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Real-time quadrupole mass spectrometry of hydrothermal gases from the unstable Pisciarelli fumaroles (Campi Flegrei): Trends, challenges and processes

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ABSTRACT

Volcanic gas sampling and post-collection chemical determination in a laboratory may preclude any real-time continuous monitoring of volcanic activity. We describe the development, and show the advantages, of a system used for the continuous monitoring of fumarolic gases discharged from the Pisciarelli site (Campi Flegrei, Southern Italy) based on a commercial quadrupole mass spectrometer (QMS-301 Omnistar^{TM}). Although numerous technical problems were addressed due to the ephemeral nature of the emission point and the harsh environment, we also report measurements of the chemical composition of the major gas species emitted from the fumarole for two different periods (in 2009 and 2012). The CO_2/H_2S, H_2S/H_2, He/CO_2 and CH_4/CO_2 molar ratios were investigated in order to detect magmatic and/or hydrothermal components in the system, while the N_2/O_2 ratio was adopted to infer other non-volcanic processes, such as air contamination and mixing with polluted surface waters. The presented methodology allows continuous gas sampling and provides the first evidence of short-term gas variations not available by direct sampling, which is often impractical and hazardous. Compared to the current techniques that are used worldwide for the full characterization of gaseous emissions, i.e. chemical analysis of traditional soda-filled under-vacuum bottles and MultiGAS surveys (laboratory-based and *in situ*, respectively), QMS-based monitoring is complementary and, in prospect, an alternative. With our method, the geochemical monitoring benefits of the real-time analysis for high sampling rates that can be made comparable to the continuous measurements of geophysical networks. This allows a better understanding of hydrothermal features, particularly of chemical fluctuations occurring on the very short-term, which is fundamental for the evaluation of the evolution of unrest episodes at Campi Flegrei, one of the most hazardous volcanic areas in the world.

1. Introduction

Several efforts have been made in geophysical and geochemical monitoring to interpret, and possibly predict, the evolution of volcanic activity. Typically, geophysical methods target the depth and size of the magmatic/hydrothermal source by inverting seismic features and ground deformation data from widespread acquisition ground networks, such as the seismic and GPS ones, in some cases integrated by satellite interferometry for ground displacements over wide areas; geochemistry can be either based on *in situ* site-specific measurements (e.g. fumarolic gases sampling and subsequent laboratory analysis, thermal profiling in boreholes), or widespread data acquisition covering wide surfaces (e.g. soil diffuse degassing).

Isolated point measurements, and subsequent laboratory analyses, yield the full concentration of fluids discharged at specific peculiar sites (fumaroles) and allow interpretation of the pressure and temperature conditions of actively degassing hydrothermal reservoirs by identifying the conditions yielding the last gas re-equilibration prior to the outlet discharge. Such an approach to the measurement of intensive parameters of the hydrothermal system must be necessarily complemented by the measurements of extensive quantities, such as the extension of the anomalous (i.e. exceeding the background value) degassing areas, and the fluxes of mass discharged at surface.

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Volcanic eruptions are frequently preceded by variations in the chemical and isotopic composition of fluids discharged from fumaroles, hot springs and also from diffuse soil emissions making observations of waters and gases basic tools to understand the magmatic-hydrothermal systems beneath active volcanoes [1–4]. In particular, diffuse CO_2 emissions have been quantified by soil-gas surveys of hydrothermal systems at volcanoes in a quiescent condition and, recently, more information have been obtained on fumarolic CO_2 emissions [5].

However, high-precision geochemical discrete sampling and measurements suffer limitations, essentially due to the necessity of accessing the point source of gas emission, avoiding any secondary phenomena (such as component removal, particularly water, or contamination). Collection of fumarolic gases is – depending on logistics and the state of volcanic activity – mostly performed discontinuously with time intervals between consecutive sample collections ranging from days to weeks or even months between consecutive sample collections [6]. Sampling frequencies are too low to allow an efficient comparison between gas data and geodetic and seismic information from continuous geophysical monitoring.

Furthermore, direct sampling poses dangers when getting close to active fumarolic sites. Steam, from both magmatic and superficial heated up sources (such as overlying lakes or groundwaters), is the most common volcanic gas, but other gases, often very toxic, are emitted during eruptive events and may impact on human health. CO_2 and H_2S, particularly, are heavier than air and may pool at ground level and result in asphyxia [7]. Another disadvantage of the direct sampling is that it requires instrumental analysis in the laboratory, which is often performed many days later making it unsuitable for tracking real-time variations on site.

Because of these difficulties, the volcanic CO_2 flux inventory (claimed as one of the most reliable gas precursors to an eruption [8]) remains sparse and incomplete for most of the active volcanoes on Earth [9]. Moreover, its estimate is further complicated by the high background atmospheric concentration, which, inexorably, can affect all measurements carried out by remote-sensing techniques [8].

High-frequency measurements of volcanic gases are a priority for obtaining a better understanding of the precursors of eruptive activity and unrest, but because increasing the frequency of on-site discrete sampling in such environments entails high risks and costs, in the last decades, automatic systems have been developed (Multi-GAS) [10–13] and several novel techniques are still in experimental phase (Tunable Diode Laser TDL [5]; Differential Absorption Lidar DIAL [8]) to become a strong tool in geochemical monitoring.

Few applications of continuous fumarolic gas monitoring systems based on quadrupole mass spectrometer have been so far discussed in literature. Continuous measurement of dissolved gas concentrations using a quadrupole mass spectrometer (QMS) was described by Takahata et al. [14]. Faber et al. [15] reported on a system which analyzed fumarolic gases pumped through a pipe to a remote station where several instruments (e.g. gas chromatograph and mass spectrometer) monitored various physical and chemical parameters. *In situ* mass spectrometer measurements of volcanic gaseous emission were conducted at several fumarolic sites using a commercial quadrupole mass spectrometer by Diaz et al. [16] at Poas (Nicaragua) and Hawaii Volcanoes. It is worth noting that QMS represented an important advancement compared to other techniques for continuous gas monitoring which have been applied on several volcanoes. Earlier attempts by Le Guern [17] were based on a portable gas-chromatograph to determine in real-time the full gas speciation at Vulcano Island (Italy), Kilauea (Hawaii, U.S.A.), and Merapi (Java, Indonesia) volcanoes. Similarly, Zimmer and Erzinger [18] and Zimmer et al. [19] showed data from a gas chromatograph-based system operating continuously at the summit of Merapi Volcano. By means of specific infrared analysers and mass spectrometer, Toutain et al. [20] monitored CO_2, He and ^{222}Rn in gases from a well located at the base of the active cone on Vulcano Island (Italy). Shimoike and Notsu [21] reported on a system to monitor volcanic gases extracted from an observation well located 3 km north of the summit of the Izu-Oshima Volcano (Japan) using IR sensors.

In this paper we extend results and possibilities offered by an our preliminary approach to continuous hydrothermal/volcanic gas monitoring [22] and demonstrate the usefulness of a quadrupole mass spectrometer, deployed at the Pisciarelli fumarolic field (Campi Flegrei, Southern Italy) to improve present-day strategies of geochemical monitoring. Considering that data processing and interpretation are relevant part of the monitoring strategy, this paper shows how the described data acquisition and treatment brings advancements in our understanding of the investigated fumarolic system, included at one of the most dangerous volcanic areas on Earth.

2. Campi Flegrei setting

2.1. Generalities

The restless Campi Flegrei caldera (CFc), often referred to as a ‘supervolcano’ [23] was formed by two major events: the Campanian Ignimbrite eruption, 39 ka ago [24,25], and the Neapolitan Yellow Tuff eruption, 15 ka ago [26]. More than 1.5 million people live within the CFc and surrounding areas, including the city of Naples. Volcanic risk has enormously increased through time as a consequence of rapid population expansion and strong, often irregular, urbanization. The previous eruption occurred in 1538 AD and was preceded by uplift episodes lasting decades [27]. The caldera resurgence is typically characterized by phases of uplift and subsidence over a range of timescales [28–31], not necessarily culminating in an eruption. The last important strong ground uplift ($\sim$3.8 m) occurred from 1969 to 1984, followed by a period of relatively slow subsidence, interrupted by minor uplifts in 1989, 1994 and 2000 [32]. Since 2005 a renewed uplift phase affects the area, at a much smaller rate [33,34], resulting in a ground uplift of 38 cm in the last ten years [35]. Together with a moderate seismicity [34], such a ground deformation is accompanied by other signs of potential reawakening, particularly variations in the chemical composition of fumarolic emission, and flux gases degassing from soils [11,36–38]. These geochemical anomalies reveal a progressive increase in the CO_2-rich magmatic contribution to fumarolic fluids since 2000, largely prevailing over the meteoric/hydrothermal contribution [37,39,36]. The area is affected by intense, diffuse degassing and fumarolic activity in both Solfatara crater and Pisciarelli fault [5], placed close to the town of Pozzuoli. Detailed geochemical analyses of the fumaroles [37–39,36,40], coupled with the measurements of soil diffuse degassing [39–41] and with physical numerical simulations of the hydrothermal system [42], suggests that magma degassing episodes have a relevant role in triggering the volcanic unrest periods that periodically affect the area [37,43,44], as strongly supported by temporal coherence between changes in gas composition and uplift [11,45]. In January 2013, based on persistence of ground uplift and gas chemistry data, the *Dipartimento della Protezione Civile* (Italian Government) raised the state of the CFc from the green level (quiet) to the yellow level (scientific attention) [46].

2.2. The fumarolic activity and state of art in geochemical monitoring at the Pisciarelli site

The Pisciarelli area is a fault-related fumarolic field located a few hundred meters east of Solfatara crater (Fig. 1). This area, the most