# ONLINE SUPPLEMENTARY MATERIAL

## ANALYTICAL METHODS

### Reflected and confocal light microscopy

Reflected light microscopy provided information about the texture and mineralogy of the reacted surface (e.g., Craig 1981). Confocal light microscopy was performed using a Leica DCM8 confocal light microscope at ANU using a blue LED light source (460 nm) and an objective magnification of 100x. Preliminary observations with both techniques were used throughout the analysis workflow to track any changes in the sample surface related to sample preparation or other analytical techniques.

### X-ray computed tomography (X-ray CT)

X-ray Computed Tomography was used to investigate the geometry of the reaction product coating with a laboratory-based HeliScanMicroCT at the CTLab at Australian National University (ANU). In order to resolve the thin reaction product layer, the sample was imaged using the ‘Sub-micron CT scanner’, which uses a LaB6 filament X-ray source and high-precision air-bearing stages for sample motion control. This source has a relatively low X-ray flux, resulting in long scan time requirements, but it also has a fine X-ray spot size capable of resolving small details (down to 300 nm). A cubic volume of 2.8 x 2.8 x 1.6 mm (in X, Y, and Z dimensions, respectively) was imaged via helical acquisition trajectory at a voltage energy of 100 keV and a tube current of 75 microAmps; the resulting voxel resolution of the scan was 0.965 micron per voxel edge; and the scan required approximately 20 hours to complete, although time could be reduced if scanning of the substrate was reduced.

To quantify coating geometry, a series of image processing steps were performed to isolate the coating from the basalt substrate; for this sample all processing was accomplished using WebMango, an internet-accessible GUI implementation of Mango (<physics.anu.edu.au/appmaths/capabilities/mango.php>). Three-phase segmentation (void, basalt, and coating) using an edge-detection algorithm and a two-phase segmentation process were used (see Sheppard 2004 for details). Then the two segmentations (basalt plus coating, and basalt only) were combined to produce a three-phase segmentation.

### X-ray photoelectron spectroscopy (XPS)

High resolution XPS analysis was performed on a Kratos Axis UltraDLD instrument fitted with a magnetic charge compensation system, at the Department of Chemistry,University of Copenhagen. The samples were handled using clean stainless-steel tools and placed into hollows in clean stainless steel sample holders (without adhesives). Samples were stored in a desiccator, and we avoided contact with other surfaces, fingers, dust and breath to minimise adventitious carbon contamination.

X-ray photoelectron spectroscopy was used over a large surveyed area (i.e., modified glass, sulfate and oxide) to determine the major elements present at the surface of the reacted glass. All spectra were collected under ultrahigh vacuum (ranging from 9x10-9 to 4x10-8 torr) in a chamber with only oil-free (scroll and turbomolecular) pumps. We used a monochromatized AlKα source and a 700 x 300 µm spot size. Survey (broad scan) spectra were collected at 160 eV pass energy and all high resolution scans at 10 eV pass energy. The energy resolution was ~0.35 eV at 10 eV pass energy. Charge compensation was adjusted to obtain the narrowest line widths. All binding energies were referenced to C from adventitious C (285 eV), although its binding energy depends on the history of the sample (Stipp and Hochella 1991). No evidence of beam damage was observed during data acquisition, and the scan was performed twice to check that the results were consistent.

### **Reflectance Fourier Transform Infrared (FTIR) spectroscopy**

Reflectance FTIR was used in both specular reflectance and attenuated total reflectance modes to interrogate the mineralogy of the reacted sample (Mernagh et al., 2018, this volume). A Bruker Tensor 27 FTIR spectrometer attached to a Hyperion microscope was used for FTIR analyses in conjunction with OPUS 7.0 software. All analyses were made over 650-1300 cm-1 with a resolution of 4 cm-1 and 200 scans. The chamber of the FTIR spectrometer was purged with a constant flow of dry air during analyses, to reduce detection of atmospheric components. Bands were identified and assigned to specific vibrations in sulfates and silicates using literature values (e.g., Lane 2007; van der Marel and Beutelspacher 1976).

We used a 20x Ge attenuated total reflectance (ATR) crystal on a with a penetration depth of 0.1 – 0.2 μm (MacDonald et al. 2000) to analyse the sulfate coating. After smoothing the spectra with a 21-point window, we applied the extended ATR correction with OPUS, using a refractive index of 1.51 (typical for sulfates), to correct the position and intensity of absorption bands in the ATR spectrum. This procedure allowed us to compare the ATR spectrum with transmission spectra in the literature, and to compare our results to specular reflectance FTIR spectra of the sample.

A specular reflectance FTIR spectrum of the surface of the coated sample was collected using a 36 x magnification objective and a 40 x 40 µm aperture; this technique detects light from the sample to several tens of microns deep (King and Larsen 2013). Specular reflectance FTIR spectra was also collected on a cross-section of the sample using a 36x magnification objective lens and 20 x 20 µm aperture. Both spectra were smoothed to a 21-point window and a Kramers-Kronig (K-K) transformation was applied (e.g., Hadni 1967; Dufresne et al. 2009; Mernagh et al. 2018, this volume).

### **Raman spectroscopy**

Micro-Raman spectroscopy was performed using a Renishaw in Via reflex microscope coupled with a Horiba Jobin-Yvon T64000 spectrometer system, located at the Research School of Physics and Engineering (RSPE) at the ANU. A 532 nm wavelength laser was used for both spot analyses and mapping of the reacted sample surface with a range of objective lens magnification (5-100x) over a spectral range of 100-1400 cm-1. The RRUFF database (Lafuente et al. 2015) was used to interpret the Raman spectra. We used Raman analysis after other non-destructive techniques (e.g., FTIR, XPS), due to the semi-destructive nature of the Raman laser beam (Delhaye and Dhamelincourt 1975).

### Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDXS)

SEM was used for high resolution, high magnification secondary electron imaging (SEI) of the coatings on reacted glasses to provide topographic information of the surface at high spectral resolution (Reed 2005; Goldstein et al. 2017; Zaefferer and Habler 2017; Dalby et al. 2018, this volume). SEM was also used to interrogate surface chemistry, using EDXS and backscattered electron images (e.g., Goldstein et al. 2017). Prior to analysis, samples were mounted on stainless steel stubs and carbon-coated. Analysis was performed using a Hitachi 4300 SE/N field emission (FE) SEM at the Centre for Advanced Microscopy at the ANU using appropriate calibration standards. Imaging and EDXS mapping and analyses were performed using a 15 kV accelerating voltage and 1 nA beam current, resulting in an interaction diameter of ~2 µm.

### **Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS)**

Trace element data was collected on unreacted and reacted basaltic glasses using an ArF excimer laser (193 nm) coupled to a Varian 820 quadrupole ICP mass spectrometer (ICP-MS) through an ANU designed and built HelEx ablation cell (Eggins et al. 1998). The isotopes analyzed for both static spot analyses and depth profiling analyses were: 23Na, 24Mg, 27Al, 29Si, 39K, 43Ca, 47Ti, 57Fe, 85Rb, 88Sr, 93Nb, 137Ba, 208Pb, 232Th, and 238U.

Trace element contents of the unreacted glass starting materials were determined using static spot analyses, with a square aperture size of 50 µm. A gas-blank (background) was measured for 120 seconds before and after ablation. The analysis time was 120 seconds, with an ablation rate of 10 Hz (10 pulses per second) and applied laser energy density of ~ 10 mJ/cm2.Analyses were calibrated using glass standard reference materials, NIST610 (Jochum et al. 2011) and BCR-2G (Columbia River Basalt, Wilson 1997). Si was used as the internal reference element because it was the highest concentration element in the substrate. Data reduction was performed using in-house software based on conventional LA-ICPMS data reduction and treatment methods (Horstwood 2008).

For chemical depth profiling analyses on SO2(g)-reacted basaltic glasses, an ablation rate of 1 Hz and a square aperture size of 100 µm were used. The laser energy density was reduced to ~2 mJ/cm2 by adjusting the mirrors within the laser apparatus. Standard reference materials (NIST610 and BCR-2G) and unreacted glass starting materials were also measured to ensure that the mass spectrometer signal was consistent with what would be expected for homogeneous solids (Figs. 9 a-c; Woodhead et al. 2008). Twenty-three different LA-ICPMS depth profiles were collected across the surface of the same SO2(g)-reacted basaltic glass sample. Multiple depth profiles with an ablation time of 600 seconds were taken to assess the variability of the reaction product coating on the sample.

### **Secondary ion mass spectrometry (SIMS)**

A SIMS depth profiling analyses were performed by monitoring the change in isotope signal strengths as a function of time (corresponding with their depth in the sample; Magee and Honig 1982; Genareau et al. 2007). We used a Cameca 6f SIMS at Arizona State University with a 10nA primary beam of 16O2-, rastered over a 125 x 125 µm2 area for ~1 to 5 hours duration. Positive secondary ions were accelerated into the mass spectrometer at 5000V. Samples were sputter-coated with ~20 nm gold coating to help alleviate charge build-up during the analysis. However, the large sputtered hole in the gold coating required us to apply a charge compensation routine where the intensity of either 40Ca+ or 23Na+ were monitored while ramping the sample voltage from 5080 to 4980V and returning the sample voltage to the centroid of the voltage *vs* intensity curve. Secondary ion intensities were determined using an electron multiplier for most elements and a Faraday cup for major, or high ion yield elements (23Na, 28Si, and 40Ca). A field aperture inserted into the path of the secondary ion beam allowed only those ions originating from a circular area ~30 µm in diameter in the middle of the crater into the mass spectrometer (this removed secondary ions from the crater walls). Analyses were performed both at low mass resolving power (M/∆M, 10% definition ~800) and also higher mass resolving powder in order to separate 32S from 16O2 and 40Ca from 24Mg16O. The isotopes measured using SIMS were 23Na, 24Mg, 27Al, 29Si, 32S, 40Ca, 56Fe, 88Sr, 93Nb, 138Ba, 208Pb, 232Th, and 238U. NIST 610 was used as a standard.

### NanoSIMS

NanoSIMS was used to map the distribution of isotopes across the sample surface at high resolution (e.g., Dalby et al. 2018, this volume). High-resolution elemental maps were carried out with a CAMECA NanoSIMS 50L at the Centre for Microscopy, Characterisation and Analysis, at the University of Western Australia. The samples were prepared in cross-section as polished one-inch epoxy mounts and gold coated to provide conductivity. Measurements were performed using a Hyperion (H200) oxygen ion (O-) source, with a spot size of approximately 100 nm, impact energy of 16 keV and a beam current of 12.5 pA. The instrument was operated in multi-collector mode with electron multipliers, allowing the simultaneous detection of seven ion species from the same analysis region. High-resolution elemental maps were acquired by rastering the beam over a field of view of 50 µm2 at a resolution of 512 × 512 pixels with a dwell time of 2.5 ms/pixel. Prior to each image, the area of interest was pre-sputtered with the primary beam. Isotopes measured were 23Na, 24Mg, 29Si, 43Ca, 47Ti, 57Fe, 85Rb, 88Sr, 138Ba, 208Pb, and 238U.

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