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Arsenic-bearing phases in South Andean volcanic ashes: Implications for As mobility in aquatic environments

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ABSTRACT

Three samples of volcanic ashes collected after eruptions of the volcanos Hudson in 1991, Chaitén in 2008 and Puyehue in 2011 were analyzed in order to define the solid speciation of arsenic and the dynamics of its release to the aqueous phase. The bulk chemical and mineralogical characterization of the samples was performed by ICP/OES, DRX, and SEM/EDS analyses. The chemical composition of the near surface region (first 2–10 nm), along with the As and Fe solid speciation was performed by XPS. Batch experiments were conducted to evaluate the kinetics of the arsenic release under variable pH conditions. The integrated analysis of these data indicates that arsenic compounds are concentrated onto the ash surface in the form of As(III)–S and As(V)–O species. The As(III) species have been assigned to arsenian pyrite, while As(V)–O compounds have been assigned to adsorbed arsenate ions or Fe arsenate salts precipitated as thin coatings.

Although the main As carrier in the studied volcanic ashes is Al-silicate glass, this phase is stable at the neutral pH that dominates the aqueous reservoirs of the area affected by ashfall. Thus, its contribution to the pool of dissolved arsenic is minor. Higher contributions are clearly associated with the more mobile As species that concentrate onto the surface of Al-silicate glass. This more available arsenic represents less than 6% of the total measured arsenic.

1. Introduction

South America is home to the longest continental volcanic region in the world. Since the Late Triassic, magmatism and volcanism have centered on the Andean region. The first documentation of volcanoes in the region was recorded by the voyages of Columbus and Pizarro in the 16th century. Since then, a large number of volcanoes in the Andes volcanic arc have erupted one or more times (Global Volcanism Program, Smithsonian Institution). In this region, Chile is the country with the largest number of historically active volcanoes. The environmental consequences, however, are mostly observed in neighboring Argentina which is located downwind, and generally receives most of the ashfall. The elevated concentrations of As that are measured in the groundwater of the Chaco-Pampean region (Central and Northern Argentina), have traditionally been assigned to the alteration of volcanic glass spread in the loessic sediments that blanket the entire region (i.e., Nicolli et al., 2012). While most of these conclusions were generated on the basis of water geochemistry analysis, little is known about the As-bearing phases associated with these materials.

Volcanic ash is generally produced by the expansion of magmatic gases. When magma ascends to the Earth's surface and pressure decreases, gases become supersaturated; bubbles nucleate and grow within the magma. The magmatic volatiles are scavenged by ash particles during their transport in the volcanic plume by gas–particle and liquid–particle interactions (Taylor and Stoiber, 1973; Oskarsson, 1980; Delmelle et al., 2007; Martin et al., 2012). As the erupted plume cools, the volatiles condense onto the ash particle surfaces (Rose, 1977; Rose et al., 1980). Pokrovski et al. (2002) studied the speciation of arsenic in eruptive gases and found that arsenic is predominantly in the form of $As(OH)_3$. Similar to other volatile compounds, $As(OH)_3$ can be adsorbed onto ash surfaces (Allard et al, 2000; Witham et al, 2005) and transported in this form along with the solid. A part of the magmatic arsenic could also be incorporated into the glass structure (i.e., Borisova et al., 2010). The partial remobilization of structural As can occur by the dissolution of aluminosilicate glass, which is produced under the extreme acid conditions that predominate within the volcanic plume due to the presence of volatile acids (i.e., HCl, H_2S, HF). Along with As, other elements, including Ca, Mg, Na and K, are also released and then precipitated, forming thin coatings onto the glass surfaces (i.e., Rose, 1977; Oskarsson, 1980; Africano and Bernard, 2000; Delmelle et al, 2007; Gislason et al, 2011).

A number of studies have already documented the relevance of compounds that are formed in the near-surface region of volcanic glasses in the rapid release of hazardous elements and nutrients to aquatic environments (i.e., Witham et al., 2005; Jones and Gislason, 2008; Ruggieri et al., 2010). The study of the chemical composition of

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this near-surface region (first 2–10 nm) thus becomes a key to understanding the mobility of natural contaminants in regions affected by ashfall. X-ray photoelectron spectroscopy (XPS) is a powerful tool used to determine the chemical composition of the top nanometers of solids and to discriminate between the electronic states of the elements. This technique has previously been applied in samples of volcanic ash collected after the eruptions of Eyjafjallajökull (2010), Grímsvötn (2011) and Chaitén (2008) volcanoes. None of these works reported concentrations of As or its electronic state.

In this study, we report XPS data coupled with a complete chemical and mineralogical characterization of three Andean ashes emitted during recent eruptions. Our aim is to identify the As-bearing phases present in the near-surface region of the glass grains. Kinetic experiments performed under different pH conditions further help us to understand the impact of As release in aqueous reservoirs affected by ash deposition studied here. To the best of our knowledge, this is the first time that surface As-bearing components in Andean volcanic ashes have been identified through the interpretation of XPS spectra.

2. Materials and methods

2.1. Sampling

Three volcanic ash samples were collected a few hours after eruptions of the Chilean volcanos Hudson (1991, 45°S 72°W), Chaitén (2008, 42°S 72°W) and Puyehue (2011, 40°S 72°W). The Hudson ash sample was collected at San Julian, a costal locality 550 km SE of the volcano. The Chaitén sample was collected at the village of Esquel, located at the eastern foot of the Andes about 110 km E of the volcano. Finally, the sample from the Puyehue eruption was collected from the roof of a house in the city of Bariloche 110 km E of the volcano.

After collection, samples were air-dried and sieved through <63 μm mesh in order to separate the silty-clayed fraction. All the results presented here refer to this fraction.

2.2. Chemical and surface characterization

Bulk chemical analysis was carried out on the ground <63 μm fraction by inductively coupled plasma optical emission spectrometry (ICP/OES) after lithium metaborate/tetraborate fusion. The validity of the results for major, minor, and trace elements was checked against the measurement of NCS DC70014 standards, which were carried out along with sample analysis.

Grain-size of the volcanic ashes was measured by laser diffraction using a Horiba LA 950 particle size analyzer. The samples were minimally dispersed to prevent the breaking up of aggregates. The precision (reproducibility) of the laser diffraction particle sizer was tested by using mixtures of glass beads (NIST traceable polydisperse particle standard PS202/3–30 μm and PS215/10–100 μm, Whitehouse Scientific). For both runs (PS202, $n = 6$ and PS215, $n = 5$) the median (D50) was certified to be within 3% of nominal value, and the percentiles D10 and D90 were within 5% of nominal values for the standards.

The specific surface area (SSA) was measured by N_2 adsorption using a computer-controlled STROHLEIN area meter II instrument.

The chemical composition of the near-surface region (2–10 nm) was determined by X-ray photoelectron spectroscopy (XPS) using a XR50, Specs GmbH operated in a hemispherical electron energy analyzer PHOIBOS 100 MCD Specs, with a pass energy of 40 eV and non-monochromatic Mg Kα source ($h\nu = 1253.6$ eV; work voltage 13 kV and power 300 W). Air dried samples were analyzed in an ultra-high vacuum (UHV). A two-point calibration of the energy scale was performed using sputtered cleaned gold (Au $4f_{7/2}$, binding energy (BE) = 84.00 eV) and copper (Cu $2p_{3/2}$, BE = 932.67 eV) samples. Broad scans were collected over a 1100-eV range and high resolution spectra were obtained for Al, Si, C, O, Na, Ca, Fe, Cl, P, F, As, S, Mg and K at a resolution of 0.14 eV per step, 200 ms per step and a pass energy of 20 eV. For energy calibration purposes, in order to correct charging effects, all photoelectron peaks (Al 2p, Si 2p, O 1s, Na 1s, Ca 2p, Fe $2p_{3/2}$, Cl 2p, P 2p, F 1s, As 3d, S 2p, Mg 2p and K 2p) were referenced against the C 1s binding energy from the aliphatic contaminants (originating from the hydrocarbon contamination of the surfaces) at 284.8 eV. In order to ensure comparability, the scan procedure was identical for all samples; no evidence of beam damage was found. For chemical composition, data were treated with the commercial software, CasaXPS, using Shirley background correction. As and Fe spectra were fitted using the software of XPSpeak 4.1 with peaks of Gaussian–Lorentzian mixed function after subtraction of a Shirley baseline. The full width at half maximum (FWHM) was fixed during the fitting. The FWHMs were 2.0, 2.1 and 2.3 eV for As $3d_{5/2}$, ferrous and ferric species, respectively. In order to provide a reasonable agreement with the measured spectrum, all spectra were fitted with the least number of components possible. Finally, the peaks corresponding to the binding energies (BE) of As and Fe species were identified by comparing them to the reported values.

2.3. Minerological analysis

Minerals present in the <63 μm size-fraction of the samples were identified by X-ray diffraction (XRD) and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) measures. XRD analysis was performed with a Philips X'Pert PRO X-ray diffractometer operating at 40 kV and 40 mA using Cu-Kα radiation. XRD data were obtained for random samples in the 2θ range from 5 to 70° (step size: 0.02; 13 s/step). The mineralogical interpretation was done using the software X'Pert HighScore, installed on the X-ray diffractometer.

SEM/EDS studies were performed with a JEOL 35 JXA-8230 electron probe microanalyzer coupled with an energy-dispersive X-ray (EDS) analyzer. The samples were prepared in graphite stubs and coated with carbon. In addition, SEM was coupled with focused energy dispersive X-ray analysis (EDAX DX4), in order to perform the elemental semi-quantification. The detection limit of EDS analysis was about 0.5% for arsenic; the spatial resolution was about 1 μm.

2.4. Kinetic experiments

Batch experiments were performed in order to evaluate the release of As throughout time under varying pH conditions. The experiments we carried out by suspending ~1.0000 g of dry ash in three solutions consisting of 20 mL of milliQ water in which the pH was initially set at 6.5, 3.0 and 10.0. The pH value of the suspensions was kept constant during the experiments by adding drops of either 0.1 M HNO_3 or NaOH solutions. Aliquots of the suspension were withdrawn after 1.5, 24, 72, 168, 240 and 336 h from the start of the experiments, centrifuged at 5000 rpm for 15 min and then filtered through a 0.45 μm cellulose membrane filter. Total As and Al contents were analyzed in acidified (1% HNO_3) dilutions by ICP-MS. Detection limits were 0.22 μg L^{-1} and 2.5 μg L^{-1} for As and Al respectively.

3. Results

3.1. Chemical and mineralogical characteristics of volcanic ashes

Table 1 shows the bulk chemical composition of the three analyzed samples. According to the TAS classification (Le Maitre, 1984), Hudson ashes are trachyandesite in type, while Puyehue show a trachydacitic composition and Chaitén ashes are mainly dacitic. Similar to bulk chemical composition, trace element contents also indicate compositional differences among the magmatic sources. The content of arsenic is remarkably higher in the Chaitén ashes than those measured in Puyehue and Hudson samples (Table 1). Surface areas for all three samples were lower than 3.5 m^2 g^{-1}.