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A new method for sampling fumarolic gases: Analysis of major, minor and metallic trace elements with ammonia solutions

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Abstract

A new method using ammonia solutions in pre-evacuated quartz bottles has been experimented for volcanic gas sampling and analysing. Various tests (reproducibility, variability and comparison with known methods such as NaOH pre-evacuated bottles and acid condensates) have been performed to check for their efficiency. By using ammonia solutions, acid gases (St, HCl, HF), carbon dioxide, noncondensible gases (N_2, Ar, …) and metallic trace elements (MTE) can be measured with standard methods (HPLC, GC, titrimetry, ICP-MS).

Results show that acid gases, CO_2 and noncondensible gases are sampled and analysed with similar efficiency in NH_4OH bottles than by using the known and accurate NaOH method. Moreover, a key point is that NH_4OH solutions, after undergoing adequate processing (oxidation and acidification) allow also precise MTE measurements by using standard ICP-MS methods. Such MTE measurements appear much more reliable than those performed on acid condensates.

Pre-evacuated ammonia bottles appear therefore as an optimum tool to collect volcanic gases and to obtain their complete chemical composition.

Keywords: volcanic gas; sampling; acid gases; noncondensible gases; metallic trace elements

1. Introduction

Volcanic gases are complex mixtures of H, C, O, S, minor acid gases (HCl, HF, HBr), trace gases (He, Ne, …) and metallic trace elements (named MTE in this work : Pb, Se, Cd, Bi …). A very reliable method for sampling such mixtures was proposed by Giggenbach (1975). It uses NaOH as a reactant in empty bottles, and is now by far the most widely used method for the detection of all the above-mentioned species except MTE (Giggenbach and Matsuo, 1991; Giggenbach et al., 2001). These last elements are commonly sampled by collecting the so-called “acid condensates”, in spite of evident sampling bias such as MTE revolatilisation and scavenging by S precipitation (Bichler and Sortino, 1995b; Toutain et al., 2000). However, the availability of high precision data for MTE concentrations in magmatic fluids is highly needed to constrain the dynamics of gas cooling (Symonds et al., 1987; Quisefit et al., 1988) and elemental flux calculations. Moreover, MTE have been shown to potentially mark fluctuations of magmatic activity (Quisefit et al., 1988; Toutain et al., 1995; Goff et al., 1998; Shevenell and Goff, 2000), making them potential tracers for monitoring

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of volcanic activity. Herein, we propose another simple and accurate method similar to that of Giggenbach (1975) but using NH_4OH reactant in place of NaOH. By using such a method, the complete and quantitative analysis of all species (acid gases, CO_2, noncondensible gases, MTE) is easily performed. In this paper, we will validate the method by 1) establishing the good reproducibility of each measurement on NH_4OH bottles and 2) comparing chemical compositions obtained on NaOH, water condensates and NH_4OH bottles collected simultaneously. We believe that this method is reliable for routine measurements in most observatory conditions as it uses classical and widespread analytical techniques (High Pressure Liquid Chromatography, Gas Chromatography, titrimetry, ICP-MS). Volcanic fluids used for this comparison are from Vulcano (Aeolian Islands, Italy) and Merapi (Java, Indonesia).

2. Previous methods

2.1. Acid condensates: an open system

Measuring MTE in volcanic gases is a constant goal since many years. Different collection systems have been employed to condense the high-temperature gas phase, including direct condensation through a silicon or silica tube (Piccardi, 1982; Gemmel, 1987; Africano, 2004), or forced condensation in a condensor cooled by cold water, snow, ethanol dry-ice or ether (Quisefit et al., 1989; Taran et al., 1995; Goff and McMurtry, 2000). Such methods are “open systems” because some species (CO_2, O_2, N_2, Ar, He, H_2, …) have to be released to the atmosphere. Moreover, as the natural flow available at most high-temperature fumarolic vents is low, it has to be forced by using either manual or electric pumping to allow a significant volume of fluid to be collected. The solution therefore obtained is supposed to contain the water, acid gases (SO_2 as $SO_4^{2-}+SO_3^-$, HCl and HF as Cl^- and F^-) and MTE, which are thought to be dissolved in the solution. Such solutions display usually very low pH values (often close to 0) and are not suitable for S (partial dissolution of sulphur species) and CO_2 measurements. Such acid condensates have 2 main advantages: significant volumes are easily sampled, and their bulk chemistry supplies analytical matrix well adapted to the usual instrumental conditions for MTE analysis.

These solutions, however, have some characteristics that are rarely discussed in the literature, except Fischer et al. (1998):

- a white to pale yellow precipitate often appears within the solution quickly after collection. This is the result of S precipitation, which acts usually with a high kinetic. Recent results on acid condensates from Kudryavy volcano (Fischer et al., 1998) show that such precipitates are potentially MTE-rich (up to 33, 8 and 5 ppm for Pb, Bi and Rh, respectively). S precipitation may also remove trace elements showing high chemical affinity with S, such as Se, Te, As (not analysed in Fischer et al. (1998)), in accord with the chemical composition of solid sulphur deposited around low temperature fumarolic vents (Greenland and Aruscavage, 1986; Toutain, 1987; Quisefit et al., 1989).
- These solid phases remain floating in solution, but are also adsorbed on the inner face of collecting flasks making S-budgets poorly constrained.
- During sampling, the collected solution may remain in the device at relatively high temperature (typically 30–50 °C, depending on gas temperature, input flow and capacity of the device) whereas the atmosphere above the solution is depressed as the result of pumping. This may lead to revolatilization of some MTE, the level of which likely increases with the volatility of the element. Bichler and Sortino (1995b) have shown that appreciable amounts of MTE were detected at the outlet of the condensate collector and concluded to their transport from the solution as volatile species, which are up to now non-identified.

All these factors probably arise in the collection of solutions depleted in the most volatile MTE, which are also those of the highest volcanological interest (As, Se, Te, Tl, Pb, Bi, Hg, Cd, Zn, Sb). Acid condensates therefore display both a very high variability and possibly non-reliable MTE concentrations even if their high absolute content is an advantage for the determination of some MTE present at low amounts in volcanic gases.

2.2. Caustic bottles: a close system

Giggenbach (1975) described a powerful method for sampling volcanic gases by using bottles under vacuum and partially filled with 4N NaOH. This procedure allows the dissolution of most of the compounds (H_2O, CO_2, SO_2, H_2S, HCl, HF, MTE), whereas non-condensable species (H_2, N2, Ar, O_2, He, CO) remain in the gas phase within the bottle. It enables considerable enrichment of the solution in trace species and operates in close system, without any leak to the atmosphere. Soda solutions were recently experimented for MTE analyses in Vulcano and Kudryavy fumarolic fluids (Bichler and Sortino, 1997;