

Development of the MultiGAS for Determining Fumarole Gas Chemistry in Geothermal Systems

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ABSTRACT

Geothermal exploration relies in part on the gas geochemistry of fumaroles, bubbling springs and steaming ground to offer insight into the nature of the fluids at depth, processes affecting them when rising to the surface, and provide estimates of the temperature of last equilibration of the gases within the reservoir. Traditional measurements involve direct sampling of the gases in pre-evacuated Giggenbach glass bottles before laboratory chemical analysis. Gas component analysis, combined with the isotope ratios of certain components (e.g., CO₂, He), provides insight into the proportion of magmatic, crustal, meteoric and atmospheric components in the fluid, and the state of equilibrium and temperature of these fluids at depth.

The Multi-component Gas Analyzing System (MultiGAS) was developed by the volcanological community over 10 years ago as a field-portable instrument for in-situ analysis of the major volcanic gas components in diffuse and dilute gas emissions. No two instruments are identical but all consist of various sensor types now capable of simultaneously analyzing for H₂O, CO₂, CO, SO₂ and H₂S.

In geothermal systems, surface manifestations are often comprised of gas emissions. In some cases, low temperatures and/or low flow rates make traditional sampling of fumaroles difficult, due to rapid vapor condensation (in water-rich fumaroles) and atmospheric contamination. The MultiGAS is best suited to these types of manifestations, providing a tool that can be used at a wide variety of locations with differing gas emission styles.

The MultiGAS has been field-tested in two very different geothermal prospect areas: one characterized by cold, CO₂-rich gas seeps and bubbling springs, and the other characterized by steaming ground and fumaroles with temperatures near the boiling point of water. Results of the MultiGAS analysis are compared with the equivalent ratios obtained from traditional sampling and

analytical procedures (where possible), in order to identify the advantages and disadvantages of this new technique. The MultiGAS allows for the rapid characterization of the gas geochemistry in the field, aids in mapping/targeting of fumaroles in a large field, and allows for the selection of the most ideal fumaroles to sample using the traditional Giggenbach method.

Introduction

Gas geochemistry is traditionally used to characterize geothermal systems; from evaluating the nature of the system (steam vs. liquid-dominated) and the nature of the gas fraction (incompressible gas vs. steam), to tracking the evolution of a production field (pressure changes). During grassroots exploration of areas with surface gas emissions, gas geochemistry is used to help define the geometry of the geothermal system at depth (e.g., zones of upflow of geothermal or magmatic fluids). Additionally, gas geochemistry is used to make estimates of the last equilibrium temperature of the gases at depth, that can help in assessing the temperature of the reservoir. Conversely, lack of equilibrium between the different gas species can provide important clues as to the pathway of the gases from the reservoir to the surface.

The goal of this study was to customize a field-portable, cost-effective instrument capable of analyzing gas compositions in-situ for use in geothermal exploration. Various prototypes of such an instrument have been built by a handful of research labs around the world, mainly for the monitoring of volcanic gas emissions (e.g., Shinohara, 2005). The instrument, commonly referred to as a MultiGAS, consists of miniaturized gas detectors (infra-red and electrochemical) that are connected in series and allow for simultaneous measurement of various gas species (e.g., CO₂, CO, SO₂, H₂S). A pressure, temperature, and relative humidity sensor allows for the calculation of water vapor content in the gas. In the last few years, commercial suppliers (e.g., Altair, Dräger) have started to manufacture a version of the MultiGAS for environmental and agricultural purposes. Although these instruments are not currently customizable, and thus not optimized for geothermal exploration, there is the potential to develop a commercial-grade product that will make this technology accessible to everyone.

In this paper we describe the development, calibration and field testing of the MultiGAS for geothermal exploration. Results from two field sites with different emission styles are compared: the thermometamorphic geothermal region of Lardarello, Italy, and the volcanic geothermal region of the Andes in southern Peru. We demonstrate that the MultiGAS is capable of characterizing the chemical nature of a suite of gas species and that ratios of various gas species are comparable to results obtained by traditional laboratory methods. Advantages and disadvantages of this technique over traditional sampling methods are discussed. The conclusion reached is that the field portability, real-time aspect and cost-effectiveness of the MultiGAS make it a promising tool for geothermal exploration in the 21st century.

Study Areas

The two sites chosen for testing of the MultiGAS are very different in terms of the nature of the geothermal system and its emissions. The first is Alterra Power's exploration lease area Mensano, located in central Italy, 20-25 km west of the city of Siena. It is adjacent to the geothermal fields of Lardarello and Radicondoli-Travale, exploited by Enel Green Power. The area corresponds to the inner zone of the Northern Apennines, a fold and thrust belt formed as a result of convergence between the African and European plates in the Cretaceous-Early Miocene. Based on core logging from the hundreds of geothermal wells drilled by Enel Green Power at their Lardarello and Radicondoli-Travale fields, the geothermal systems are hosted in both metamorphic and sedimentary rock units. Heat is supplied through a combination of thinned crust due to regional extension and < 3 Ma magmatic intrusions. The gas emissions sampled are located in the area of Montemiccioli, where cold gas seeps emanate from a deep crustal shear zone (Magma Energy Italy, confidential internal report).

The second area discussed is one of Alterra Power's proposed exploration lease areas in southern Peru called Pinchollo. It is located in the province of Arequipa, approximately 80 km to the N-NW of the city of Arequipa. The concession area and the fumarole sampled is located around Hualca Hualca volcano in the district of Chivay. Hualca Hualca volcano, and neighboring Sabancaya and Ampato volcanoes, are part of the active volcanic arc of Southern Peru (Cordillera Volcanica del Sur). This volcanic arc sits atop thick continental crust, a result of the combined effects of crustal shortening due to convergence between the Nazco oceanic plate and the South American continent, and magmatic addition. The geothermal manifestations in southern Peru consist mainly of hot springs, silica sinter deposits, ground alteration and fumaroles/steaming ground. Heat is supplied by the repeated magmatic activity in the area, ongoing since the Cenozoic.

Instrument and Calibration

The MultiGAS consists of temperature, pressure and relative humidity sensors (to calculate H₂O vapor content), SO₂, H₂S, and CO electrochemical cells and CO₂ non-dispersive infra-red (NDIR) detectors from Alphasense Ltd. The SO₂ sensor has a range of 2000 ppm and a sensitivity of 1.5 ppm. The H₂S sensor has a range of 2000 ppm and a sensitivity of 0.5 ppm. We use two CO₂ sensors with ranges of 0.5 and 5 % and sensitivities of 10 and

100 ppm, respectively. The CO sensor has a range of 1000 ppm and a sensitivity of 0.5 ppm. The sensors are integrated into one common sample chamber but we have designed the instrument in order to have flexibility in terms of the gas species analyzed (Figure 1). As such, the sensors can be added or removed from the sample chamber depending on which gas species need to be analyzed, or for maintenance. Additionally, if the concentration range of a sensor needs to change, a new sensor calibrated by Alphasense to meet the new specification can be integrated into the sensor package. A maximum of eight sensors can be used simultaneously.

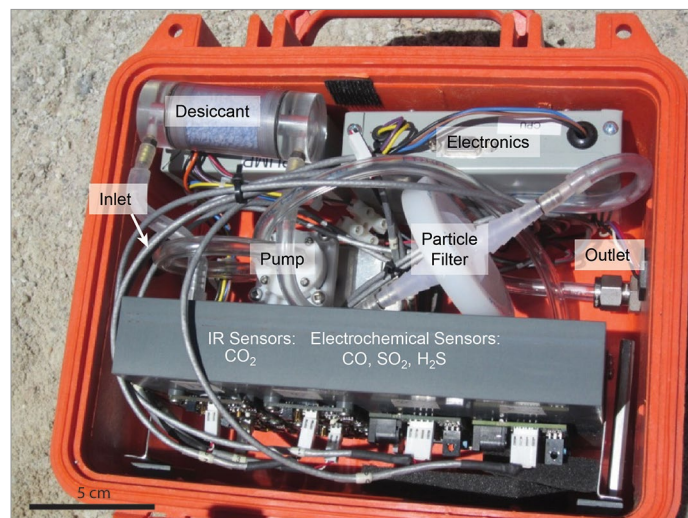


Figure 1. Components of the MultiGAS sensor package. The H₂O sensor (temperature and relative humidity) is located outside the box (not in view).

The sensor package is hosted in a rugged waterproof case (Pelican brand) with an inlet and outlet for the gas as well as two military-style cable connections: one to connect the temperature and humidity sensor, which sits outside the box, and the other to connect the cable that sends data to and receives power from the

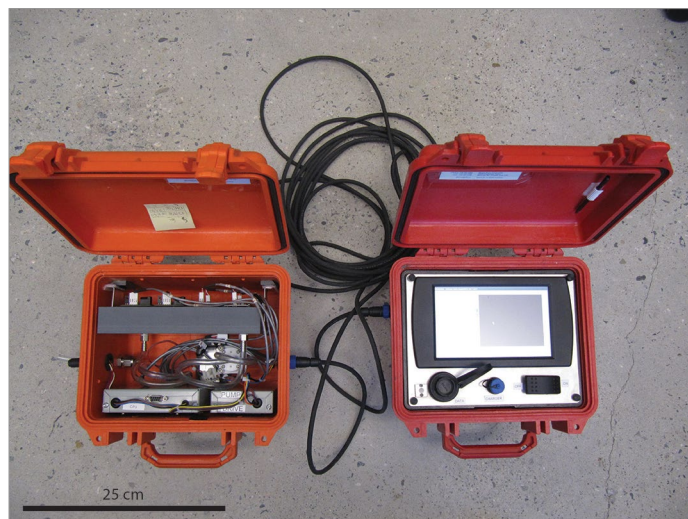


Figure 2. MultiGAS sensor package (left) and computer and battery package (right).

computer and Li-ion batteries, housed in a second Pelican case (Figure 2). Particle and desiccant filters are in the line leading to the sample chamber, in order to eliminate contamination or interference by particles and water vapor. Finally, a pump is placed at the end of the line to pull the gas through the sample chamber and expel it from the system.

Although the electronic boards for the sensors are calibrated in the factory by Alphasense, the electrical signal from the board is amplified and converted to a digital signal before being recorded on the computer. As a result, the exact amplification, gain and range of the digital signal for each sensor channel must be calibrated. We perform this calibration in the laboratory using test gases of variable but known concentration (e.g., 100, 500, 1000 ppm or 0.5, 1, 2 wt. % CO₂), which we flush through the sensors, recording the resulting “digital counts”. An empirically derived scaling factor and baseline is obtained by fitting a linear equation to the data, thereby allowing us to convert digital units to concentration values (Figure 3).

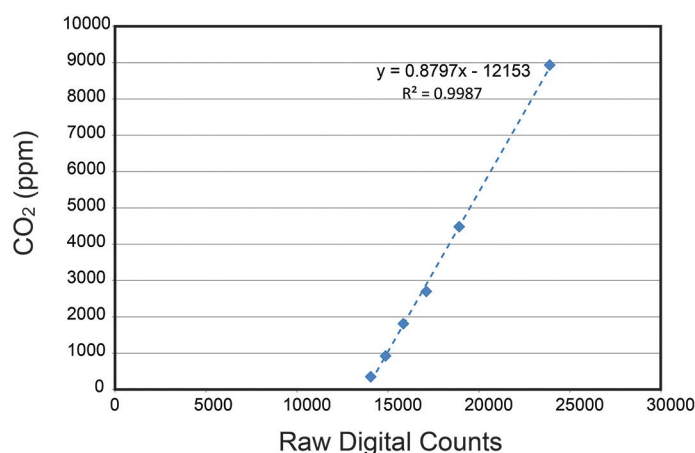


Figure 3. Laboratory calibration data for the 0-5000 ppm CO₂ sensor.

Sampling Methodology and Data Analysis

Gases were sampled at ambient temperature (10-30 °C) and at varying distances from the vent (a few cm to a few m) (Figure 4 and Figure 5). As the gases exit the vent they mix with the atmosphere (dilute) and in the case of high-temperature fumaroles, the gases also cool as they mix with air. Therefore, the MultiGAS analyzes variably diluted geothermal gases, and the proportion of geothermal gas/atmosphere will depend on both the distance sampled from the vent and the flux of the gas from the vent. As such, absolute concentrations of the gas species measured by the MultiGAS cannot be compared directly to gas compositions measured in a laboratory from samples collected in pre-evacuated (vacuum) bottles and for which air contamination has been avoided. However, assuming the gases do not react chemically upon mixing with air at these low temperatures, the concentration ratio of the different chemical species should be constant regardless of the amount of dilution by air that occurs (Figure 6a). The only specie for which this does not apply is H₂O because atmospheric humidity, sometimes up to a few wt. % H₂O vapor, can be quite variable, even on the time scale of tens of minutes (Figure 6b). For the other gas species (CO₂, CO, H₂S and SO₂), atmospheric

concentrations are either nil (CO, H₂S, SO₂) or nearly constant (CO₂) over these time scales.

In theory, the ratio of two gas species can be obtained by plotting the raw concentration data for one specie against the other and extrapolating the slope of the line (Figure 6). In practice, gas compositions are not always constant over time and therefore natural fluctuations over the sampling period (tens of minutes) will result in variable species ratios (scatter on the raw concentration cross-plot). Another complication arises when sensor response times are not all equal (Figure 7). For example, given that the sensor for H₂O vapor is located outside the sensor package, it encounters the gases before the sensors inside the case. To circumvent this problem, we use maximum concentrations as the gas/air ratio changes over time (peaks and troughs on a concentration-time plot) and ratio the corresponding maximum values recorded at each peak (Figure 7). The average of these peak concentration ratios gives us an idea of the time-averaged composition of the gas, which will have a higher standard deviation for gas vents with a changing composition over time.



Figure 4. Close-up sampling of a small, cold CO₂-rich gas seep, Mensano, Italy.



Figure 5. Sampling of a diffuse steam-rich gas plume, Peru.

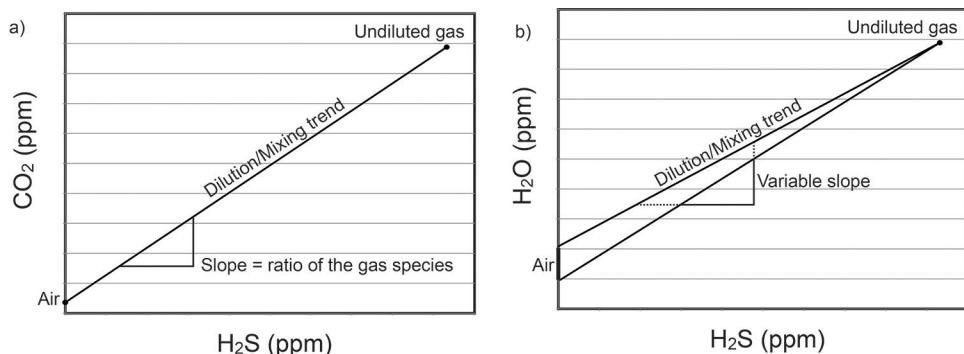


Figure 6. Theoretical mixing lines between geothermal gases and air assuming negligible chemical reaction of the species.

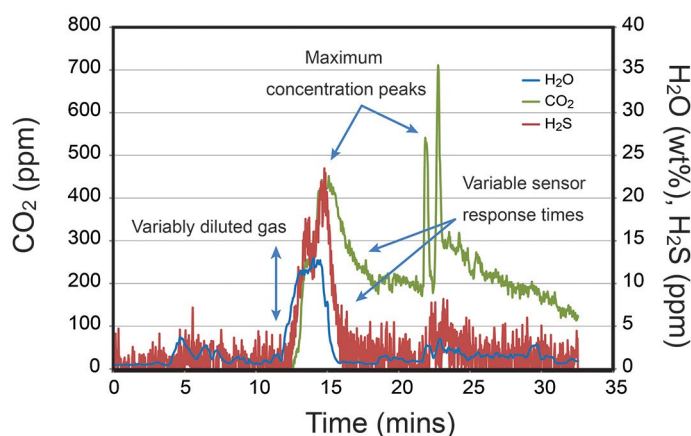


Figure 7. An example from Peru of the time-series signal response from the MultiGAS for a wet geothermal gas variably diluted by air. The effect of variable sensor response time is shown. The ratio of the maximum peak concentrations is used to characterize the composition of the gas.

Results

Italy

Low temperature gas vents (15 °C) at Montemiccioli (Figure 8) were surveyed with the MultiGAS in May 2012. At the same time,



Figure 8. Cold gas seeps through the forest ground at Montemiccioli, Italy. Bubbling was observed through the standing water found in some places. Gas venting could also be heard.

they were sampled via traditional methods (with a pre-evacuated “Giggenbach”-style bottle) and analyzed for chemical and isotopic composition at the laboratory facilities in the Department of Earth Sciences at the University of Florence. These laboratory results reveal that they are CO₂-rich (98.3 mol %) with some trace amounts of methane (0.74 mol %) and H₂S (0.04 mol %) as well as traces of He, N₂ and Ar. The relative proportion of these latter three gases (He, N₂ and Ar) suggest that the Montemiccioli gases are a mixture of

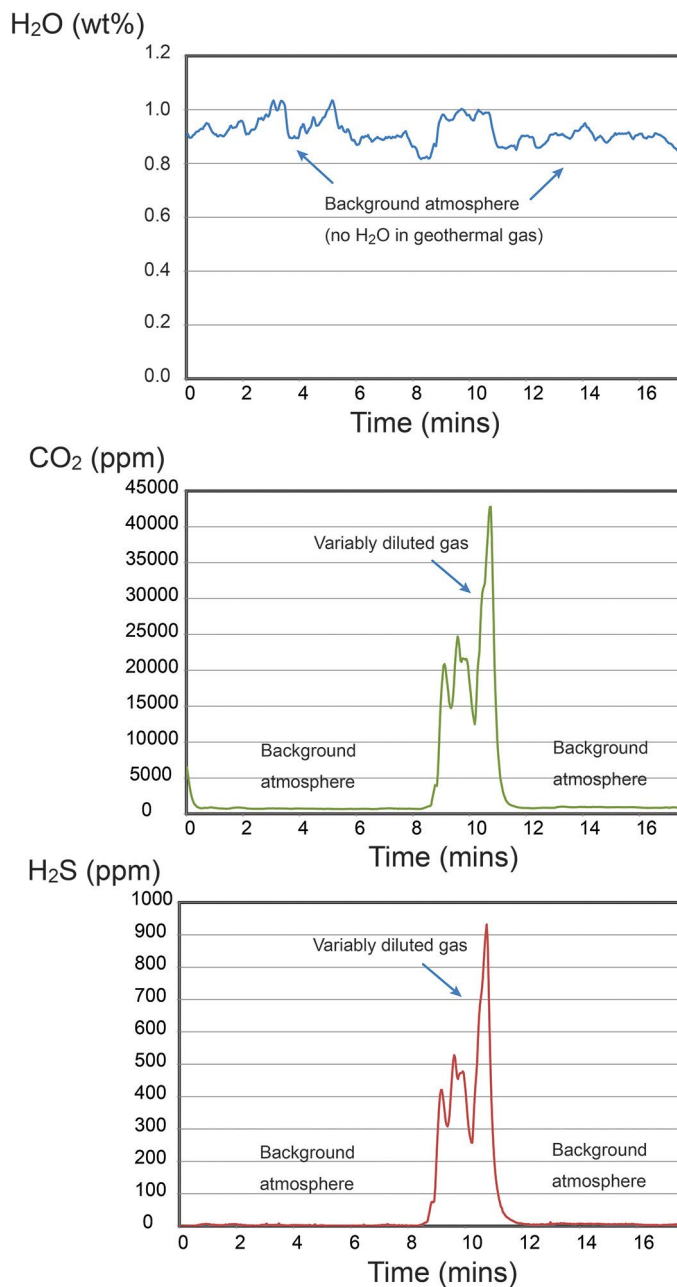


Figure 9. MultiGAS results at Montemiccioli showing the variable gas/air mixture recorded over time.

crustal-derived and magmatic-derived gases. ^{13}C isotope values are -7.32, which, coupled with a He isotope R/Ra ratio (ratio of $^3\text{He}/^4\text{He}$ in the sample divided by the ratio in air) of 1.21 (Minissale et al., 1997), confirms the link to deep, magmatic gases.

The MultiGAS results confirm that the Montemiccioli gases are CO_2 -rich, dry (no H_2O was detected above background atmospheric values) with minor amounts of H_2S (Figure 9). The $\text{CO}_2/\text{H}_2\text{S}$ weight ratio of the gases can be assessed with a simple binary plot of the two species, whose concentration varies over a wide range due to variable dilution with air over the sampling period (Figure 10). This weight ratio of $\text{CO}_2/\text{H}_2\text{S}$ obtained from the slope of the line passing through the data is ~ 48 . The lab results, converted to weight ratio, reveal a $\text{CO}_2/\text{H}_2\text{S}$ ratio of ~ 3000 . The discrepancy between the MultiGAS and lab results suggests either a calibration issue or a cross-sensitivity (interference) issue with the MultiGAS, because it is unlikely that the actual chemistry of the gas changed significantly in the time between the two sampling periods. Given that the MultiGAS was calibrated in the lab prior to field deployment, the most likely explanation for the discrepancy is a cross-sensitivity issue that would cause the apparent CO_2 content measured by the MultiGAS to be lower, or the H_2S content to be higher than it should be. According to interference tests performed by Alphasense, SO_2 , NO_2 , NO and Cl_2 are the main interference species, none of which are present in the Montemiccioli gases. Unfortunately, Alphasense has no cross-sensitivity data for organic gases (methane, ethane, propane, etc.), which have been found to have a strong, but negative, interference on some H_2S sensors (e.g., ISC Model TX 418 from Industrial Scientific Corp.; Austin et al., 2006). More lab testing needs to be conducted in order to identify all possible interferences on the sensors used in the MultiGAS.

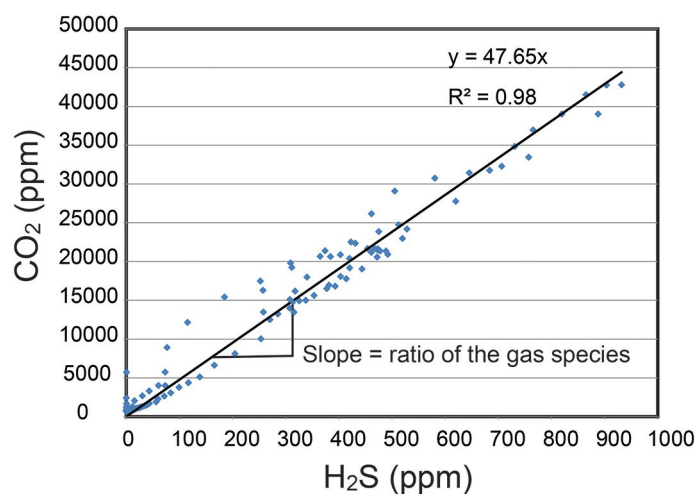


Figure 10. CO_2 versus H_2S concentration in the variably diluted gas from Montemiccioli as analyzed by MultiGAS over a period of 18 minutes.

Peru

High temperature ($\sim 86^\circ\text{C}$; boiling temperature of water at the fumarole elevation), wet geothermal gas emanates from a series of fumaroles in an area called Puye Puye, on the flank of Hualca Hualca volcano (Figure 11). MultiGAS measurements at the most vigorous fumarole were made in September 2011 and were combined with traditional gas sampling for laboratory analysis. The

samples were analyzed at the GNS Science laboratory facilities in New Zealand. Results of these analyses reveal that the gases are steam-dominated (98.9 mol % H_2O) with minor amounts of CO_2 (~ 1 mol %) and even smaller amounts of H_2S , CH_4 and N_2 (~ 1 , 1.5 and 1.7 mol %, respectively in the dry gas fraction). The ^{18}O and deuterium isotopic composition of the condensed steam fraction suggests the water is likely meteoric in origin and has undergone low temperature boiling, as its isotopic composition is depleted in both ^{18}O and deuterium compared to local meteoric water at similar elevation (Figure 12; Giggenbach and Stewart, 1982).



Figure 11. Steam-rich fumarole at Puye Puye, Peru.

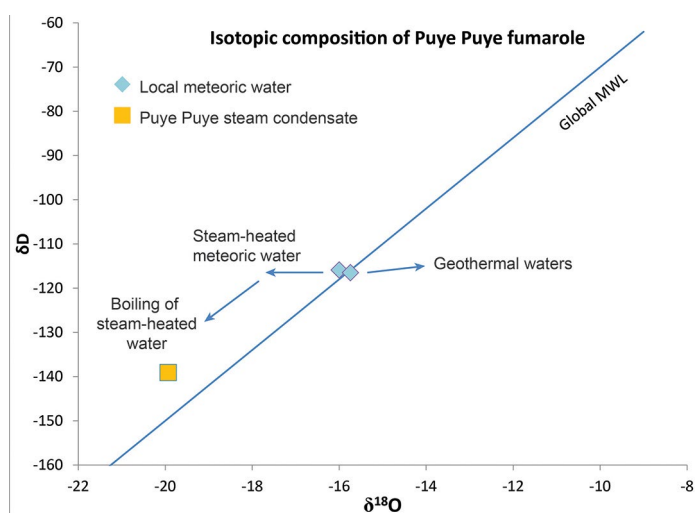


Figure 12. Isotopic composition of Puye Puye steam condensate and nearby local meteoric waters. Isotopic shifts related to mixing, steam-heating and boiling of the meteoric water is shown schematically.

The MultiGAS results confirm that the Puye Puye gases are H₂O-rich with small amounts of CO₂ and H₂S (Figure 7). The H₂O/CO₂, H₂O/H₂S and CO₂/H₂S weight ratios of the gases are estimated using the average of the maximum values recorded as each peak (Figure 7). The average of these peak concentration ratios and their associated standard deviation are compared to the average of the laboratory analyses in Figure 13. There is relatively good agreement between the two datasets.

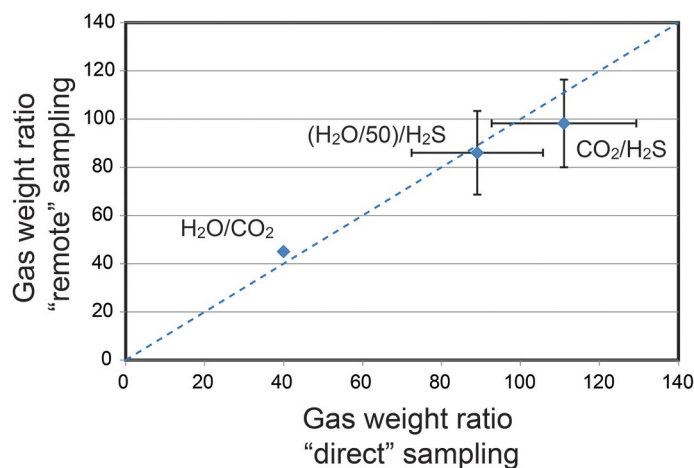


Figure 13. Results of the MultiGAS ("remote") and laboratory ("direct") analyses for Puye Puye, Peru.

Discussion and Conclusions

These data represent preliminary results of field testing of the MultiGAS and highlight the potential of this instrument to provide real-time gas composition data that is comparable to laboratory analyses of samples collected in the traditional manner (with pre-evacuated glass bottles). The key characteristic of the MultiGAS is that it reports gas species ratios, not absolute concentrations, as these are variably diluted by atmosphere.

These tests also highlight some un-resolved issues, related mainly to the potential cross-sensitivity of the various sensors to different interfering gases. Miniaturized sensor technology is constantly improving; new sensors are coming onto the market (e.g., CH₄ and other organic compounds), which will allow us to test more rigorously the effects of cross-sensitivity of the sensors.

The main shortcomings of the MultiGAS compared to traditional sampling are first, its inability to analyze minor constituents such as He, Ar, N₂, O₂ and H₂ either because the sensors do not currently exist, or the concentration of these species is too low (e.g., He, H₂) and/or is too high in air (e.g., Ar, N₂, O₂) making detection in the dilute plume of gas difficult. However, it is possible to connect the MultiGAS inlet directly to a funnel/tube that isolates the geothermal gas, thereby minimizing atmospheric dilution and increasing the detectable gas concentration. In this case though, the user runs the risk of saturating the major species (CO₂, H₂S). Additionally, the MultiGAS is not currently capable of analyzing the isotopic composition of the gases, which is crucial to the geochemical characterization of geothermal gases.

The main advantages of the MultiGAS are that it provides real-time and continuous measurement of gas composition, leading to more cost-effective field work by targeting prospective areas during exploration and determining the most appropriate fumarole for traditional sampling. It can also be used for testing and monitoring of the gas/steam fraction in wells.

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