

Identification of the As-bearing phases in fresh volcanic Andean ashes

G. Bia, L. Borgnino, M.G. García & D. Gaiero

Centro de Investigaciones en Ciencias de la Tierra (CICTERRA), CONICET and Universidad Nacional de Córdoba, Argentina.

ABSTRACT: The sources and dynamics of arsenic in fresh volcanic ashes collected during the eruptions of Hudson (1991) and Puyehue (2011) volcanoes have been studied. The chemical and mineralogical compositions of both volcanic ashes were analyzed by ICP/OES, DRX, and SEM-EDS. Batch experiments were conducted to evaluate the kinetics of the arsenic release under variable pH values. Results indicate that the release is enhanced under both acidic and alkaline conditions. Besides, the positive linear trends found between Fe and As concentrations in the leachates ($p=0.0107$ milliQ water; $p=0.0022$ pH 3; and $p=0.0081$ pH 10) suggest that arsenopyrite or/and its alteration product scorodite is an important As-bearing phase present in the ash samples. This phase would be the main responsible of the As release under acidic conditions. At higher pH, other mechanisms are involved: desorption from Fe (hydr)oxide coatings (at neutral to slightly alkaline conditions) and dissolution of both arsenopyrite and volcanic glass at pH higher than 9.

1 INTRODUCTION

Large regions of Argentina are affected by the deposition of great amounts of volcanic ashes, a geological material responsible for the natural contamination that affects water reservoirs and soils. A number of studies assign the high concentrations of As measured in groundwaters of the Chaco-Pampean plain to the alteration of volcanic glass and rock fragments spread in the loessic sediments that blanket the entire region (e.g., Nicolli *et al.*, 2012). Most of these conclusions were achieved on the basis of water geochemistry analysis, but little is known about the As concentrations and As-bearing phases present in loess and in the volcanic particles themselves. Some authors suggested that natural contaminants (such as As, V, F and Hg) in volcanic glass are associated with thin coatings of soluble salts and secondary Fe-bearing phases (oxides and sulfides) precipitated onto the particles surface (i.e., Delmelle *et al.*, 2007; Borgnino *et al.*, 2013).

The aim of this work is to identify the As-bearing phases present in two fresh Andean volcanic ashes, in order to assess the mechanisms that control the release of this natural contaminant to the water.

2 METHODS AND EXPERIMENTAL

2.1 Sampling and chemical and mineralogical analyses

Two volcanic ash samples were collected immediately after the eruptions of the Hudson (1991) and Puyehue (2011) volcanoes in nearby regions to them. The bulk chemical composition was determined by ICP/OES after acid digestion. Minerals present in the samples were identified by X-ray Diffraction (XRD) and SEM/EDS measurements. The chemical composition of the

near-surface region was determined by X-ray photoelectron spectroscopy (XPS).

2.2 Arsenic release experiments in volcanic ash

Batch experiments were performed in order to determine the kinetics of the As release. The experiments we carried out under different pH conditions. Three suspensions were prepared with 1.0000 g of dry ash and 20 mL of milli Q water (pH 6.5), HNO_3 10^{-3} M (pH 3.0) and NaOH 10^{-3} M (pH 10.0), respectively. The pH value was kept constant by adding either 0.1 M HNO_3 or NaOH solutions. Aliquots of the suspension were withdrawn after 1, 24, 72, and 168 hours of the experiment start, and filtered through a $0.45 \mu\text{m}$ cellulose membrane filter. Total As and Fe contents were analyzed in acidified (1% HNO_3) dilutions by ICP-MS. Detection limits were $0.22 \mu\text{g L}^{-1}$ and $6 \mu\text{g L}^{-1}$ for As and Fe, respectively.

3 RESULTS AND DISCUSSION

3.1 Chemical and mineralogical characteristics of volcanic ashes

Hudson and Puyehue volcanic ashes show andesitic and dacitic composition respectively. Frequent glass grains are observed by SEM and the obtained XRD patterns are typical of amorphous compounds. The chemical characterization of single grain minerals in the Hudson ash sample allowed to identify the presence of Ti and Fe (hydr)oxides, gypsum, illite and chromite associated with altered volcanic glass. Some anhedronal crystals of pyrite were also found. In the sample of Puyehue, primary minerals such as andesine, quartz, and cristobalite were recognized, and, using mapping, some minority phases were identified such as gypsum, Fe (hydr)oxides and pyrite.

3.2 Kinetics experiments

Figure 1a illustrates the results obtained from the kinetics experiments performed with suspensions of the Hudson ashes in milli Q water, HNO₃ and NaOH solutions. As observed, the kinetic process involves two stages: a first step, which occurs during the first hour, followed by a second much slower step that involves a gradual release of As that reaches equilibrium after 150 h. The Puyehue ashes followed the same trend (not shown).

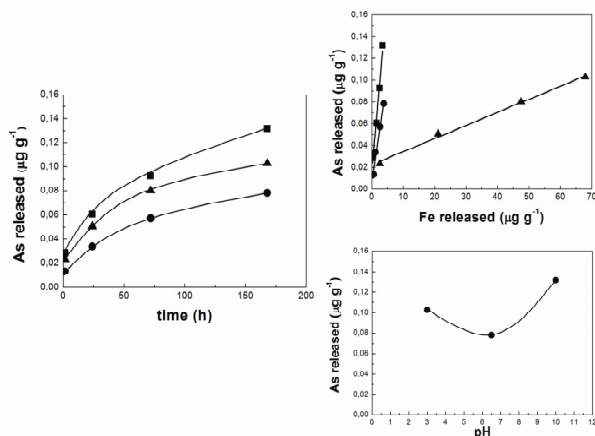


Figure 1. (a) Kinetics curves showing the release of As with time, (b) relationship between As and Fe, in leachates of the Hudson ashes. Circles: milliQ water; triangles: pH 3; squares: pH 10 (c) As released as a function of pH.

Figure 1b shows the relationship between As and Fe measured in the leachates of the Hudson volcanic ash. The observed trends, that are identical to those determined in experiments performed with the Puyehue sample, suggest that these two elements have a common source or a similar mechanism of release. Under alkaline and neutral conditions, the As/Fe ratio is markedly higher (Figure 1b) than under acidic conditions. This behavior could explain the presence of different arsenic sources, more likely pyrite grains and Fe (hydr)oxide coatings detected by SEM/EDS. Arsenopyrite can dissolve under both acidic and alkaline pH conditions. Besides, at high pH the dissolution of amorphous volcanic glass could not be ruled out, as its dissolution is favored (pH > 9). The positive linear trend observed between Na and As concentrations in the leachates may support this last hypothesis. Taking into account that the composition of the ashes is dominated by Na silicates, the measured increase in Na concentration could be a consequence of the volcanic glass dissolution. Another process that may release As to the solution at high pH is desorption from Fe (hydr)oxides that were identified by SEM/EDS analysis, as thin coatings associated with altered volcanic glass.

In view of this results, dissolution of arsenopyrite predominates at acidic pH, while at higher pH (> 8) desorption from Fe (hydr)oxide coatings is probably the main mechanism of As release. Highly alkaline

conditions (pH > 9) ignite the dissolution of the volcanic glass.

It is important to mention that no individual As minerals were detected by either XRD or SEM-EDS. The detection of low levels of As by this last method is not adequate when Mg-bearing minerals are also present, due to the overlap of peaks. XPS is a surface-sensitive technique that permits to determine the chemical composition of the nearsurface region (2–10 nm). The results obtained here may indicate that when the ash samples are in contact for 90 min with acidic and alkaline solutions, the proportion of As atoms in the nearsurface region is lower than in the untreated sample. This trend agrees with the results obtained in the kinetic experiments above mentioned.

4 CONCLUSIONS

The enhanced release of arsenic at both, acidic and alkaline pH, and the positive linear trends between Fe and As concentrations (p=0.0107 milliQ water; p=0.0022 pH 3; and p=0.0081 pH 10) suggest that arsenopyrite or/and its alteration product scorodite (FeAsO₄·2H₂O) is an important As-bearing phase present in the ash samples. This phase would be the main responsible for the As release under acidic conditions. At higher pH, other mechanisms are involved: desorption from Fe (hydr)oxide coatings (at neutral to slightly alkaline conditions) and dissolution of both arsenopyrite and volcanic glass. The latter strongly dissolves at pH higher than 9, which explains the increased release of As observed at alkaline pH values.

ACKNOWLEDGEMENTS

Authors wish to acknowledge the assistance of CONICET and UNC for the support facilities used in this investigation. G. Bia acknowledges a doctoral fellowship from CONICET.

REFERENCES

- Borgnino, L., Garcia, M.G., Bia, G., Stupar, Y., Le Coustumer, Ph. & Depetris, P.J. 2013. Mechanisms of fluoride release in sediments of Argentina's central region. *Science of the Total Environment* 443: 245-255.
- Delmelle, P., Lambert, M., Dufrene, Y., Gerin, P. & Oskarsson, N. 2007. Gas/aerosol-ash interaction in volcanic plumes: new insights from surface analyses of fine ash particles. *Earth Planet. Sci. Lett.* 259: 159-170.
- Nicoli, H.B., Bundschuh, J., Blanco, M. del C., Tujchneider, O.C., Panarello, H.O., Dapeña, C. & Rusansky, J.E. 2012. Arsenic and associated trace-elements in groundwater from the Chaco-Pampean plain, Argentina: Results from 100 years of research. *Science of the Total Environment* 429: 36-56.