	9	7	5	2	07	977
		61°			None												
	13°50'20.9	2°48.28"			demonstrab	58.9	0.4	19.	4.6	1.5	0.0	2.5	1.9	1.3	0.2	0.0	
SS43	0"N	W	Harder rock, just above surface of SS creek	Dacite III	le	5	5	59	2	2	4	9	0	2	8	04	359
		61°			None												
	13°50'57.9	3°32.80"	Agglomerate boulder 300 m south of		demonstrab	58.9	0.6	18.	4.3	2.0	0.0	6.5	2.3	1.6	0.1	0.0	
SS44	0"N	W	Sourfrère	Andesite	le	4	1	28	9	4	9	3	9	7	2	03	419
		61°			None												
	13°50'27.7	3°10.03"			demonstrab	60.7	0.5	16.	6.2	1.7	0.1	4.1	2.4	0.9	0.1	0.0	
SS10	3"N	W	Soft sand and gravel tuff	Andesite	le	4	9	38	5	5	0	4	1	5	1	05	307
		61°			None												
	13°49'5.67	2°57.92"			demonstrab	60.7	0.6	17.	6.6	2.0	0.1	5.3	2.7	1.2	0.1	0.0	
SS07	"N	W	On road to Tete Paul trail	Andesite	le	0	9	03	0	4	2	1	5	0	1	04	378
		61°															
	13°51'7.92	2°18.24"		Carbona			0.0	0.4	0.4	0.3	0.0	53.	0.0	0.0	0.0	<0.	
SS18	"N	W	Travertine at Jerusalem Falls	te	n/a	1.12	1	0	2	2	3	34	8	2	4	002	187
<u>Dacitic samples with mass loss or mass gain of Al</u>																	
		61°	Hardish "block" of pseudobreccia below old	Minor Al		69.0	0.6	15.	2.9	0.1	<0.	0.0	0.1	0.4	0.0	0.0	
SS17A	13°50'19.9	2°45.70"	geothermal borehole	Dacite	loss	5	8	65	4	9	01	3	4	0	4	05	94

	0"N	W															
		61°															
	13°50'25.4	2'49.34"	80 m downstream from tourist pool: altered		Minor Al	68.4	0.5	12.	3.7	1.4	0.0	2.6	1.4	1.4	0.0	0.0	
SS25	6"N	W	exterior	Dacite	loss	6	4	78	6	3	6	2	7	1	9	06	430
		61°															
	13°50'15.1	2'45.70"			Minor Al	68.3	0.5	11.	2.5	0.3	<0.	0.1	0.2	0.5	0.0	0.0	
SS31B	0"N	W	Fizzy Pool: sediment sample	Dacite	loss	8	3	26	7	3	01	4	9	7	5	02	275
		61°															
	13°50'17.4	2'46.20"	Muddy sediment at junction of clear water		Minor Al	70.0	0.4	10.	4.2	0.4	0.0	1.2	0.8	0.6	0.0	0.0	
SS38	5"N	W	and blackish water creeks	Dacite	loss	4	6	53	5	6	3	0	4	9	6	02	302
		61°															
	13°50'16.0	2'47.35"			Minor Al	66.1	0.4	10.	7.2	0.5	0.0	1.4	0.9	0.5	0.0	0.0	
SS33	0"N	W	Witches Cauldron: rock sample	Dacite?	loss	3	8	90	2	6	4	3	6	9	5	02	333
		61°															
	13°50'15.7	2'46.30"			Moderate	73.4	0.5	7.5	4.6	0.2	0.0	0.2	0.2	0.6	0.0	0.0	
SS32B	5"N	W	Lake Placid: rock sample	Dacite?	Al loss	3	1	5	5	0	1	4	7	1	6	02	331
		61°															
	13°50'15.1	2'45.70"			Moderate	77.6	0.6	7.5	0.7	0.0	<0.	0.1	0.4	0.7	0.0	<0.	
SS31A	8"N	W	Gabriel's crater, at Fizzy Pool: rock sample	Dacite	Al loss	8	0	0	5	7	01	0	5	4	6	002	747
		61°															
	13°50'16.1	2'47.47"			Major Al	84.9	0.8	4.4	0.2	<0.	<0.	<0.	0.1	0.4	0.0	<0.	
SS34	0"N	W	Witches Cauldron: black mud	Dacite	loss	1	1	7	1	01	01	01	8	8	3	002	296
SS32A		61°	Lake Placid: rock sample	Dacite	Major Al	89.3	0.6	2.7	0.5	0.0	<0.	0.0	0.1	0.3	0.0	<0.	846

	13°50'15.7	2'46.30"			loss	6	2	5	2	3	01	9	6	0	3	002	
	5"N	W															
		61°															
	13°50'20.0	2'47.35"			Major Al	91.3	0.7	1.2	0.4	0.0	<0.	0.0	0.1	0.0	0.0	0.0	
SS35	0"N	W	Witches Cauldron: rock sample	Dacite	loss	9	4	9	2	3	01	6	2	2	3	02	715
		61°															
	13°50'19.8	2'48.12"			Extreme Al	94.0	0.7	0.3	0.2	<0.	<0.	0.0	0.0	0.0	0.0	<0.	
SS40	0"N	W	Whitish rock with porphyritic texture	Dacite	loss	3	4	9	2	01	01	9	2	1	2	002	578
		61°															
	13°50'18.2	2'48.50"			Extreme Al	28.3	0.2	0.2	0.2	<0.	<0.	<0.	<0.	0.0	<0.	<0.	
SS39	5"N	W	Tim's Pool flank: rock sample	Dacite	loss	2	6	4	1	01	01	01	01	2	01	002	242
		61°															
	13°50'16.8	2'47.40"			Extreme Al	36.1	0.5	0.1	1.7	<0.	<0.	0.0	<0.	<0.	<0.	<0.	
SS36	0"N	W	Top of Sulphur Slope	Dacite	loss	5	1	3	2	01	01	1	01	01	01	002	313
		61°															
	13°50'21.3	2'46.60"				50.2	0.4	20.	0.9	0.0	<0.	0.1	1.8	1.2	0.1	0.0	
SS14A	0"N	W	Above old geothermal borehole	Dacite	Al gain	5	2	62	6	8	01	4	0	7	1	06	333
		61°															
	13°50'10.6	2'37.50"				53.5	0.3	19.	1.3	0.0	<0.	0.2	1.1	1.8	0.4	0.0	124
SS48	8"N	W	Bedded volcanoclastic	Dacite	Al gain	6	9	27	8	4	01	0	0	2	8	09	2
		61°															
	13°50'25.3	2'49.56"	80 m downstream from tourist pool: very			45.3	0.3	20.	0.3	0.0	<0.	0.1	1.5	2.3	0.1	0.0	
SS26	0"N	W	altered	Dacite	Al gain	1	6	64	1	2	01	1	7	2	6	06	374

		61°															
	13°50'27.6	2°51.72"	150 m downstream from tourist pool: very			45.7	0.3	20.	0.7	0.0	<0.	0.0	0.9	3.6	0.1	0.0	
SS22	0"N	W	altered	Dacite	Al gain	2	4	53	1	1	01	6	8	6	7	06	861
		61°															
	13°50'20.3	2°46.28"				62.7	0.2	18.	1.3	0.0	<0.	0.1	0.4	0.8	0.3	0.0	
SS15	0"N	W	Pseudobreccia, domainal alteration	Dacite	Al gain	7	6	21	9	1	01	8	9	8	4	06	509
		61°															
	13°50'20.1	2°48.10"			Major Al	23.2	0.1	24.	7.1	0.1	0.0	4.8	1.1	0.8	0.2	0.0	
SS41	0"N	W	Very altered volcanic, putty-like	Dacite	gain	5	6	42	6	0	1	5	9	5	3	03	165
		61°															
	13°50'19.9	2°45.70"	Whitish soft "maxtrix" of pseudobreccia		Major Al	39.3	0.1	34.	0.7	0.0	<0.	0.1	1.2	0.6	0.3	0.0	
SS17B	0"N	W	below old geothermal borehole	Dacite	gain	5	9	38	3	4	01	6	2	3	2	07	829

Notes: Second and third rows in table give analytical methods and detection limits,

respectively

LF200: lithium borate fusion of sample powder (>5 g) followed by ICP-ES (majors elements) and ICP-MS (trace elements)

AQ200: Sample splits of 0.5 g are leached in hot modified aqua regia, then analysed by ICP-ES or ICP-MS

TC003: Total C and S by

Leco furnace

Table 1 cont.

LO	TO		TO																																					
	Su	T/	T/																																					
I	m	C	S	Cu	Pb	Zn	Au	Ag	As	Bi	Sb	Tl	Se	Cd	Hg	Ni	Sc	V	Ni	Co	Rb	Sr	Cs	Sn	W	Mo	Ga	U	Be											
				mg	mg	µg/	µg/	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg										
%	%	%	%	/kg	/kg	kg	kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg											
LF		TC	TC	AQ	AQ	AQ	AQ	AQ	AQ	AQ	AQ	AQ	AQ	AQ	AQ	LF	LF	LF	AQ	LF	LF	LF	LF	LF	LF	LF	AQ	LF	LF	LF										
20	LF2	00	00	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20										
0	00	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0										
0.	0.0	0.0	0.0													0.0																								
1	1	2	2	0.1	0.1	1	0.5	0.1	0.5	0.1	0.1	0.1	0.5	0.1	1	20	1	8	0.1	0.2	0	1	0.1	1	0.5	0.1	0.5	0.1	1	1										
3.	99.	0.0	<0.													<0.	<0.			<0.	<0.	<0.	0.0	<2													28			16.
3	91	2	02	8.0	1.7	33	5	1	5.9	1	0.2	1	5	1	6	0	8	37	1.5	4.3	45	1	0.6	1	0.6	1.5	6	3.7	3											
0.	99.	<0.	<0.													<0.	<0.			<0.	<0.	0.0	<2													30			15.	
2	90	02	02	3.3	1.5	19	5	1	0.5	1	0.2	0.1	5	1	5	0	8	25	1.8	5.5	63	2	1.9	1	0.9	0.3	3	2.5	2											
0.	99.	<0.	<0.													<0.	<0.			<0.	<0.	<0.	<2													30			15.	
4	90	02	02	6.0	1.4	16	5	1	2.1	1	0.1	1	5	1	01	0	10	45	1.7	6.0	65	0	2.8	1	0.8	0.3	0	2.9	<1											
2.	99.	0.0	<0.													<0.	<0.			<0.	<0.	<0.	<2													31			16.	
0	91	4	02	4.2	1.3	16	5	1	1.6	1	1	0.2	5	1	01	0	6	16	1.1	4.4	71	3	3.7	1	1.0	0.3	1	3.1	2											
1.	99.	<0.	0.0													<0.	<0.			<0.	<0.	0.0	<2													30			17.	
7	90	02	7	5.8	3.8	13	5	1	4.0	0.4	1	0.2	5	1	2	0	8	33	0.9	5.8	56	8	3.3	2	1.2	0.5	2	2.8	2											
1.	99.	<0.	<0.	3.7	1.0	8	<0.	<0.	1.5	<0.	<0.	<0.	<0.	<0.	<0.	<2	8	31	0.8	4.9	67	30	3.9	1	0.9	0.2	17.	2.6	3											

0	90	02	02				5	1		1	1	1	5	1	01	0					5						2		
1.	99.	0.0	<0.				<0.	<0.		<0.	<0.		<0.	<0.	0.0	<2					29						17.		
2	90	2	02	2.7	1.7	11	5	1	4.7	1	1	0.1	5	1	1	0	7	30	0.8	4.7	66	0	3.8	2	0.9	0.3	3	2.8	1
1.	99.	<0.	<0.				<0.	<0.		<0.	<0.		<0.	<0.	0.0	<2					29						17.		
3	90	02	02	2.4	3.0	9	5	1	6.1	1	1	0.1	5	1	3	0	7	28	0.8	5.3	64	3	3.4	2	0.9	0.3	7	2.6	<1
3.	99.	0.0	0.1				<0.	<0.		<0.			<0.	<0.	0.2	<2					30						17.		
4	90	7	3	6.2	1.8	21	5	1	9.2	1	0.2	0.2	5	1	1	0	9	42	1.4	5.9	65	9	1.9	1	0.7	1.2	1	2.6	<1
1.	99.	<0.	0.0				<0.	<0.		<0.	<0.	<0.	<0.	<0.	0.0	<2					30						16.		
1	90	02	5	4.3	1.2	10	5	1	1.8	1	1	1	5	1	2	0	8	32	0.9	5.5	69	0	3.8	2	0.8	0.2	4	2.8	<1
2.	99.	0.0	0.0					<0.		<0.		<0.	<0.	<0.	0.1	<2					27						15.		
1	90	5	2	5.8	1.5	21	0.5	1	1.7	1	0.2	1	5	1	0	0	10	38	1.5	6.3	60	5	2.0	1	1.1	0.3	8	2.5	1
2.	99.	<0.	0.0	11.			<0.	<0.		<0.		<0.	<0.	<0.	0.2	<2					28						15.		
1	89	02	6	7	2.5	25	5	1	1.2	1	0.1	1	5	1	8	0	11	75	2.5	6.9	62	9	2.0	1	0.7	0.8	5	2.2	2
3.	99.	<0.	0.0				<0.	<0.		<0.	<0.	<0.	<0.	<0.	0.4	<2					28						15.		
0	90	02	2	9.2	1.8	19	5	1	3.0	1	0.1	1	5	1	8	0	12	64	2.0	7.7	41	1	3.7	1	0.7	0.3	2	2.6	2
5.	99.	0.0	0.4				<0.	<0.		<0.		<0.	<0.	<0.	0.1	<2					23						14.		
7	90	3	1	6.1	2.0	18	5	1	2.3	1	0.1	1	5	1	0	0	12	62	1.4	7.4	47	8	1.5	<1	0.7	0.2	9	2.0	2
12	99.	0.1	1.3				<0.	<0.		<0.	<0.		<0.	<0.	0.5	<2					36						16.		
.6	91	9	2	2.3	7.0	2	5	1	1.1	1	1	0.2	5	1	6	0	13	65	0.2	0.3	60	6	3.1	1	0.6	0.2	6	2.7	<1
24	99.	1.0	6.8	18.			16.			<0.			28.		17.	<2					15						12.		
.2	93	7	7	2	5.7	84	9	0.1	1.8	1	0.5	0.4	7	0.2	51	0	10	49	3.0	8.1	30	8	1.9	<1	0.7	0.8	3	2.2	<1
24	99.	0.0	6.8				<0.	<0.		<0.			<0.	<0.	3.1	<2					63						24.		
.4	90	5	5	2.6	2.0	2	5	1	4.7	1	0.4	0.1	5	1	5	0	12	67	0.5	0.4	31	8	1.7	1	0.7	1.6	7	2.4	<1

10	99.	0.1	0.2	11.	20.			<0.	24.				<0.	<0.	0.5	<2					10					15.			
.6	95	1	1	5	2	8	1.4	1	1	0.4	0.3	0.5	5	1	1	0	14	55	0.3	1.1	40	5	2.3	2	1.0	1.1	8	2.6	<1
4.	99.	0.1	0.8	10.				<0.	<0.						3.2	<2					22						13.		
1	92	7	8	9	5.4	60	5	1	2.6	1	0.1	0.2	1.3	0.1	7	0	8	40	2.4	5.4	44	6	3.4	1	0.9	0.5	1	2.0	1
6.	99.	0.0	1.1					<0.		<0.			<0.	<0.	2.5	<2					41						17.		
5	91	5	7	5.9	2.1	7	0.7	1	4.5	1	0.1	0.2	5	1	7	0	8	36	0.6	2.0	65	9	2.6	2	0.9	0.4	4	2.8	1
2.	99.	0.1	0.0					<0.	<0.				<0.	<0.	0.6	<2					23						12.		
0	91	0	9	8.4	4.4	36	5	1	3.7	1	0.1	0.1	5	1	4	0	9	41	1.9	6.9	51	3	4.1	1	0.6	0.5	5	2.1	1
22	99.	0.0	6.3		12.			<0.	<0.	<0.	<0.	<0.		<0.	9.2	<2		12				41			<0.		56.		
.8	92	2	3	2.0	9	2	5	1	5	1	1	1	5.1	1	4	0	5	6	0.3	0.2	10	2	0.5	1	5	0.4	4	1.9	<1
36	99.	0.1	22.					<0.					<0.	<0.	2.6	<2					28								
.9	94	1	42	3.7	9.0	3	1.4	1	4.9	0.1	0.2	1	5	1	3	0	8	42	0.3	0.8	28	9	4.2	1	0.8	0.6	8.2	2.0	1
7.	99.	0.0	0.0	38.	10.			<0.					<0.	<0.	0.0	<2					12						15.		
6	92	5	2	4	3	60	2.2	1	2.6	0.2	0.5	0.5	5	1	9	0	11	61	4.4	6.5	63	6	6.4	2	0.9	0.2	0	3.7	1
23	99.	0.0	6.3					<0.		<0.			<0.	20.	<0.	4.0	<2					47					22.		
.1	91	5	9	2.2	5.4	<1	5	0.1	3.9	1	0.3	1	8	1	9	0	10	75	0.4	0.7	31	2	0.7	1	0.9	0.5	8	1.1	<1
22	99.	0.0	5.8					<0.	<0.		<0.	<0.	29.	<0.	0.9	<2		15		<0.		36					33.		
.0	92	2	5	4.2	2.6	3	5	1	1.8	1	1	1	3	1	0	0	8	0	0.2	2	23	3	0.9	<1	1.3	0.4	0	1.2	<1
20	99.	0.0	5.2		10.			<0.	<0.				<0.		<0.	1.7	<2					36					26.		
.6	93	3	4	3.2	9	3	5	1	1.2	1	0.2	1	5.1	1	2	0	10	76	0.7	1.2	11	5	0.4	<1	3.9	0.3	1	1.8	<1
19	99.	0.1	4.3	17.				<0.					<0.	<0.	8.2	<2		11				13					26.		
.7	80	2	3	6	7.7	4	6.3	1	8.4	0.2	0.3	1	5	1	6	0	15	1	0.4	0.5	15	62	1.0	2	1.2	0.4	7	1.6	<1
8.	99.	0.0	1.7	20.	3.3	58	<0.	<0.	2.5	<0.	<0.	0.3	<0.	<0.	0.5	<2	16	63	2.5	10.	50	16	3.0	<1	0.8	0.4	14.	2.3	1

6	92	9	9	7			5	1		1	1		5	1	0	0			0		2					4			
4.	99.	0.1	0.0				<0.	<0.	<0.	<0.	<0.	<0.			0.1	<2					28					16.			
8	89	8	5	7.6	3.1	74	5	1	5	1	1	1	5	0.1	3	0	13	63	3.1	7.5	67	0	3.5	<1	0.8	0.3	9	2.3	2
6.	99.	0.0	<0.	46.				<0.	15.				<0.		0.0	<2		10		11.	24			<0.		15.			
4	88	4	02	2	5.5	77	2.1	1	2	0.4	0.2	0.2	5	0.2	4	0	16	4	9.1	8	35	4	2.9	2	5	0.5	0	1.9	<1
3.	99.	0.0	<0.	60.				<0.		<0.			<0.	<0.	<0.	<2		11		12.	26					17.			
3	88	3	02	3	2.6	38	1.7	1	2.8	1	0.1	0.1	5	1	01	0	17	5	4.6	5	47	0	3.1	1	0.5	0.3	1	2.3	<1
43	99.	12.	<0.				<0.	<0.		<0.	<0.	<0.	<0.	<0.	<0.	<2					24			<0.	<0.	<0.	<0.		
.9	71	36	02	1.6	0.3	2	5	1	7.2	1	1	1	5	1	01	0	<1	<8	0.6	0.7	1	34	0.2	<1	5	1	5	1	<1
10	99.	0.1	0.6				<0.			<0.			<0.	<0.	1.0	<2										16.			
.8	96	2	0	6.7	1.8	7	5	0.2	8.9	1	0.1	0.1	5	1	1	0	10	60	0.6	1.6	14	24	0.5	1	1.1	0.2	2	3.6	<1
7.	99.	<0.	1.0				<0.	<0.		<0.	<0.	<0.	<0.	<0.	0.2	<2					24					19.			
2	91	02	9	3.7	4.6	9	5	1	2.1	1	1	1	5	1	7	0	8	50	1.1	4.8	45	3	3.1	1	0.7	0.3	0	2.2	<1
15	99.	0.4	6.1	10.			<0.	<0.		<0.			30.		24.	<2					12					11.			
.8	96	7	0	1	6.1	38	5	1	6.9	1	0.2	0.6	8	0.1	38	0	7	34	2.6	5.9	14	7	0.8	<1	0.9	0.4	4	2.6	<1
11	99.	0.1	4.6					<0.		<0.			26.	<0.	11.	<2					14								
.4	95	7	9	7.0	4.2	23	0.6	1	0.6	1	0.4	0.3	6	1	83	0	7	38	2.6	6.0	27	0	2.2	1	0.8	0.7	9.7	2.2	<1
11	99.	0.1	6.2	10.				<0.		<0.			32.		12.	<2					15					10.			
.5	93	6	4	5	5.5	53	1.1	1	3.6	1	0.3	0.4	6	0.1	70	0	7	38	4.3	8.6	24	9	2.3	1	0.6	1.5	5	2.1	<1
12	99.	0.1	7.1	10.				<0.		<0.			44.		33.	<2					14					10.			
.4	94	7	2	5	6.6	18	1.5	1	9.8	1	0.3	0.4	1	0.1	83	0	4	43	3.0	5.9	22	4	1.6	1	0.9	0.5	2	2.6	<1
11	99.	0.1	3.3	3.2	8.7	2	<0.	<0.	3.6	<0.	0.2	<0.	21.	<0.	31.	<2	3	35	1.0	0.4	9	18	0.5	2	1.6	0.6	9.4	2.2	<1

[illegible]

.6	86	3	0					5	1	1								1	8	0					0					5	1							
15	99.	0.0	2.8									<0.	<0.	0.6	<2					10				<0.				19.										
.3	86	7	9	4.9	8.6	3	1.6	0.1	4.2	0.2	0.2	0.5	5	1	3	0	5	45	0.3	0.6	7	44	0.5	<1	5	0.3	3	1.5	<1									
37	99.	0.0	15.	22.					<0.					<0.					1.2	<2					15.					52	<0.				10.			
.7	90	5	37	0	2.4	18	5	0.1	7.4	1	0.4	0.7	6.9	0.1	3	0	10	82	4.0	8	55	8	0.4	<1	5	0.6	5	1.0	<1									
22	99.	0.0	3.8					<0.	<0.					<0.	<0.	0.3	<2					10					76	<0.										
.8	88	7	5	3.3	4.6	5	5	1	2.9	1	1	0.1	5	1	3	0	12	0	0.4	0.7	9	0	1	<1	3.1	0.2	8.0	2.1	<1									

Table 1 cont.

																				Al2O		Zr/	Zr		N	Nb	Th	Th	(La/
																				3/TiO	Zr/A	TiO	/	Zr/	b/	/T	/Z	/Y	Yb)
Hf	Th	Ta	Nb	Y	Zr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	2	I2O3	2	Y	Nb	Y	h	r	b	n
mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg									
/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg									
LF	LF	LF	LF	LF	LF	LF	LF	LF	LF	LF	LF	LF	LF	LF	LF	LF	LF	LF	LF	LF									
20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20									
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0									
								0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0									
0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	2	0	5	2	5	1	5	2	3	1	5	1										
				15.	10	22.	44.	4.9	18.	3.3	0.9	3.0	0.4	2.8	0.5	1.5	0.2	1.3	0.2				6.	20.	0.		0.		
2.9	7.8	0.4	5.3	9	7.2	9	8	5	20	3	0	0	4	6	0	7	1	7	3	42.0	6.2	261	7	2	3	0.7	07	5.7	11.4
				14.	12	20.	39.	4.2	15.	2.6	0.7	2.6	0.3	2.3	0.4	1.4	0.2	1.5	0.2				8.	21.	0.		0.		
3.0	7.4	0.5	5.5	2	0.7	6	2	5	10	1	3	1	9	9	7	6	2	0	5	40.9	7.0	287	5	9	4	0.7	06	4.9	9.3
				13.	10	22.	43.	4.5	16.	2.7	0.8	2.5	0.3	2.3	0.4	1.4	0.2	1.2	0.2				7.	21.	0.		0.		
2.8	7.9	0.4	4.8	6	3.3	5	5	6	50	0	4	5	9	9	5	5	0	7	1	40.9	6.0	246	6	5	4	0.6	08	6.2	12.0
				14.	12	22.	43.	4.6	17.	2.8	0.8	2.7	0.4	2.3	0.4	1.4	0.1	1.3	0.2				8.	21.	0.		0.		
3.4	7.8	0.5	5.7	7	0.1	9	9	3	30	8	5	3	1	6	7	6	9	2	2	40.8	7.2	293	2	1	4	0.7	06	5.9	11.8
				13.	12	21.	44.	4.3	15.	2.9	0.9	2.5	0.3	2.3	0.4	1.3	0.1	1.2	0.2				9.	19.	0.		0.		
3.3	8.6	0.5	6.2	2	1.4	6	2	3	90	2	1	3	8	9	4	2	9	9	2	40.1	6.7	270	2	6	5	0.7	07	6.7	11.4
3.1	7.7	0.5	5.8	14.	11	22.	43.	4.7	16.	2.9	0.8	2.8	0.4	2.4	0.4	1.4	0.2	1.2	0.2	40.0	6.6	264	7.	19.	0.	0.8	0.	6.2	12.4

																						1										
					68.	25.	40.	2.9	7.4	1.0	0.1	0.7	0.1	0.6	0.1	0.4	0.0	0.4	0.0						5.	22.	0.			0.	13.	
1.8	5.8	0.3	3.0	4.5	8	4	1	9	0	1	9	3	2	9	4	5	6	4	8	60.4	3.4	202	3	9	7	0.5	08	2	39.2			
																						1										
					60.	38.	61.	5.3	14.	2.4	0.8	3.5	0.5	1.9	0.2	0.3	0.0	0.2	0.0						5.	27.	0.			0.	20.	
1.6	5.7	0.2	2.2	3.9	9	8	2	6	50	7	2	9	0	6	1	8	4	8	5	70.0	3.3	234	6	7	6	0.4	09	4	94.1			
					35.	20.	40.	5.2	21.	3.6	1.3	2.5	0.3	1.5	0.3	0.7	0.1	0.7	0.1						4.	27.	0.			0.		
1.0	3.9	0.1	1.3	7.6	1	2	2	1	80	5	4	0	2	3	1	1	0	2	0	152.6	1.4	219	6	0	2	0.3	11	5.4	19.1			
																						3										
					40.	27.	66.	7.0	19.	2.2	0.6	1.2	0.1	0.3	0.0	0.1	0.0	0.1	0.0						3.	21.	1.			0.	60.	172.
1.1	6.6	0.1	1.9	1.2	2	9	5	2	70	8	3	5	1	8	4	3	2	1	2	180.9	1.2	212	5	2	6	0.3	16	0	3			

Table 2

Sample no.	SS17B	SS31A	SS31B	SS34	SS36	SS37	SS38	SS42
Primary rock (based on lithochemical data)	Dacite	Dacite	Dacite	Dacite	Dacite	Dacite II	Dacite	Dacite I
Al mobility (based on lithochemical data)	Al +++	Al - -	Al -	Al - - -	Al - - -	None	Al -	None

Table 2a. Modal mineralogy determined by XRD								
Kaolinite	56.3	nd	trace	nd	nd	nd	nd	13.6
Smectite	nd	nd	61.1	nd	nd	nd	53.3	nd
Quartz	6.1	25.9	14.5	6.2	20.8	21.6	16.2	18.2
Cristobalite	2.4	5.9	6.9	nd	nd	nd	6.2	nd
Plagioclase	nd	nd	nd	nd	nd	39.0	16.9	nd
K-feldspar	nd	nd	nd	nd	nd	nd	nd	10.0
Muscovite	nd	nd	nd	nd	nd	7.3	nd	nd
Cummingtonite-Grunerite	nd	nd	nd	nd	nd	7.6	nd	nd
Ca amphibole	nd	nd	nd	nd	nd	1.3	nd	nd
Clinopyroxene	nd	nd	nd	nd	nd	1.0	nd	nd
Natroalunite	19.4	4.1	1.7	2.2	nd	nd	nd	3.0
Alunite	3.0	3.0	5.3	6.6	nd	nd	4.0	3.3
Sulfur	nd	nd	8.0	nd	60.6	nd	nd	nd
Pyrite	nd	nd	2.4	nd	0.7	nd	3.4	nd
Amorphous	12.7	61.1	nd	85.0	17.9	22.2	nd	51.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 2b. Modal mineralogy determined by MLA								
Sulphur	0.00	0.14	0.06	0.01	56.90	0.01	0.57	0.00
Pyrite	0.02	0.09	2.36	0.05	1.77	0.29	3.11	0.02
Jarosite	0.01	0.00	0.00	0.00	0.00	0.00	0.04	0.08
Fe sulphate	1.10	0.31	2.07	0.32	0.16	0.49	1.74	0.64
Alunite-Fe sulphate	0.00	0.00	0.05	0.00	0.00	0.02	0.24	0.21
Alunite-Natroalunite	3.49	1.30	1.14	2.69	0.00	0.12	1.83	0.91
Alunite-Natroalunite with silica hydroxide	3.70	7.93	3.19	5.04	0.02	0.23	1.92	1.70
Quartz	1.63	26.62	11.00	7.18	16.00	12.78	19.10	11.72
Silica oxyde/hydroxide	1.62	18.13	12.78	21.76	9.93	8.84	17.41	8.10
Silica hydroxide with C	0.04	3.97	0.86	25.30	0.35	1.11	2.21	0.52
Al-bearing silica hydroxide with C, S and Cl	2.49	20.79	22.97	28.31	11.71	5.94	10.65	2.26

Table 3

Water sample location	Date	pH	Temperature (°C)	SO ₄ (mg/kg)	Cl (mg/kg)	HCO ₃ (mg/kg)	NO ₃ (mg/kg)	F (mg/kg)	Br (mg/kg)	Fe (mg/kg)	Mg (mg/kg)	Ca (mg/kg)	Na (mg/kg)	K (mg/kg)	TDS (mg/kg)	Al (mg/kg)	Mn (mg/kg)	Zn (ug/kg)	As (ug/kg)	Cd (ug/kg)	Pb (ug/kg)	δ18O water (VSMOW)	δD water (VSMOW)
(see Figure 4 map)																							
Black Water	25/03/				389	435.			0.0	10.	62.	174	240	10.	254				≤0.				
Pool *	2014	7	37.2	46.1	.2	8	--	5.7	6	7	2	.6	.9	4	6	3.0	0.0	≤3	2	2.6	1.1		
Black Water	22/07/				390	197	3.3	≤0.	0.1	79.	410	102	133	225	359								
Pool	2014	7	45.4	64.6	.4	4.0	9	01	0	6	.4	.9	.6	.1	6	2.1	0.9	≤3	4.6	3.6	7.3		
Black Water	19/01/			540.	186	0.00	0.8		0.0	73.	38.	85.	104	14.	136					≤0.			
Pool	2017	7	41.5	7	.1	1	0	0.1	7	4	8	8	.5	8	3	3.2	1.9	≤3	1.9	2	5.3	-0.43	-6.2
Clear Water	25/03/				32.	567.	7.7	10.	0.3		11.	56.	158	0.0					≤0.				
Pool *	2014	7	28.1	22.2	2	5	9	2	3	8.2	5	6	.6	1	434	0.5	0.0	6	2	2.6	1.8		
Clear Water	21/07/			109.	50.	978.	0.6	≤0.	0.0	79.	108	96.	138	126	105								
Pool *	2014	7	27.0	6	7	8	2	01	5	6	.3	4	.7	.8	4	0.0	0.3	≤3	3.1	3.0	6.9		
Clear water	19/01/				18.	159.	0.7		0.0		15.	43.	33.							≤0.			
Pool	2017	7	32.7	83.2	6	4	8	0.1	7	8.8	1	9	0	7.7	496	2.3	0.6	26	0.8	2	6.2	-2.57	-8.5
	25/03/			227.	49.	199.	≤0	15.	0.1	10.	11.	42.	145	16.									
Fizzy Pool *	2014	6	45.8	6	3	6	02	1	3	0	5	5	.6	5	539	5.7	0.0	37	8.3	2.9	2.5		

	21/07/			351.	57.	221.	1.4	≤0.	0.0	88.	40.	47.	100	76.									
Fizzy Pool *	2014	7	79.4	6	5	4	7	01	3	5	7	7	.7	6	766	9.2	0.1	≤3	7.0	4.2	5.9		
	18/01/			131	11.	0.00	1.0		0.0	117	70.	33.	210	95.	152	92.				≤0.			
Fizzy pool ‡	2017	6	87.4	2.8	1	1	2	0.1	2	.1	5	0	.2	3	2	1	0.3	≤3	4.6	2	0.7	10.41	7.3
French Wall	18/01/			273.	19.	0.00	0.1		0.0		14.	53.	29.		131			≤0.	≤0.				
bubbler ‡	2017	6	47.8	2	6	1	2	0.2	6	5.0	2	2	3	5.3	402	.1	1.1	197	2	2	8.6	-2.96	-10.5
	25/03/			348.	58.		≤0		0.2			42.	174										
Lake Placid *	2014	7	63.7	5	8	95.7	02	9.8	4	9.2	9.3	7	.4	5.8	850	1.9	0.0	≤3	2.4	2.5	0.9		
	21/07/			547.	87.	162.	1.7	10.	0.5	88.	72.	46.	105	164									
Lake Placid *	2014	7	82.3	7	3	0	8	2	7	5	3	6	.4	.5	945	2.0	0.1	≤3	5.9	4.9	5.5		
	18/01/			701.	18.	0.00	0.5	≤0.	0.1	24.		49.	166	48.	101	367			12.	≤0.			
Lake Placid ‡	2017	7	59.8	3	8	1	3	01	8	4	9.2	2	.5	2	9	.5	0.4	85	4	2	3.8	11.70	11.7
	18/01/			125	71.	149.	0.4		0.2	10.	205	268	46.	24.	209		12.			≤0.			
Painted Pool	2017	7	67.9	8.8	4	0	7	0.2	0	3	.6	.2	0	7	9	3.6	0	52	2.1	2	3.8	14.11	13.9
SS creek	18/01/			524.	58.	0.00	0.0		0.1		25.	128	62.	13.		76.				≤0.			
confluence	2017	7	60.4	0	8	1	3	0.2	0	8.4	9	.5	9	0	823	8	2.7	51	4.3	2	4.3	9.25	8.1
Small green	25/03/			528.	30.		≤0	26.	0.3	10.	14.	87.	177	18.									
gasser *	2014	7	78.6	5	8	84.7	02	4	6	0	2	7	.3	4	894	1.9	0.0	≤3	1.7	2.5	0.9		
Small green	22/07/	7	85.4	100	50.	52.4	0.9	8.4	0.0	79.	145	98.	140	120	165	3.5	0.3	≤3	2.9	3.6	8.4		

± 5 % of the average

‡ Indicates samples with anomalous AI

concentrations

Table 4

Sample no.	Sample type	XRD (most to least abundant)	$\delta^{18}\text{O}$ ‰	δD ‰	$\delta^{34}\text{S}$ ‰	Total S %
SS49	Weakly altered dacite	qtz, plag, alk fspar, amph, biot (thin section)	9.7	-41		
SS17B	Altered volcanic	kaol, natroalun, amorp, qtz, alun, crist	13.4	-42, -48	-5.26	3.62
SS31A	Altered volcanic	qtz, amorph, crist, natro, alun	18.5	-56	-5.94	3.20
SS42	Altered volcanic	amorph, qtz, kaol, alk-fspar, alun, natro	15.1	-63	-5.03, -5.83	1.26
SS31B	Geothermal pool mud	smect, qtz, sulfur, alun-natro, crist, py	20.6, 19.7	-67	-7.79	5.84
SS34	Geothermal pool mud	amorph, alun, qtz, natro			-6.61	2.05
SS38	Geothermal pool mud	smect, plag, qtz, crist, alun, py			-8.34	4.46
SS36	Crumbly S-rich volcanic	sulfur, qtz, amorph, trace py	13.7	-104	-12.87	60.46
SS39	Crumbly S-rich volcanic	(not analysed)	20.8	-99	-15.82	61.61

Table 5

Sample no.	Chemical type	Al mobility	K																							
			Si	Ti	Al2	Fe	M	M	Ca	Na	2	P2	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			O2	O2	O3	O	gO	nO	O	2O	O	O5														
													mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg
			%	%	%		%	%	%	%	%	%	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg	/kg

Precursor**compositions (LOI-****free)**

Average	Dacite I	66.	0.	17.	3.	1.	0.	5.	3.0	1.	0.1	23.	43.		16.											
		08	45	73	98	61	09	29	0	62	0	0	8	4.7	8	3.0	0.9	2.7	0.4	2.5	0.5	1.5	0.2	1.4	0.2	
Average	Dacite II	72.	0.	14.	4.	1.	0.	3.	2.1	1.	0.0	16.	30.		11.											
		29	43	30	17	43	10	83	9	16	7	3	2	3.2	4	2.1	0.7	2.0	0.3	1.9	0.4	1.2	0.2	1.2	0.2	
Average	Dacite III	64.	0.	21.	4.	1.	0.	2.	2.0	1.	0.3	11.	20.													
		90	50	57	58	67	04	85	9	45	1	3	0	2.1	8.0	1.3	0.5	1.3	0.2	1.3	0.3	0.9	0.1	1.0	0.1	
Average	Andesite	63.	0.	18.	5.	2.	0.	5.	2.6	1.	0.1	19.	38.		16.											
		64	67	24	47	06	11	64	6	35	2	4	6	4.4	7	3.4	0.9	3.5	0.5	3.4	0.7	2.0	0.3	1.9	0.3	

Calculated mass**changes (wt %)**

		None	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		demonstra	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
SS12	Dacite I	ble	2.9	01	0.6	5	5	0	2	0.0	0	0	1.3	3.8	0.6	2.6	0.6	0.1	0.4	0.1	0.5	0.1	0.2	0.0	0.1	0.0
		None	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		demonstra	0.	-	0.	0.	0.	0.	0.	0.	0.	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SS49	Dacite I	ble	0.3	02	0.3	2	1	0	2	0.1	1	1	2.1	4.0	0.4	1.4	0.3	0.1	0.1	0.0	0.1	0.0	0.0	0.0	0.1	0.0
		None	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		demonstra	0.	-	0.	0.	0.	0.	0.	0.	0.	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SS20	Dacite I	ble	3.4	00	0.6	3	1	0	9	0.3	1	1	1.0	2.7	0.2	0.9	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0
		None	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		demonstra	0.	-	0.	0.	0.	0.	0.	-	0.	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SS19	Dacite I	ble	1.5	02	0.4	1	3	0	1	0.1	1	2	0.7	1.7	0.1	1.2	0.0	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.0	0.0
		None	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		demonstra	-	0.	-	0.	0.	0.	0.	-	0.	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SS04	Dacite I	ble	4.2	01	0.2	0	0	0	1	0.1	2	2	2.0	0.7	0.5	1.3	0.1	0.0	0.3	0.0	0.2	0.1	0.2	0.0	0.1	0.0
		None	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		demonstra	0.	-	0.	0.	0.	0.	0.	-	0.	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SS06	Dacite I	ble	0.6	00	0.1	1	0	0	5	0.1	1	1	0.5	1.1	0.2	0.6	0.1	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.1	0.0
		None	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		demonstra	0.	-	0.	0.	0.	0.	0.	-	0.	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SS05	Dacite I	ble	1.2	01	0.3	1	1	0	1	0.1	1	3	0.5	2.1	0.0	0.1	0.0	0.0	0.1	0.0	0.2	0.0	0.1	0.0	0.0	0.0
		None	0.	-	0.	0.	0.	0.	0.	-	0.	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SS08	Dacite I	demonstra	2.0	00	0.1	0	0	0	1	0.1	1	0	2.2	2.1	0.4	0.9	0.3	0.0	0.2	0.0	0.1	0.0	0.0	0.0	0.0	0.0

		ble																								
		None		-		-		-		-																
		demonstra	-	0.	-	0.	0.	0.	1.	-	0.	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	
SS27	Dacite I	ble	3.9	01	0.3	6	1	0	1	0.3	0	1	0.7	3.3	0.6	4.0	0.7	0.1	0.7	0.1	0.5	0.1	0.3	0.1	0.3	0.0
		None				-																				
		demonstra		0.	-	0.	0.	0.	0.		0.	0.0														
SS03	Dacite I	ble	0.0	00	0.6	1	0	0	3	0.0	1	1	1.4	1.6	0.3	1.6	0.2	0.0	0.2	0.0	0.0	0.0	0.1	0.0	0.0	0.0
		None				-			-		-	-														
		demonstra	-	0.	-	0.	0.	0.	0.	-	0.	0.0	-	-	-	-	-	-	-		-					
SS47	Dacite I	ble	2.4	01	0.3	1	0	0	4	0.1	1	1	1.6	4.2	0.4	1.7	0.2	0.1	0.2	0.0	0.1	0.0	0.0	0.0	0.1	0.0
		None																								
		demonstra	-	0.		0.	0.	0.	0.		0.	0.0	-	-												
SS50	Dacite I	ble	0.3	03	0.5	6	2	0	0	0.0	0	1	1.9	2.5	0.1	0.9	0.3	0.1	0.3	0.1	0.4	0.1	0.2	0.0	0.3	0.0
		None									-	-														
		demonstra		0.		0.	0.	0.	0.	-	0.	0.0														
SS11	Dacite I	ble	0.6	03	0.3	4	6	0	0	0.1	4	1	1.2	1.0	0.2	0.5	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		None								-	-	-		-												
		demonstra	-	0.		0.	0.	0.	1.	-	0.	0.0	-	10.	-	-	-	-	-		-					
SS24	Dacite I	ble	6.7	03	0.1	3	5	0	6	0.7	3	1	4.1	4	1.2	4.4	0.7	0.1	0.4	0.0	0.2	0.0	0.1	0.0	0.1	0.0
		None				-	-	-	-																	
		demonstra	-	0.		3.	1.	0.	5.	-	0.	0.1		18.		10.		-	-	-	-	-	-	-	-	-
SS42	Dacite I	ble	6.0	01	1.3	1	4	1	0	2.4	1	9	8.7	9	2.7	1	0.5	0.1	0.7	0.1	0.9	0.2	0.5	0.1	0.4	0.1
SS21	Dacite I	None	-	0.	-	0.	-	-	-	-	-	0.0	-	-	-	-	-	-	-	-	-	-	-	0.0	0.0	0.0

		demonstra	8.8	01	0.2	8	1.	0.	4.	2.3	0.	5	8.2	13.	1.5	5.0	0.7	0.2	0.5	0.1	0.4	0.1	0.2			
		ble					1	1	5		8			0												
		None	-			-	-	-	-																	
		demonstra	10.	0.	-	3.	1.	0.	5.	-	1.	0.1				-	-	-	-	-	-	-	-	-	-	
SS28	Dacite I	ble	3	01	0.1	5	6	1	2	1.7	4	0	8.0	9.8	0.3	2.1	1.2	0.5	1.4	0.3	1.7	0.4	1.1	0.2	1.0	0.2
		None				-	-	-	-		-	-	-	-		-										
		demonstra	-	0.	-	2.	1.	0.	4.	-	0.	0.0	10.	23.	-	10.	-	-	-	-	-	-	-	-	-	
SS30	Dacite I	ble	5.3	03	0.2	4	0	1	5	2.2	6	7	7	5	2.7	2	1.8	0.6	1.6	0.2	1.4	0.2	0.6	0.1	0.6	0.1
		None				-	-		-																	
		demonstra	-	0.		0.	0.	0.	0.	-	0.	0.0	-	-	-	-	-		-							
SS37	Dacite II	ble	0.1	00	0.1	1	1	0	2	0.1	0	1	1.2	2.3	0.2	0.6	0.1	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	
		None		-		-	-	-	-																	
		demonstra	-	0.	-	2.	1.	0.	0.		0.	0.0									-	-	-	-	-	
SS2A	Dacite II	ble	9.4	01	0.2	8	0	1	6	0.3	7	5	5.6	9.5	0.7	2.0	0.2	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.1	
		None										-														
		demonstra		0.	-	0.	0.	0.	0.		0.	0.0														
SS29	Dacite II	ble	0.1	00	0.1	1	1	0	2	0.1	0	1	1.1	2.3	0.2	0.6	0.1	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	
		None		-		-	-	-	-																	
		demonstra	17.	0.		3.	1.	0.	3.	-	1.	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	
SS45	Dacite II	ble	1	01	0.6	7	4	1	7	1.7	9	3	0.9	6.8	1.3	5.8	1.5	0.6	1.6	0.2	1.4	0.3	0.8	0.1	0.8	
		None				-	-	-	-																	
		demonstra		0.		3.	1.	0.	3.	-	0.	0.0	10.	15.			-	-	-	-	-	-	-	-	-	
SS2B	Dacite II?	ble	6.9	00	0.2	3	2	1	3	0.5	5	9	8	9	1.0	0.6	0.2	0.4	0.3	0.1	0.5	0.1	0.4	0.1	0.4	

		None	-			-	-	-	-			-														
		demonstra	11.	0.		0.	0.	0.	2.	-	0.	0.0														
SS09	Dacite II	ble	5	03	0.8	4	5	1	6	1.0	2	5	2.5	9.1	1.2	5.6	1.0	0.3	0.7	0.1	0.7	0.1	0.2	0.0	0.1	0.0
		None	-			-	-	-	-																	
		demonstra	17.	0.		2.	1.	0.	3.	-	1.	0.0			-	-	-	-	-	-	-	-	-	-	-	-
SS23	Dacite II	ble	5	04	0.3	6	4	1	8	1.4	7	5	3.8	0.9	0.7	5.1	1.6	0.6	1.6	0.2	1.4	0.3	0.9	0.1	0.9	0.1
		None	-			-	-	-	-					-												
		demonstra	16.	0.	-	3.	1.	0.	3.	-	1.	0.0	-	10.	-	-	-	-	-	-	-	-	-	-	-	-
SS13	Dacite II	ble	4	05	0.4	6	4	1	8	1.8	7	3	2.2	5	1.4	5.8	1.2	0.4	1.3	0.2	1.6	0.3	1.1	0.2	1.1	0.2
		None	-			-	-	-	-																	
		demonstra	14.	0.	-	3.	1.	0.	3.	-	0.	0.0			-	-	-	-	-	-	-	-	-	-	-	-
SS46	Dacite II	ble	1	05	0.7	3	3	1	7	1.4	8	5	6.2	4.9	0.1	2.1	0.7	0.5	0.9	0.1	1.0	0.2	0.6	0.1	0.7	0.1
		None	-			-	-	-	-																	
		demonstra	0.	-	3.	1.	0.	2.	-	0.	0.1	31.	49.							-	-	-	-	-	-	-
SS01	Dacite III	ble	0.6	01	0.3	4	6	0	6	1.1	6	8	4	5	3.6	9.1	1.3	0.1	0.5	0.0	0.3	0.1	0.4	0.1	0.5	0.1
		None	-			-	-	-	-																	
		demonstra	0.	0.	0.	0.	0.	0.		0.	0.0															
SS43	Dacite III	ble	0.0	00	0.0	0	0	0	0	0.0	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		None	-			-	-	-	-																	
		demonstra	-	0.		1.	0.	0.	1.	-	0.	0.0					-	-		-	-	-		-		-
SS44	Andesite	ble	2.0	03	0.9	3	1	0	2	0.2	4	1	2.8	5.7	0.6	1.8	0.0	0.1	0.3	0.0	0.5	0.1	0.4	0.0	0.2	0.0
SS10	Andesite	None	4.9	0.	0.2	0.	-	0.	-	0.1	-	0.0	-	-	-	-	-	0.0	-	0.0	-	0.0	0.0	0.0	0.0	0.0

		demonstra	00		9	0.	0	1.		0.	0	1.3	3.8	0.4	1.3	0.2		0.2		0.3						
		ble					1		0		3															
		None							-		-	-														
		demonstra	-	0.	-	0.	0.	0.	0.		0.	0.0	-	-	-	-										
SS07	Andesite	ble	2.2	03	1.0	5	0	0	3	0.1	1	1	1.5	2.1	0.2	0.5	0.2	0.1	0.5	0.1	0.7	0.1	0.4	0.0	0.3	0.1
			-			-	-	-	-		-	-	-	-		-										
		Minor Al	16.	0.	-	2.	1.	0.	5.	-	1.	0.0	17.	31.	-	10.	-	-	-							
SS17A	Dacite	loss	8	04	6.6	1	5	1	3	2.9	3	7	1	5	3.3	8	1.4	0.4	0.3	0.1	1.5	0.4	1.3	0.2	1.2	0.2
						-	-		-		-	-														
		Minor Al	-	0.	-	1.	0.	0.	3.	-	0.	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SS25	Dacite	loss	6.0	03	6.5	0	4	0	0	1.7	4	2	4.8	9.8	1.2	5.0	0.9	0.4	0.7	0.1	0.8	0.1	0.4	0.1	0.4	0.1
						-	-	-	-		-	-	-	-		-										
		Minor Al	-	0.	-	1.	1.	0.	5.	-	1.	0.0	11.	23.	-	10.	-	-	-	-	-	-	-	-	-	-
SS31B	Dacite	loss	2.5	05	7.3	8	3	1	2	2.7	1	5	6	1	2.6	1	1.7	0.6	1.8	0.3	1.6	0.3	0.9	0.1	0.8	0.1
			-			-	-	-	-		-	-	-	-		-										
		Minor Al	-	0.	-	0.	1.	0.	4.	-	1.	0.0	13.	25.	-	10.	-	-	-	-	-	-	-	-	-	-
SS38	Dacite	loss	2.5	03	8.2	5	2	1	2	2.2	0	4	0	1	2.7	0	1.8	0.6	1.7	0.3	1.4	0.3	0.8	0.1	0.6	0.1
			-	-			-	-	-		-	-	-	-		-										
		Minor Al	13.	0.	-	1.	1.	0.	4.	-	1.	0.0	13.	27.	-	10.	-	-	-	-	-	-	-	-	-	-
SS33	Dacite?	loss	1	06	9.0	2	2	1	1	2.2	2	6	8	4	2.9	5	1.8	0.5	1.8	0.2	1.6	0.3	0.8	0.1	0.6	0.1
			-	-	-	-	-	-	-		-	-	-	-		-										
		Moderate	15.	0.	12.	1.	1.	0.	5.	-	1.	0.0	14.	29.	-	11.	-	-	-	-	-	-	-	-	-	-
SS32B	Dacite?	Al loss	6	10	5	1	5	1	1	2.8	2	6	1	1	3.2	3	2.0	0.7	1.8	0.3	1.7	0.3	0.9	0.1	0.7	0.1

			-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		Moderate	12.	0.	12.	3.	1.	0.	5.	-	1.	0.0	12.	26.	-	12.	-	-	-	-	-	-	-	-	-	-
SS31A	Dacite	Al loss	0	03	5	5	6	1	2	2.7	1	6	8	9	3.1	2	2.4	0.7	2.3	0.3	2.1	0.4	1.2	0.2	1.1	0.2
			-		-	-	-	-	-		-	-	-	-		-										
		Major Al	15.	0.	15.	3.	1.	0.	5.	-	1.	0.0	19.	37.	-	15.	-	-	-	-	-	-	-	-	-	-
SS34	Dacite	loss	4	04	1	9	6	1	3	2.9	3	8	5	4	4.2	9	2.8	0.8	2.4	0.3	2.0	0.4	1.1	0.1	0.9	0.1
			-		-	-	-	-	-		-	-	-	-		-										
		Major Al	-	0.	15.	3.	1.	0.	5.	-	1.	0.0	17.	36.	-	14.	-	-	-	-	-	-	-	-	-	-
SS32A	Dacite	loss	2.9	01	8	6	6	1	2	2.9	4	8	4	6	4.0	6	2.6	0.9	2.4	0.3	2.1	0.4	1.2	0.2	1.0	0.2
			-		-	-	-	-	-		-	-	-	-		-										
		Major Al	-	0.	16.	3.	1.	0.	5.	-	1.	0.0	22.	42.	-	16.	-	-	-	-	-	-	-	-	-	-
SS35	Dacite	loss	3.7	06	9	7	6	1	2	2.9	6	8	2	5	4.6	2	2.9	0.9	2.6	0.4	2.4	0.4	1.3	0.2	1.2	0.2
			-		-	-	-	-	-		-	-	-	-		-										
		Extreme Al	-	0.	17.	3.	1.	0.	5.	-	1.	0.0	21.	39.	-	13.	-	-	-	-	-	-	-	-	-	-
SS40	Dacite	loss	2.5	05	5	8	6	1	2	3.0	6	8	1	4	4.1	6	2.2	0.9	1.9	0.3	1.6	0.3	0.9	0.1	0.7	0.1
			-		-	-	-	-	-		-	-	-	-		-										
		Extreme Al	12.	0.	17.	3.	1.	0.	5.	-	1.	0.0	20.	39.	-	14.	-	-	-	-	-	-	-	-	-	-
SS39	Dacite	loss	6	04	3	6	6	1	3	3.0	6	9	2	1	4.1	1	2.6	0.9	2.3	0.3	2.0	0.4	1.0	0.1	0.8	0.1
			-		-	-	-	-	-		-	-	-	-		-										
		Extreme Al	32.	0.	17.	2.	1.	0.	5.	-	1.	0.0	22.	42.	-	16.	-	-	-	-	-	-	-	-	-	-
SS36	Dacite	loss	4	03	6	5	6	1	3	3.0	6	9	4	6	4.5	2	2.9	0.9	2.6	0.4	2.2	0.4	1.2	0.2	1.0	0.2
			-	0.		-	-	-	-	-	-	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SS14A	Dacite	Al gain	4.5	07	7.6	2.	1.	0.	5.	0.8	0.	4	3.9	10.	1.5	5.8	1.7	0.6	1.9	0.3	1.8	0.3	1.1	0.1	0.9	0.2

							9	5	1	1		1				0										
							-	-	-	-																
			-	0.		2.	1.	0.	5.	-	0.	0.4	29.	37.			-	-	-	-	-	-	-	-	-	-
SS48	Dacite	Al gain	0.4	03	5.9	5	6	1	0	1.6	6	9	6	7	2.9	5.2	0.2	0.3	0.8	0.2	1.4	0.3	1.0	0.1	0.8	0.1
						-	-	-	-																	
			-	0.	11.	3.	1.	0.	5.	-	1.	0.1	23.	34.						-	-	-	-	-	-	-
SS26	Dacite	Al gain	3.0	05	0	6	6	1	1	0.8	6	3	5	2	2.3	6.6	0.8	0.3	0.1	0.1	1.4	0.4	1.2	0.2	1.1	0.2
						-	-	-	-																	
			0.	12.	3.	1.	0.	5.	-	3.	0.1	14.	16.	-	-	-	-	-	-	-	-	-	-	-	-	-
SS22	Dacite	Al gain	2.1	06	9	0	6	1	2	1.5	8	6	9	0	0.2	5.7	1.5	0.6	1.7	0.2	1.5	0.3	0.8	0.1	0.7	0.1
						-	-	-	-																	
			47.	0.	15.	1.	1.	0.	5.	-	0.	0.5	46.	66.								-	-	-	-	-
SS15	Dacite	Al gain	0	02	1	7	6	1	0	2.1	0	2	9	4	5.0	9.4	1.5	0.6	3.7	0.5	1.0	0.1	0.8	0.1	0.9	0.1
						-	-																			
		Major Al	0.	56.	15	1.	0.	9.		1.	0.6	38.	78.	11.	49.											
SS41	Dacite	gain	4.4	04	3	5	3	1	4	0.6	0	0	2	0	1	3	8.1	3.2	4.8	0.6	2.1	0.5	0.7	0.1	0.8	0.1
						-	-	-	-																	
		Major Al	36.	0.	71.	2.	1.	0.	4.		0.	0.7	49.	129	13.	34.				-	-	-	-	-	-	-
SS17B	Dacite	gain	3	05	7	3	5	1	9	0.2	0	4	6	3	6	5	3.0	0.8	0.5	0.1	1.5	0.4	1.1	0.2	1.1	0.2

HIGHLIGHTS

- Geothermal waters of Sulphur Springs are Na/Ca–SO₄ type and are meteoric in origin.
- Volcanic rocks are chemically and mineralogically altered by acid-sulphate waters.
- S-isotopic data imply a magmatic gas source for the S. Many rocks are high in Hg-Se.
- Even in the most altered rocks, Zr and Ti have remained essentially immobile.
- Mass change calculations, however, reveal that Al, P and the REE can be mobilized.

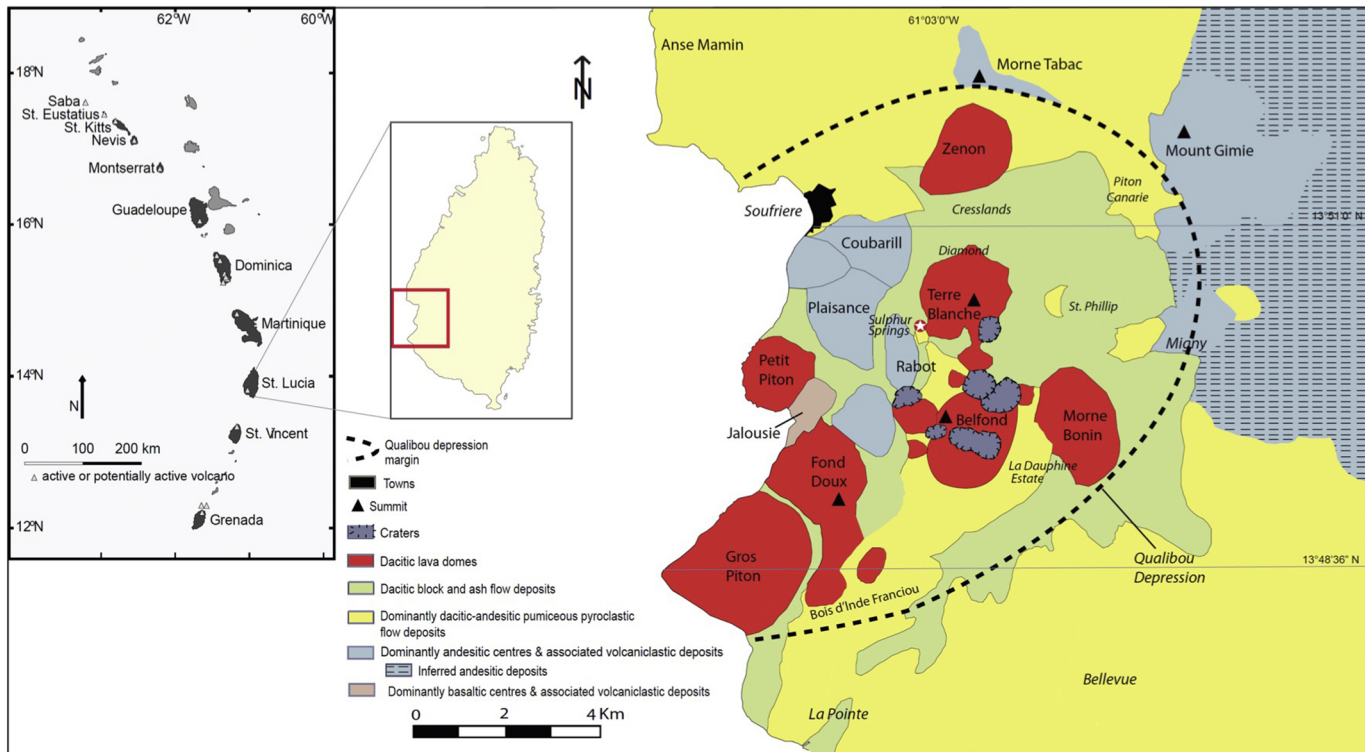


Figure 1

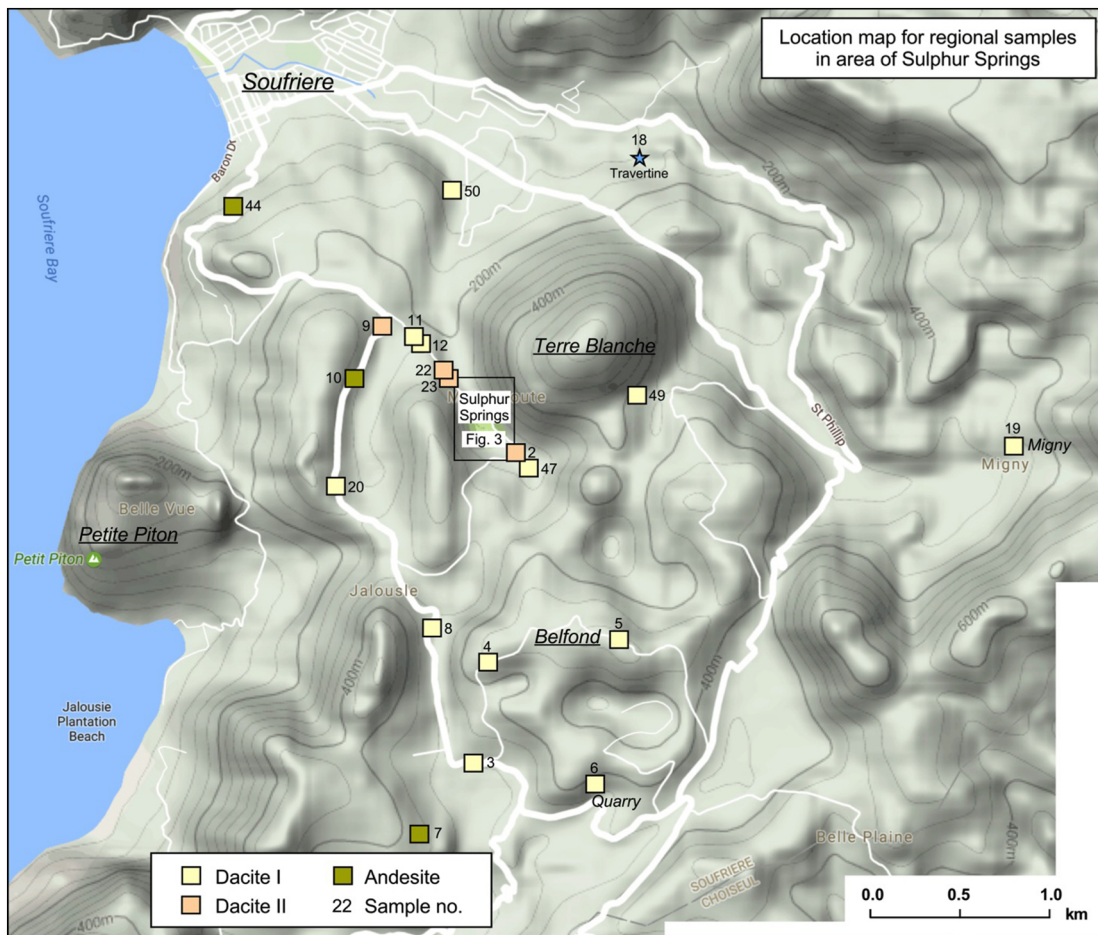


Figure 2

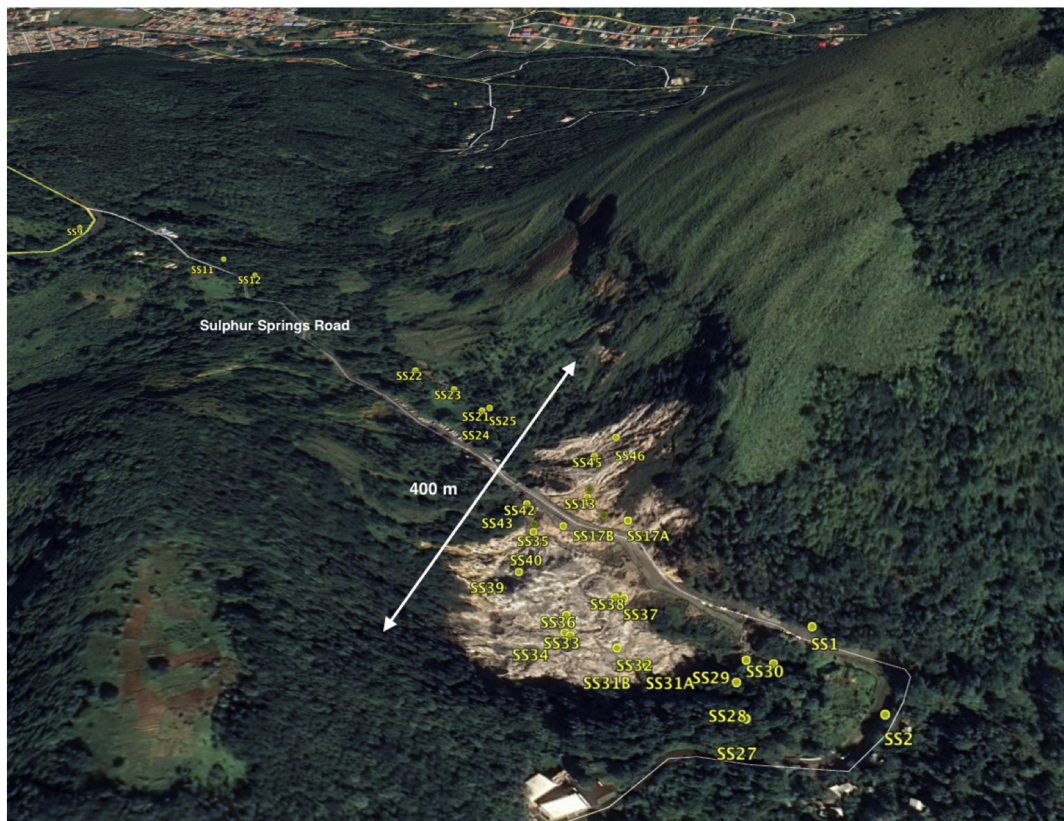


Figure 3

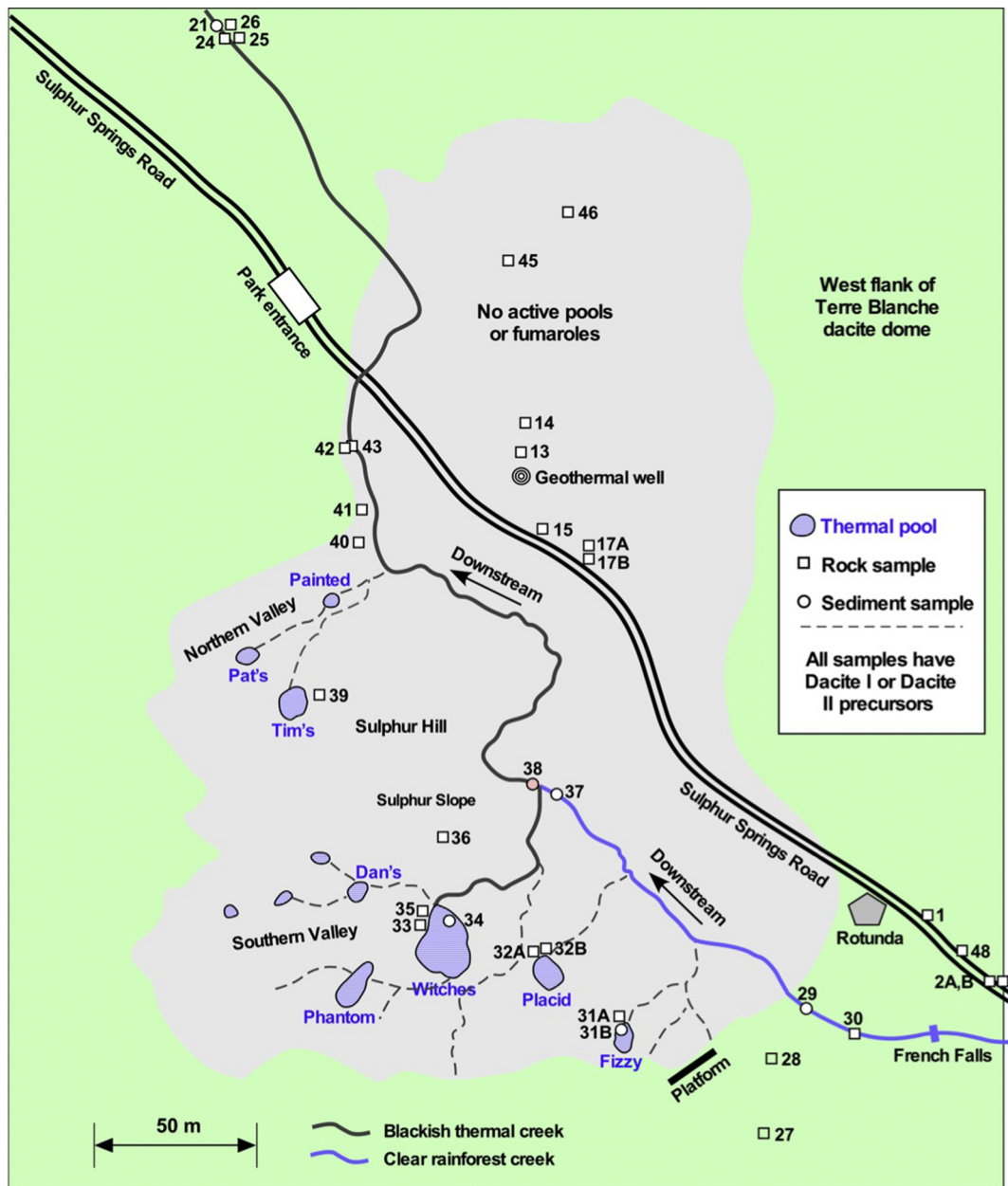


Figure 4



a.



b.



c.



d.



e.



f.

Figure 5



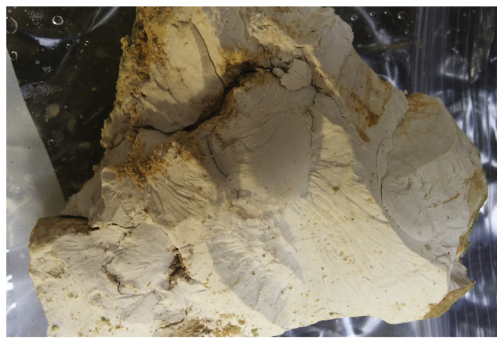
a.



b.



c.



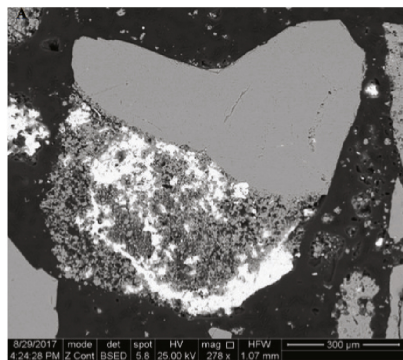
d.



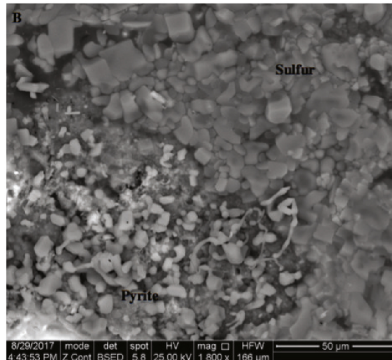
e.



f.



g.



i.

Figure 6

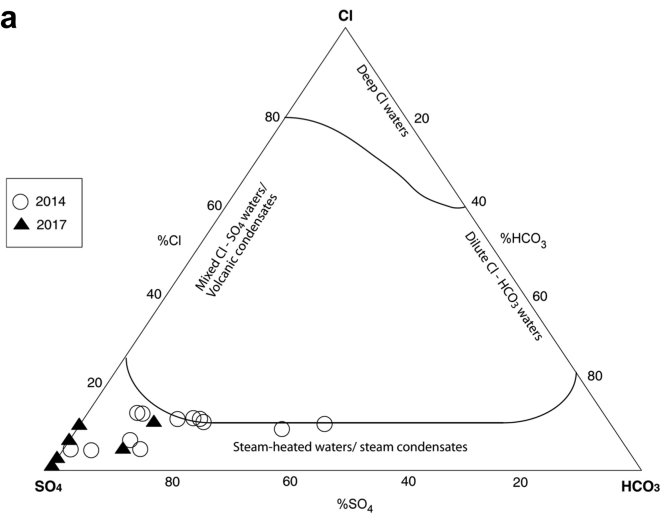
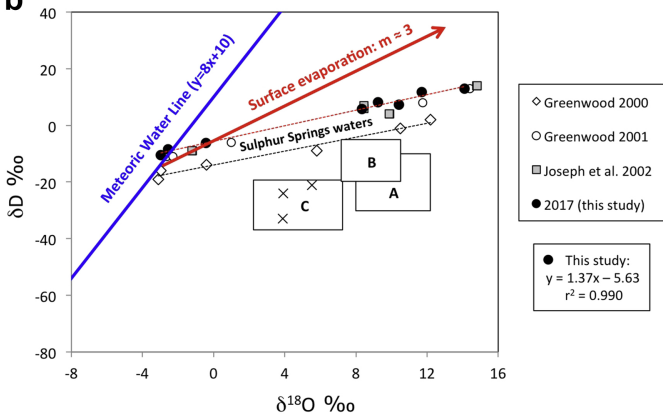
a**b**

Figure 7

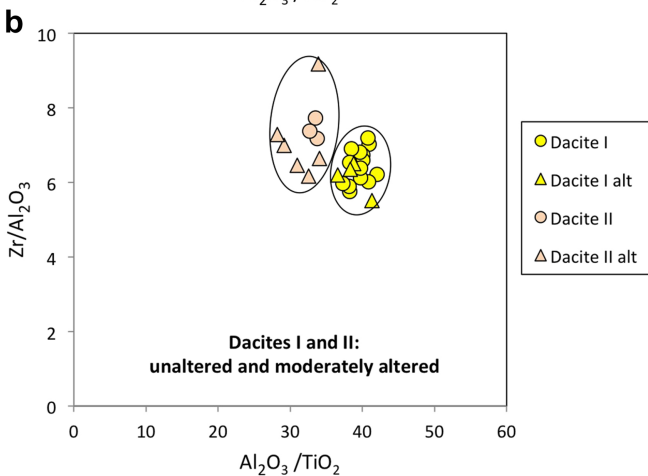
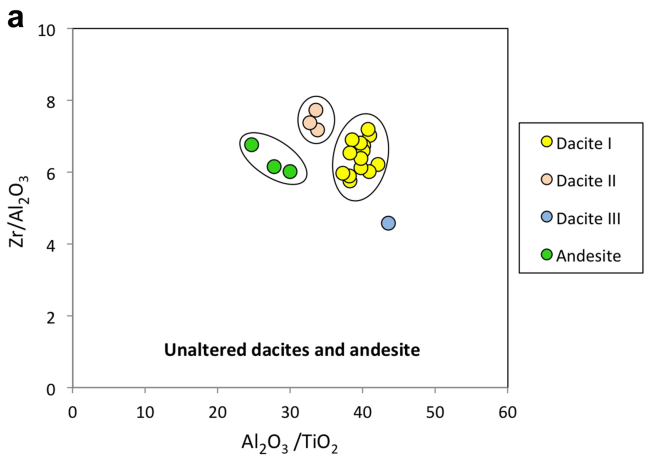


Figure 8

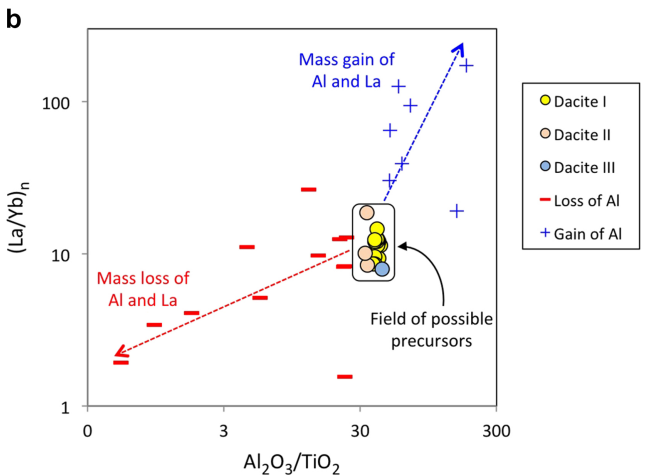
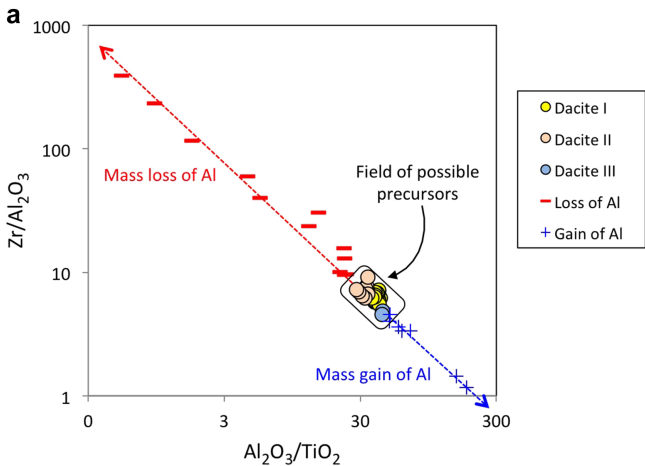


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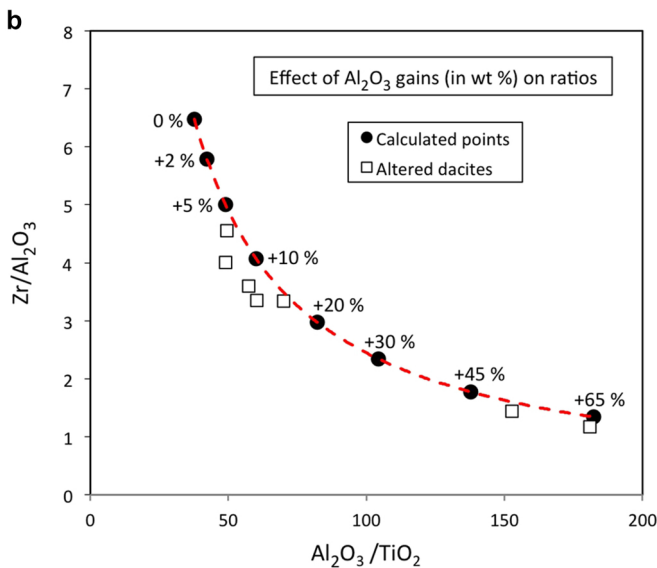
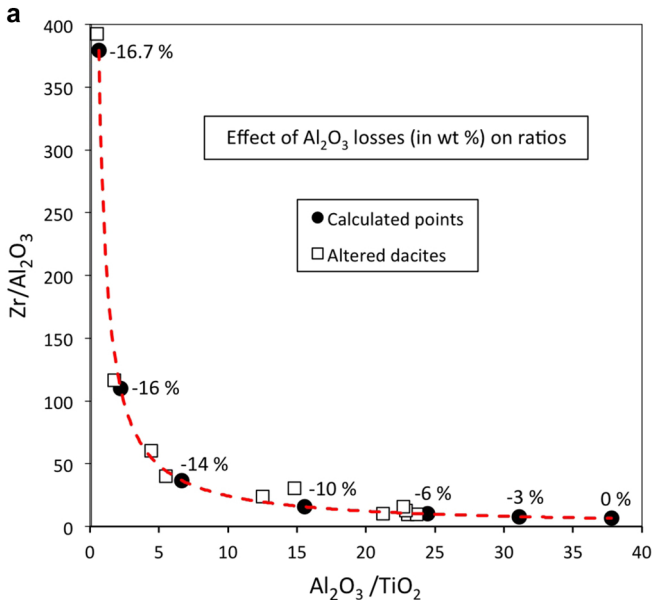


Figure 10

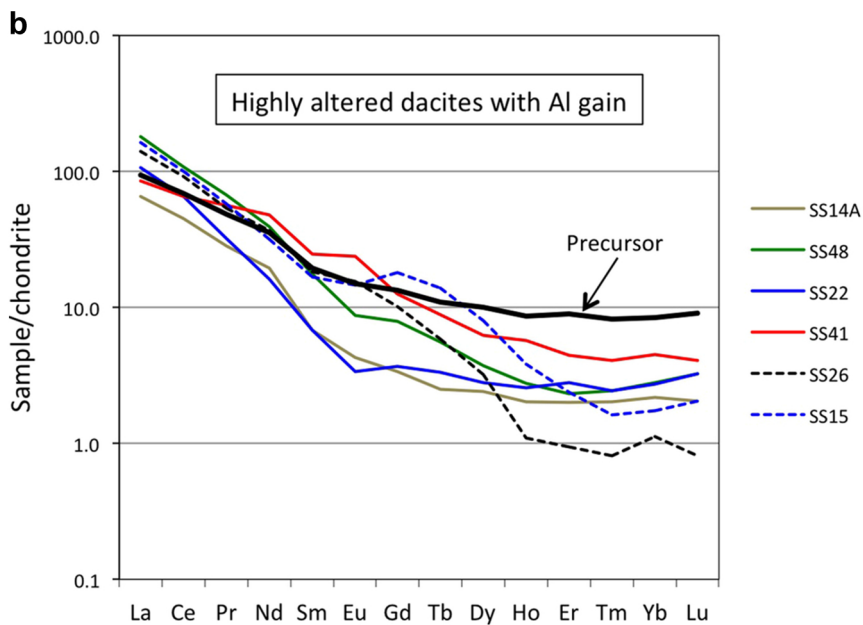
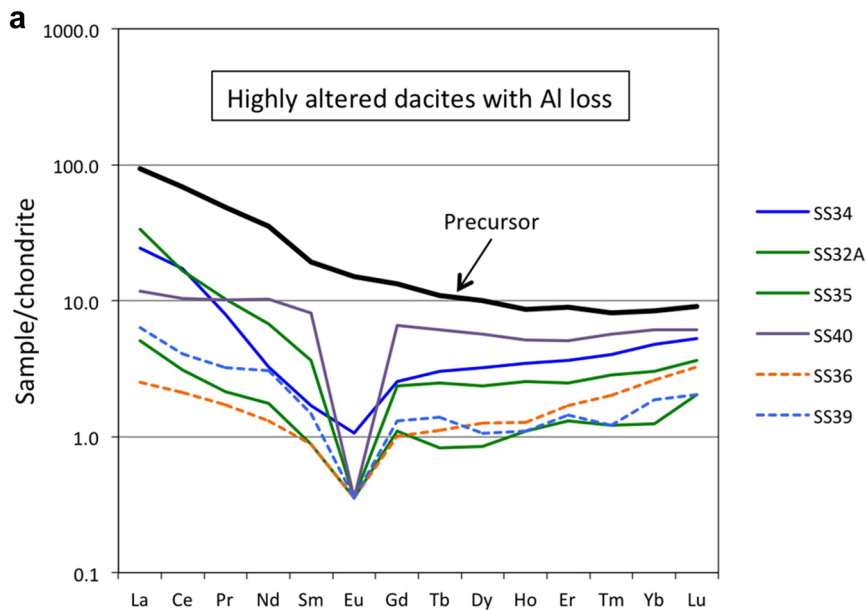


Figure 11

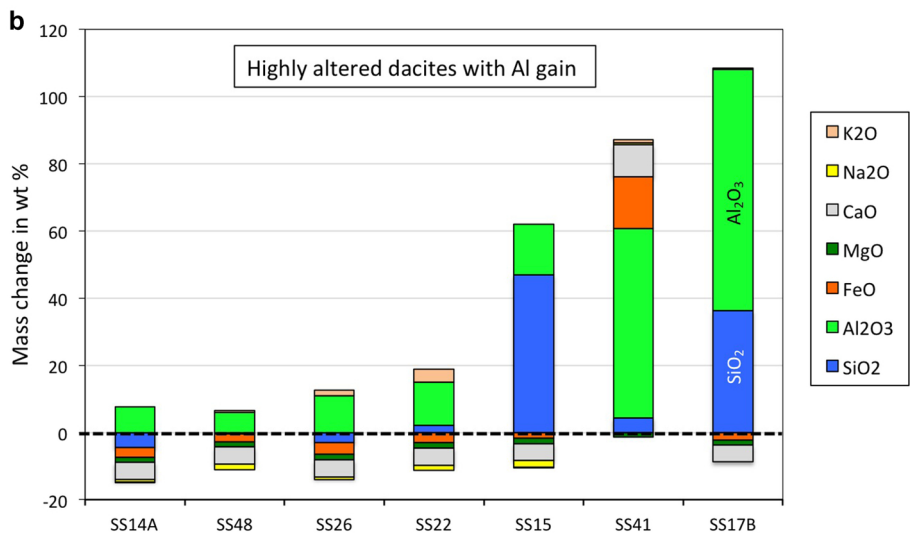
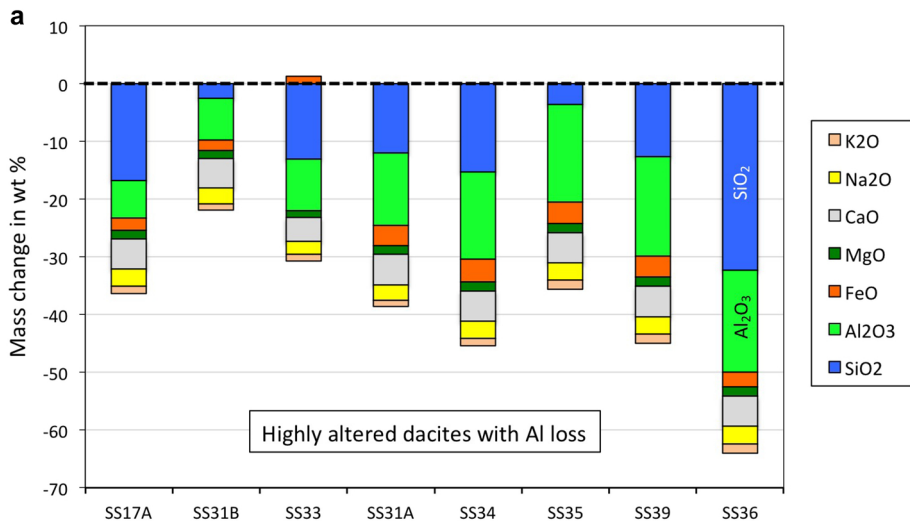


Figure 12

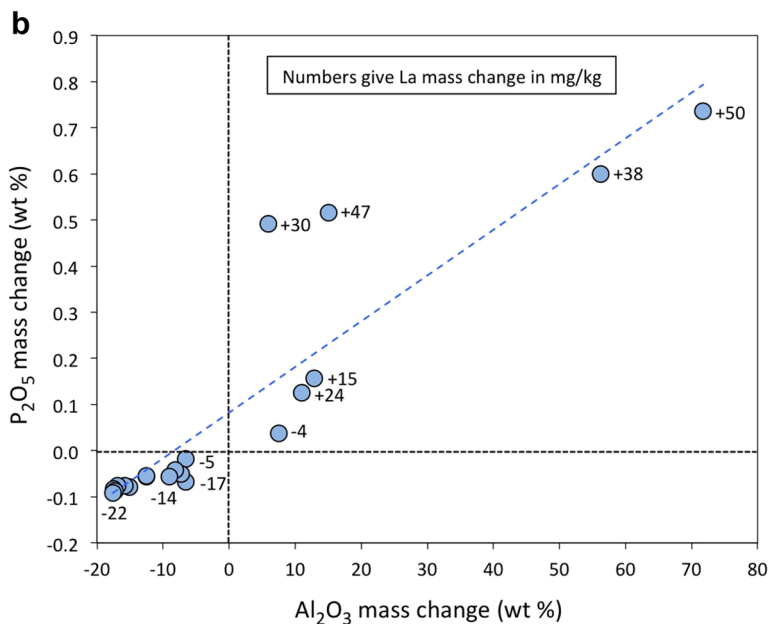
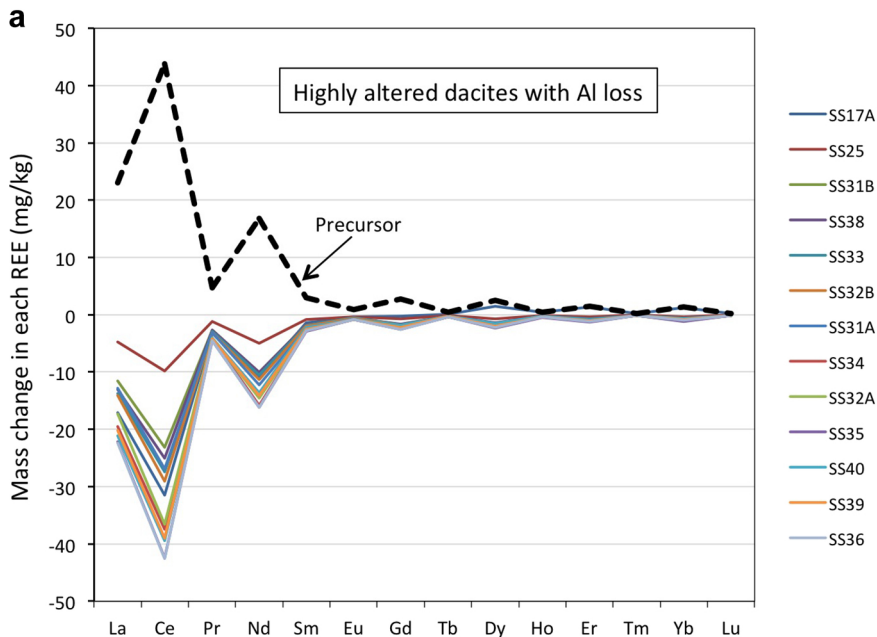


Figure 13

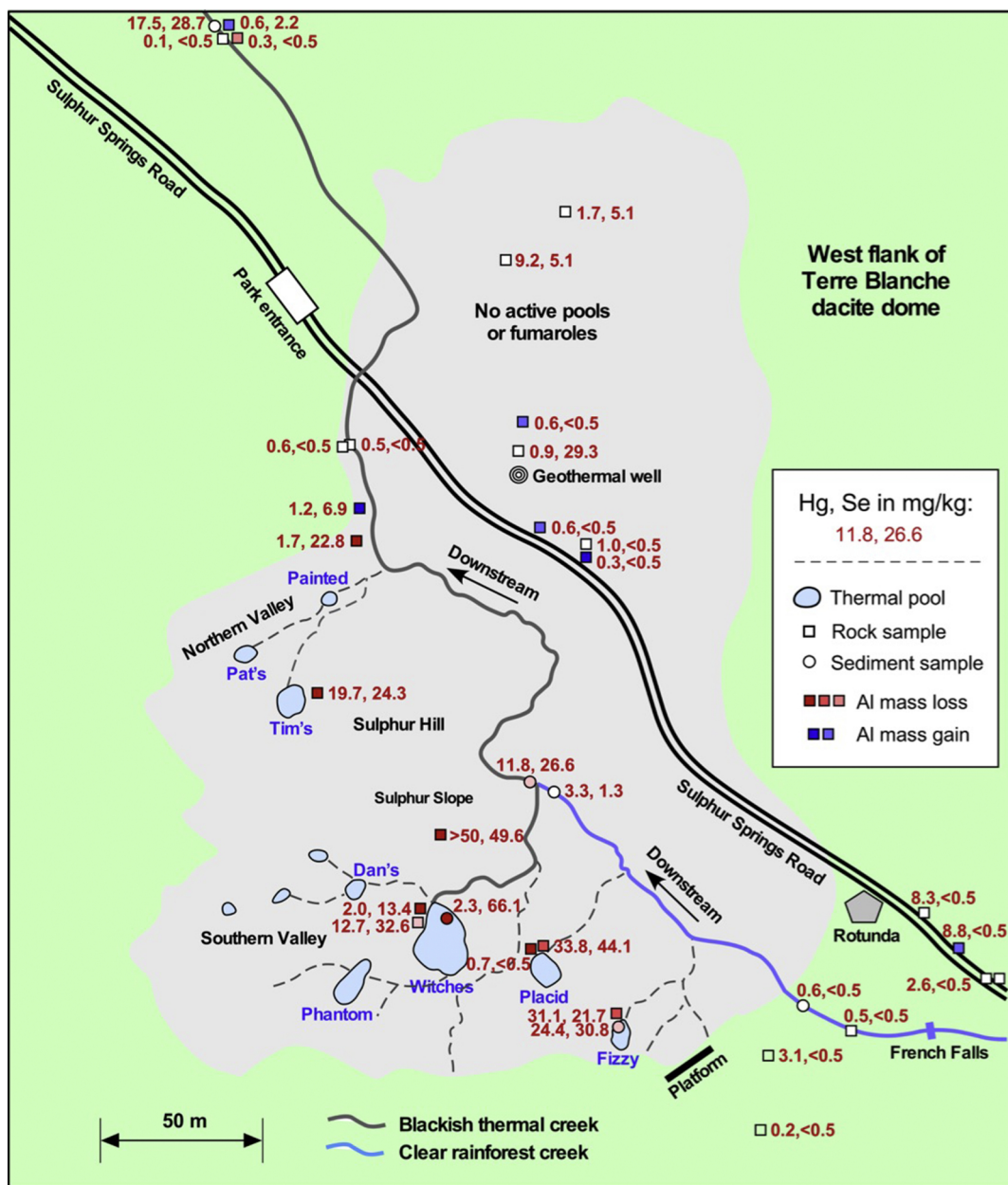
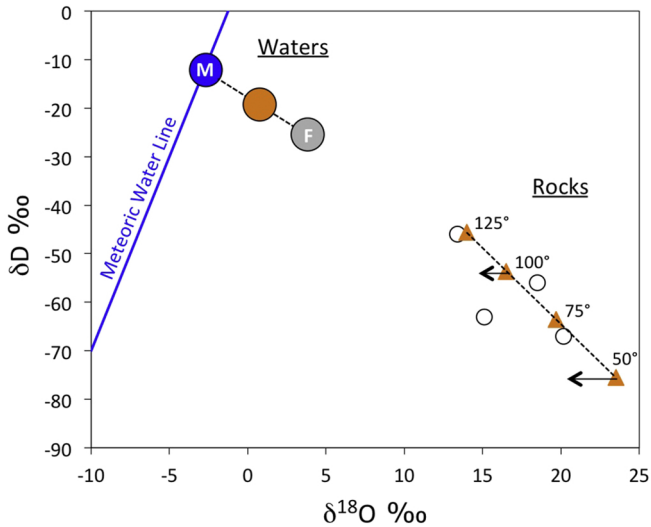


Figure 14



○ Altered rocks at Sulphur Springs

▲ Calculated WR values using 50:50 mix of M & F waters

Assemblage used:
40 % kaol, 30 % opal, 20 % smect, 10 % sulfates

Figure 15

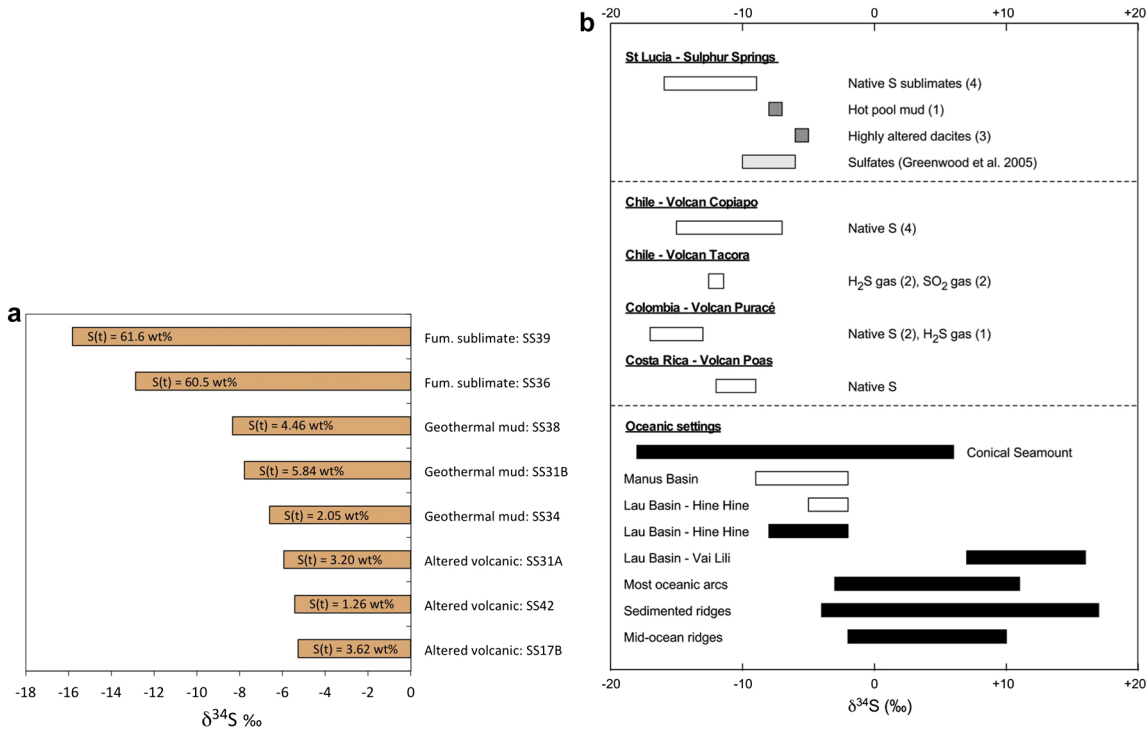


Figure 16