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11 April 2012

Analysis of ash from Colima volcano for the assessment of health hazard

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Introduction

Two ash samples from Colima volcano were sent to Durham University by Nick Varley, University of Colima. We have carried out analyses to test for potential health hazard. Samples are as follows:

Sample ID	Date Collected
COL A09/09	08/08/2009
COL A03/10	21/03/2010

Table 1: Sample information

Methods

The following analyses were carried out:

1. Major element analysis (bulk composition) using X-ray Fluorescence.
2. Grain size distributions by laser diffraction[1] using a Malvern Mastersizer 2000 with Hydro Mu.
3. Imaging of particle morphology by Scanning Electron Microscopy.
4. Crystalline silica quantification (cristobalite and quartz) using X-ray Diffraction with static position-sensitive detection (XRD-sPSD)[2].
5. Particle surface area determined by the BET method of nitrogen adsorption.
6. Surface reactivity measured by hydroxyl radical generation and iron release.
7. Red blood cell lysis (haemolysis) as an indicator of potential toxicity.

Results

Bulk composition analyses confirmed that the ash samples are andesitic.

Sample	SiO_2	$Na_2O + K_2O$
COL A09/09	58.77	5.69
COL A03/10	59.12	5.40

Table 2: Total alkali silica results determined by XRF reported as oxide wt. %.

The grain size distribution between the two samples varied greatly (table 3), but both contained substantial quantities of respirable material. Dome collapse eruptions are expected to generate ash with 10-18 vol. % sub-4 µm material[1,3].

Bin	Fraction	COL A09/09	COL A03/10
< 1 µm	Ultra-fine	3.63	1.63
< 2.5 µm	"	8.29	5.20
< 4 µm	Respirable	18.43	8.15
< 10 µm	Thoracic	32.97	21.72
< 15 µm	Inhalable	44.36	30.38
< 63 µm	Sievable	78.54	60.81

Table 3: Quantity of material in health-pertinent size fractions in cumulative vol. %. < 63 µm is included as this is the reasonable cut-off size for sieving.

The ratio of the < 4:<10 µm fractions is usually ~ 1:2, as observed for COL A09/09[1]. The fact that this ratio is not seen for COL A03/10 indicates that this sample underwent some winnowing prior to collection.

Both samples contained approximately 5 wt. % crystalline silica as cristobalite (table 4). There was negligible quartz in the samples, however minor quantities were identified by XRD.

Sample	Cristobalite	Quartz
COL A09/09	5.57	0.54
COL A03/10	5.32	0.62

Table 4: Amount of crystalline silica in the samples. Results are reported with a ±3 wt. % error.

The general morphology of the ash was similar to previously-observed volcanic ash samples. Particles were sub-angular and blocky (figure 1), with no differences observed between the bulk and respirable fractions. No fibrous particles were observed.

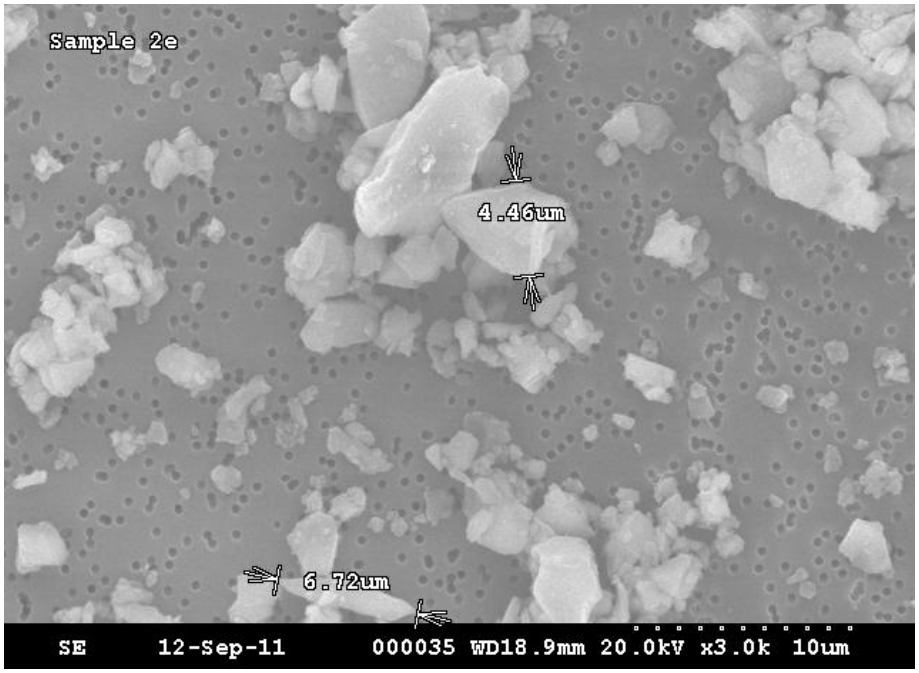

Figure 1. SEM image of the respirable fraction.

Particle surface reactivity was low when run alongside comparative ash samples (figure 2). The sample generated similar numbers of hydroxyl radicals to the andesitic Soufrière Hills sample (MBA 5/6/99), and fewer than the basaltic Etna sample. Poorly coordinated iron removed from the surface of the particles was also low (iron catalyses the generation of the hydroxyl free radical), as expected for an andesitic sample. Data are reported per unit surface area. The specific surface area for sample COL A03/10 was 0.7067 m^2 g^{-1}.

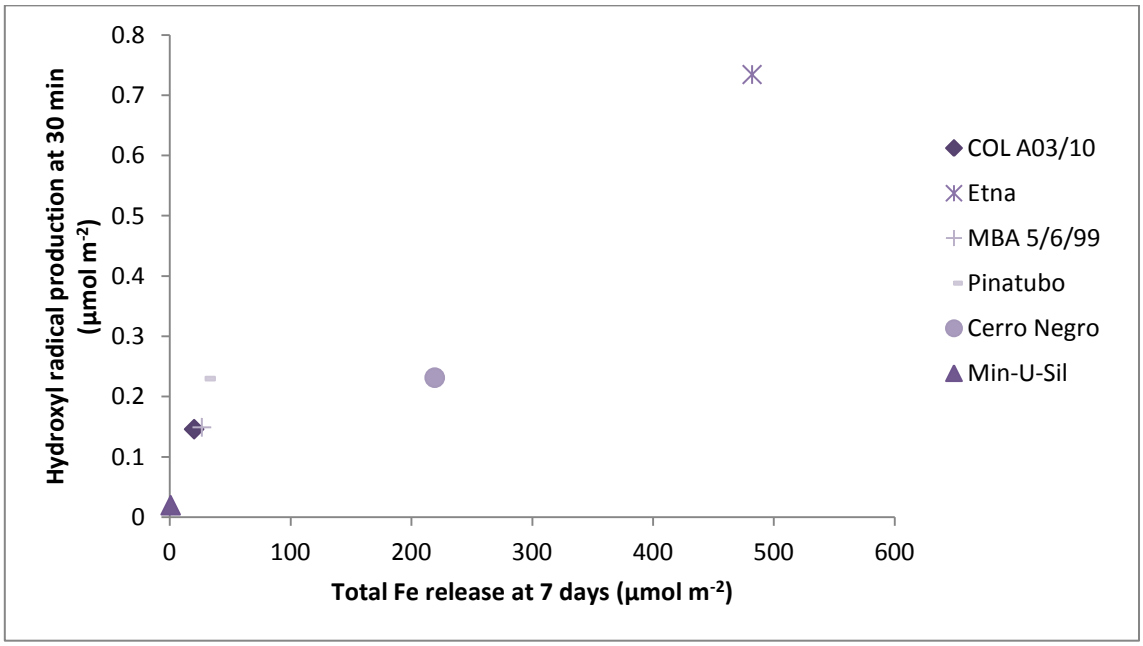

Figure 2: Hydroxyl radical generation after 30 minutes against total iron released at day 7 for COL A03/10 plus Min-U-Sil quartz standard and 4 regularly used comparative samples: Cerro Negro (1995), Etna (2002), Pinatubo (1991), Soufrière Hills (MBA 5/6/99). Min-U-Sil quartz values are those published in Horwell et al.(2007)[4]

Haemolysis (red blood cell membrane rupture) was performed on both the bulk ash sample COL A03/10 as well as a separated respirable fraction. The respirable fraction showed increased haemolytic potential compared to the bulk sample, and was only slightly elevated above the negative control TiO_2 (1.92 vs. 1.62 % haemolysis at the top dose). Relative to the positive quartz control used (DQ12), however, the respirable fraction was nearly 20 times less active at the top dose.

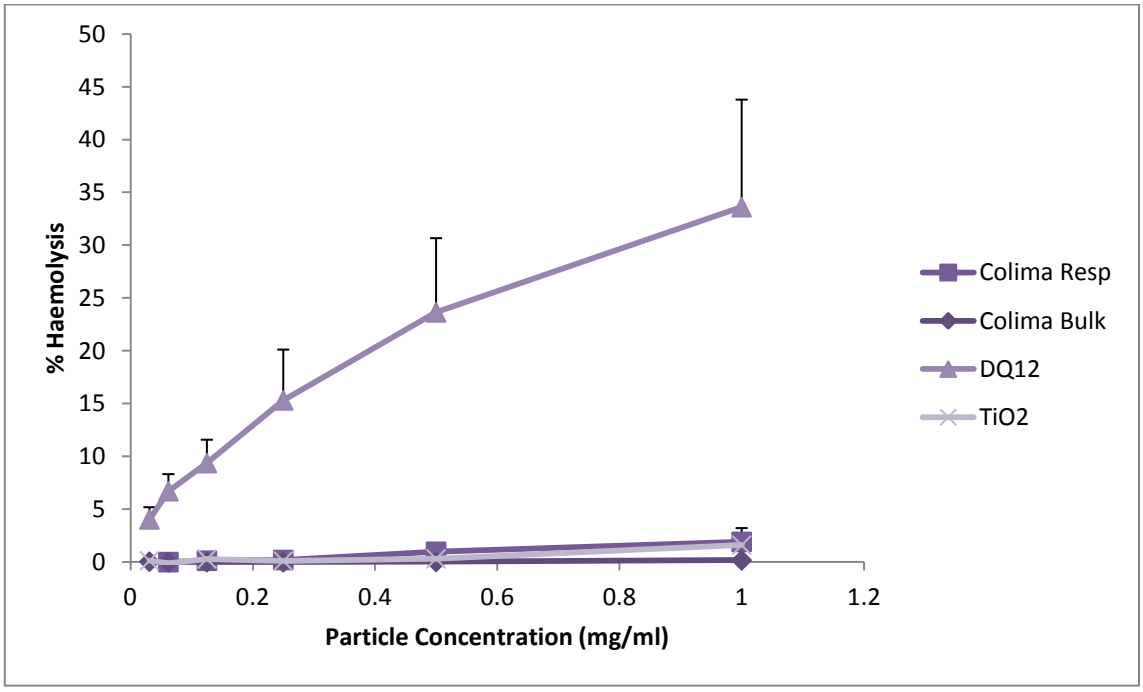

Figure 3: Haemolysis dose-response results for the bulk and respirable fraction of sample COL A03/10. Results are the mean of three runs and errors are reported as the standard error of the mean.

Discussion

The substantial respirable component of both samples warranted further characterisation of the physico-chemical properties and surface reactivity of the ash. The crystalline silica observed results from the presence of cristobalite in the dome rock, which was confirmed through identification in thin sections of dome material.

Particle reactivity experiments were carried out on COL A03/10, which was the sample for which we had more material. Reactivity in the lung determined by iron-catalysed free radical generation[5, 6] and the ability of particles to damage cellular membranes were both low when compared with other well-characterised ash samples and positive controls.

The obvious pinkish colour of the ash indicates either a readily oxidized iron phase or that the ash has been exposed to the environment. The iron component, however, was not easily mobilised in iron release experiments (figure 2), with both oxides being removed equally (10.73 µmol m^{-2} Fe^{2+} and 9.44 µmol m^{-2} Fe^{3+}). As such, we would expect little reactive iron to be available in the lung for hydroxyl radical generation.

From a health perspective, the ash is very fine and exposure could result in particle deposition in the lung. Although reactivity is low, we recommend limiting exposure as well as limiting re-suspension by wetting material prior to clean-up. We would further recommend a rapid analysis of fresh material following a more violent eruption of Colima (e.g., 2005) or dome collapse.

Acknowledgements

Many thanks to Nick Marsh (Department of Geology, University of Leicester) for carrying out XRF and to Chris Rolfe (Department of Geography, University of Cambridge) for carrying out grain size analyses.

Further information

Further information is available on all techniques upon request.

References

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