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Shallow Hydrothermal Gas Sampling and Analysis as an Exploration Tool for Magmatic Geothermal Sources

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ABSTRACT

Hydrothermal soil gas sampling and analysis procedure is a promising geothermal exploration tool for establishing magmatic sources, resource temperature estimates and siting locations for surface geophysics and slim holes. The procedure draws from established work from volcanic research, environmental soil vapor surveys and mineral exploration techniques. The hydrothermal soil gas survey takes gas samples in suspected areas of magmatic activity from an average depth of six feet by using driven soil gas probes and prepared glass gas sampling bottles. The collected gas is then analyzed for hydrothermal gases of magmatic origin, i.e., CO₂, CH₄, CO, He, H₂S, and H₂ and the air-derived gases N₂, O₂ and Ar.

Recent hydrothermal gas sampling areas were located on an island of the lesser Antilles. The locations of the gas samples were based on areas of the most recent geothermal activity, accessibility in terms of drilling, plant construction and transmission line logistics and land control. Within these areas, nineteen gas sampling locations were identified, sampled and analyzed.

Soil gas and headspace gas of water samples were analyzed for CO₂, H₂S, CH₄, CO, N₂, Ar, O₂, He, and H₂ contents. Detection limits vary depending on the gas species. The soil gas samples reported here represent a mixture of components: 1) air (N₂, O₂, Ar), 2) shallow organic volatiles (some of the N₂, and some of the CH₄), and 3) a deep component (CO₂, H₂, H₂S, He). The deep component represents inputs from a) the mantle/magma and b) the hydrothermal fluid that moves from an area close to the magma towards the ocean.

For the two samples that have the highest CO₂ contents and CO₂/Ar ratios the CO₂/N₂ and the CO₂/Ar geothermometer give quite similar results; 141°C and 125°C for the crater and 136°C and 110°C for a flank sample. Notably, the H₂S/Ar geother-

nometer and the widely-used CO₂-CH₄-H₂S-H₂ geothermometer give results within ± 10°C for most samples. The CO₂-CH₄ geothermometer, gives a temperature of 323 °C for the crater sample, which is realistic for deep temperatures in the magmatic hydrothermal systems of active volcanoes. For the flank samples that had detectable CH₄ values ranged from 221 to 271 °C, again realistic for the deep temperatures of volcano-hosted geothermal systems.

Introduction

Hydrothermal gas sampling and analysis procedure is a promising geothermal exploration tool. Our procedure draws from established work from volcanic research, environmental soil vapor surveys and mineral exploration techniques (Lechler 2009 et. al.). The hydrothermal soil gas survey takes gas samples in suspected areas of magmatic activity from an average depth of six feet by using driven soil gas probes, prepared glass gas sampling bottles and /or copper tubes. The collected gas is then analyzed for hydrothermal gases of magmatic origin CO₂, CH₄, CO, He, H₂S, and H₂ and the air-derived gases N₂, O₂ and Ar. Using comparative concentrations the following may be determined:

- Presence or absence of hydrothermal gases of magmatic origin.
- Differentiation between amagmatic or magmatic sources for soil gases.
- Temperature estimates of the geothermal source based on multiple gas geothermometers.
- Geometry and/or location of geothermal source.
- Relative depth to magmatic source.
- Relative fracture effective porosity versus porous medium effective porosity.
- Siting locations for exploration slim holes and surface geophysical studies.

Determination of Soil Gas Sampling Locations

Prior to collecting hydrothermal soil gas samples a geologic study of the site is completed to determine the sampling grid for the geothermal source production field, background sample locations, and selection of the site that indicated the highest potential geothermal source which may or may not be in the projected production field. The geologic study covers four major areas; physical geology, petrology, hydrogeology, and structural geology. The physical geology study covers the climate, topography, stratigraphy, seismic activity, weathering and erosion patterns, and identification of geothermal indicia. The petrology study reviews the mineral alteration, mineral assemblages, rock type, geochemistry, genesis, and textures. The hydrogeology study researches previous works on the aquifer types and parameters (deep and shallow) and the low temperature geochemistry of wells and springs. The structural geology map and aerial photo review is to determine potential fault traces and structural controls in the proposed sampling area.

Using the previous discussed reviews and studies a sampling grid is proposed to cover the potential geothermal production field. Since there may be large areas of low geothermal potential in the geothermal source areas more than one sampling grid is proposed to maximize the effectiveness of the sampling pattern. Other sampling areas are background sampling locations and the sampling locations with the highest potential for collection of magmatic/hydrothermal gases. The background locations are areas within a reasonable distance of the sites identified in the initial geologic study as locations of the lowest geothermal source potential and are used to assist in calibration of the gas analysis results. The areas of the highest potential geothermal source may be within or outside the sampling grid and may be from gas samples taken from soils at depth, wells, springs, vents or other geothermal features. These gas samples are the high base line and are used to normalize, compare and calibrate the soil gas results.

Soil Sampling Technique

The soil gas samples are collected by driving a series of specialized rods with a hammer drill or slide hammer to a depth averaging to six feet below ground surface. A low vacuum is then applied to the tubing and soil probe to purge atmospheric air. The sampling depth varies depending on the geology encountered. The minimum depth is based on the ability to seal the sampling point from atmospheric air and to maximize the gathering of soil gases of hydrothermal origin. The maximum depth is dependent on the regolith, equipment capabilities, and practicality based on time and benefits of deeper sampling points.

The steps of the hydrothermal soil gas sampling are as follows:

- Create a pilot hole to desired depth with a solid rod using a hammer drill or slide hammer.
- Drive a hollow vapor recovery point and rod with a special sampling screen and attached tubing to the vapor recovery point into the pilot hole with a hammer drill or slide hammer.
- Seal the bore hole annulus to prevent atmospheric con-

tamination

- Attach tubing to a purging pump and purge air from the tubing and fittings using a low vacuum
- Attach a prepared sample bottle or copper tube under vacuum to the purged tubing system
- Through a series of valves isolate the sampling bottle from the purge system to collect a gas sample by opening the sample bottle or copper tube valve
- Shut the sample bottle valve or cold weld the copper tube and remove the sample container from the soil gas sampling apparatus

General Analytical Procedures

The soil gas samples are analyzed in the Volcanic Fluids Analyses Laboratory at the University of New Mexico in the Department of Earth and Planetary Sciences by Dr. Tobias Fischer. The analytical system consists of two instruments connected to a high vacuum system. The first instrument is a Pfeiffer Quadrupole Mass Spectrometer (QMS) with mass range 0 to 120 Atomic Mass Units (AMU), the second is a gas chromatograph with Discharge Ionization Detector (DID). Calibration of both instruments is performed using commercially available gas mixtures that resemble the expected sample gas composition. The gas sample is connected to a high vacuum system (10^{-6} torr) and expanded into the vacuum line. The first split is admitted to the QMS system which operates in continuous flow mode and the sample aliquot was pumped through the QMS with a turbo pump. Approximately 200 measurements were made of the relative amounts of He, Ar, N₂, and O₂ in the sample using the QMS. These species have minimal mass interferences and are therefore ideal to be determined by QMS. The second split of the gas sample is admitted to the GC via a 10 port valve and the vacuum line. The DID combined with a MolSieve and a HayeSep column allows for the separation and analyses of CO₂, N₂, Ar+O₂, H₂, CH₄ and CO. The results from the QMS and GC are combined to obtain the complete composition of the major and trace components of the gas samples. In a separate analytical run H₂S is analyzed by QMS, however, interference with O₂ at masses 32 and 34 prohibited accurate determination of H₂S in air contaminated samples by QMS and results in high detection limits of approximately 0.04%. We have now developed a GC analytical procedure to measure H₂S more accurately in these types of samples.

Case Study

A recent hydrothermal gas sampling project was conducted on one of the lesser Antilles islands. The locations of the gas samples were based on the studies discussed previously and areas of the most recent geothermal activity, accessibility in terms of drilling, plant construction and transmission line logistics and land control. Within these three areas nineteen magmatic gas sampling locations were identified and sampled. The high base line sample to which all samples were compared to was the crater sofotara vent gas sample. Sample density was based on the grid specifics discussed earlier.

Soil gas and headspace gas of water samples were analyzed for CO₂, H₂S, CH₄, CO, N₂, Ar, O₂, He, and H₂ contents. Detection limits vary depending on the gas species. Although samples have a high air content, i.e. N₂ of 69 to 79% and O₂ contents ranging from 17 to 20%, all samples have CO₂ contents that are significantly above air. CO₂ content is highest in the Crater fumarole at 12%. The CO₂ source is likely of deep/magmatic/hydrothermal origin and samples with the highest ratios also show the highest CO₂ contents. Three samples show detectable CH₄ but these also have among the highest N₂ contents and N₂/Ar ratios suggesting that CH₄ is of shallow origin, likely the result of decaying organic matter. Hydrogen contents of all samples are close to detection limit (0.001%). Helium is not detected in the soil gas samples but detection limit of the instrument is about 100 ppm and some samples may contain elevated He contents compared to air (6 ppm). Hydrogen sulfide is above the detection limit of 0.04 % only in the Crater sample. The Lesser Antilles island is located on a subduction zone and gas discharges in such a setting are characterized by CO₂/He ratios of 50,000 – 100,000 (i.e. Giggenbach, 1996; Fischer, 2008). These high ratios are due to CO₂ being contributed from the subducting oceanic crust and sediments. Therefore it is not surprising that at 3 –12 % CO₂, helium is at or below air levels. Gas geothermometers generally applied to estimate the deep temperatures of hydrothermal systems rely on either gas-mineral or gas –water equilibrium and are often calibrated or tested with geothermal well data. In the case of ‘immature’ hydrothermal systems, that are common on active volcanoes, these equilibria are not always achieved and results need to be interpreted with caution. The soil gas samples reported on here represent a mixture of components: 1) air (N₂, O₂, Ar), 2) shallow organic volatiles (some of the N₂, and some of the CH₄), and 3) a deep component (CO₂, H₂, H₂S, He). The deep component represents inputs from a) the mantle/magma and b) the hydrothermal fluid that moves from an area close to the magma towards the ocean. As the fluid moves to the ocean, it degasses some of its magmatic components (CO₂, H₂, H₂S, He) and picks up some of the organic/crustal components (N₂, some of the CH₄). Therefore, the most reliable geothermometer is one that uses the magmatic components (CO₂, H₂, H₂S). Geothermometers that use Ar assume that Ar is derived from air dissolved in water (i.e. Giggenbach, 1991). In the case of the soil gases, however, Ar is swamped by air-derived Ar making the application of the H₂-Ar geothermometer a challenge. In addition H₂ contents are close to detection limit due to the high air content of the samples. Despite these issues, geothermometers that utilize a deep component and pair it with an air-derived component are promising. In this case the air-derived components (Ar and N₂) are assumed to originate from air-saturated water (Arnórsson et al., 1998).

In soil gases, the air components are mixtures between gases dissolved in air-saturated water at depth and air between the water table and the sampling tube. Based on the available data, it is unknown how much air is derived from the water itself and how much from the soil above the water table; therefore the temperature estimates likely represent the top part of the geothermal reservoir. For the two samples that have the highest CO₂ contents and CO₂/Ar ratios, the CO₂/N₂ and the CO₂/Ar geothermometer of Giggenbach (UNITAR report) give quite similar results; 141°C and 125°C for crater and 136°C and 110°C

for a flank sample. Notably, the H₂S/Ar geothermometer of Arnórsson et. al. (1998) and the widely used CO₂-CH₄-H₂S-H₂ geothermometer of D’Amore and Panichi (1980) give results within ± 10°C for most samples. The discrepancies between the CO₂ and H₂S geothermometers are within 30°C. Clearly, secondary processes such as addition or removal of CH₄, CO₂, H₂ and H₂S during the passage of the gases through air and likely water-saturated soil affects the relative abundances of these species sampled at the surface. The CO₂-CH₄ geothermometer, Norman and Bernhart (1982), gives a temperature of 323 °C for the crater sample, which is realistic for deep temperatures in the magmatic hydrothermal systems of active volcanoes. For the flank samples that have detectable CH₄ values range from 221 to 271 °C, again realistic for the deep temperatures of volcano-hosted geothermal systems. Both CO₂-CH₄ geothermometers are dependent on the CO₂/CH₄ ratio of the gas sample where a lower ratio results in higher temperatures. Therefore, if CH₄ oxidizes in the soil or CO₂ precipitates as calcite or dissolves in shallow pore waters, this ratio would decrease, resulting in higher measured temperatures.

Conclusions

Sampling and analysis of hydrothermal soil gases includes, and should be combined with, the following:

- Well-planned systematic sampling plan
- Complete chemical analyses of gases
- Application of established techniques that allow the evaluation of air contamination
- Gas geothermometry
- Gas ratio comparisons
- Extensive on site surveying of topography, fault traces, structures, geothermal indicia, dikes, lithologic textures and contacts and hydrothermal alteration grades and patterns

Hydrothermal soil gas sampling and analysis establishes a powerful technique to assess the geothermal potential of a region. Future work in this field should test whether hydrothermal soil gas surveys and predicted conditions below the surface can be confirmed by drilling experiments and production of geothermal fluids.

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