SUPPORTING INFORMATION FOR

Production of atmospheric organosulfates via mineral-mediated photochemistry

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1  Experimental and sample characterization details

1.1  Solar simulator and photochemical reactor

A schematic of the photochemical reactor set-up employed in these experiments is presented in Figure S1. The spectral irradiance of the solar simulator employed in the present study (at a working distance of 203 mm) is presented in Figure S2. The spectral match with the AM1.5G reference spectrum, which reflects the solar radiation spectrum in the mid-latitudes (i.e. at a solar zenith angle of 48.2°), is also presented in Figure S2; according to the specifications of the solar simulator, the spectral fit falls within the Class A limit associated with both the IEC and ASTM standards (400–1100 nm).

1.2  2-Nitrobenzaldehyde (2-NB) chemical actinometry

In order to compare the photon flux in our experiments with that present in the ambient environment, we used chemical actinometry of 2-nitrobenzaldehyde. In these experiments, aqueous solutions of 2-NB (10 μM) were placed in the quartz photochemical reactor and illuminated for 0–540 seconds. Quantification of 2-NB was accomplished using an Agilent 1100 HPLC system equipped with a binary pump, autosampler, thermostatted column compartment held at 30°C, and variable wavelength UV absorbance detector set to 258 nm. Separation of 2-NB from its photolysis products was performed using an Atlantis® dC18 column (Waters, 3 μm, 150 × 2.1 mm) under isocratic conditions (60% acetonitrile, 40% ultrapure water) at a flow rate of 0.3 mL min⁻¹. An injection volume of 50 μL was used for all separations. As shown in Figure S3, 2-NB exhibited first-order loss kinetics. The photodecay rate constant for 2-NB, j(2-NB), was (1.89 ± 0.02) × 10⁻³ s⁻¹ (here, the error reflects the uncertainty associated with the first-order fit of 2-NB loss kinetics).

1.3  Control experiments and quality assurance / quality control (QA/QC).

The methanol clean-up procedure described in the main text was validated using recovery tests, the results of which are shown in Figure S4. In these tests, which were performed in triplicate, 0.142 g Na₂SO₄ was weighed into a 15 mL centrifuge tube; then, 1 mL of a 50 μg mL⁻¹ mixed potassium hydroxyacetone sulfate and potassium propyl sulfate standard was added and the mixture was vortexed to dissolve the sulfate salt. After addition of 2.5 mL of
methanol to precipitate sulfate, the tube was vortexed for 30 s and centrifuged for 5 min at 3000 rpm. The supernatant was removed, filtered (0.2 µm nylon filter, VWR), and analyzed as described in the main text. Recoveries are reported as the ratio of (dilution-corrected) peak areas for the processed analyte mix to peak areas for the initial 50 µg mL⁻¹ mix.

In order to verify that the observed organosulfate products arose from photochemistry rather than dark reactions, a comprehensive set of control experiments were performed in stoppered glass vials wrapped in Al foil. For experiments exploring TiO₂ loading (Figure 1 in manuscript), the following controls were performed: 0, 20, 40 min stirring; 10 mM methacrolein; 1 M Na₂SO₄; 0.5 mg mL⁻¹ TiO₂. For experiments exploring the sulfate anion concentration dependence (Figure 2), the following controls were performed: 0 and 30 min stirring at all Na₂SO₄ and (NH₄)₂SO₄ concentrations shown in Figure 2; 10 mM methacrolein; 0.5 mg mL⁻¹ TiO₂. For experiments exploring the methacrolein concentration dependence (Figure 3), the following controls were performed: 0 and 30 min stirring at all methacrolein concentrations shown in Figure 3; 1 M Na₂SO₄ or (NH₄)₂SO₄; 0.5 mg mL⁻¹ TiO₂. For experiments using natural minerals (Figure 4), the following controls were performed: 0 and 30 min stirring using all minerals shown in Figure 3; 10 mM methacrolein; 1 M Na₂SO₄; 0.5 mg mL⁻¹ mineral loading. Prior to analysis, all control samples were subjected to the same clean-up procedure described in Section 2.2 of the main text. No organosulfate production was observed in any of these experiments.

In order to verify that organosulfates observed in experiments conducted using natural mineral samples (Figure 4) did not arise from photochemistry of mineral-associated organics, we also performed one set of experiments in which minerals were illuminated in the absence of methacrolein (0 and 30 min stirring; 1 M Na₂SO₄; 0.5 mg mL⁻¹ minerals). No organosulfate products were observed in these control experiments.

1.4 Sample preparation and characterization

1.4.1 Sample preparation. Prior to use, natural minerals were first broken down using a steel percussion mortar; after removing any steel contamination by passing a weighing paper-covered magnet over the samples (in the case of ilmenite, this was not done because some magnetite was interspersed with the sample; see below), samples were ground to a fine powder using an agate mortar and pestle. In order to avoid sample cross-
contamination, high-purity Brazilian quartz was ground in ethanol in the steel and agate mortars between samples. After this cleaning procedure, the mortars were rinsed with water and ethanol prior to re-use. Visual inspection, coupled with electron microprobe analysis (see Section 1.4.3) suggested that the mica sample contained calcite and iron oxide (i.e. rust). Prior to grinding, therefore, calcite was removed by placing the sample in 1 M HCl for 1.5 h and rust was removed by placing the sample in a solution of Super Iron OUT (56 g in 1.4 L; Summit Brands) for 30 min. A Dremel rotary tool was subsequently used to remove residual contamination. In the case of ilmenite, microscopy was used to aid in the manual removal of contaminants—tentatively identified as goethite/hematite, ferrocolumbite, Ti-bearing magnetite, and possibly anatase/rutile—from the broken-down sample. Anatase did not receive additional treatment beyond grinding.

1.4.2 Surface area determination. The Brunauer–Emmett–Teller (BET) surface areas of commercial TiO$_2$ and the natural minerals anatase and ilmenite were determined using an Autosorb iQ automated gas sorption analyzer (Quantachrome Instruments) with N$_2$ as adsorbate. Prior to BET analysis, samples were degassed at room temperature for 1.5 h; then, if the rate of pressure increase in the sample cell was less than 26 mTorr min$^{-1}$, the sample was removed from the degassing station for analysis. Otherwise, the rate of pressure increase was tested every 15 minutes until this condition was met. These results are shown in Table S2.

1.4.3 Electron microprobe analysis. An electron microprobe (JEOL JXA-8900R) was used to examine grains of anatase, ilmenite, and mica. The minerals were mounted in epoxy, polished, and carbon-coated (25 nm thickness) prior to analysis. In addition to back-scattered electron images, quantitative compositional data were acquired from spot analyses of the minerals using wavelength-dispersive spectrometry and Probe for EPMA software. Thirteen elements were measured (Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Zn, and Nb) with the following conditions: 20 kV accelerating voltage, 20 nA probe current, and a 1 µm beam diameter for all minerals except mica, for which a 5 µm beam was used. Total count times of 20 s were used for both peaks and backgrounds for all elements except V, Zn, and Nb, for which 30 s was used. The X-ray lines and diffraction crystals were: Na Kα, TAP (thallium hydrogen phthalate); Mg Kα, TAP; Al Kα, TAP; Si Kα, TAP; K Kα, PET (pentaerythritol); Ca Kα, PET; Ti Kα, PET; V Kα, PET; Cr Kα, PET; Mn Kα, LIF (lithium
fluoride); Fe Kα, LIF; Zn Kα, LIF; and Nb La, PET. Corrections were applied to V for interference by Ti, to Cr for interference by V, and to Mn for interference by Cr. X-ray intensity data were reduced following Armstrong. The reference standards consisted of metals, synthetic inorganic materials, and natural minerals. These results (expressed as oxide weight percent) are shown in Table S3.

1.4.4 Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) analysis. The Edmonton road dust sample was examined using scanning electron microscopy (SEM; JEOL JSM-6010LA) with energy dispersive spectroscopy (EDS) analysis for elemental mapping. A carbon coating was applied to the road dust sample prior to analysis to increase the conductivity of the sample. Three full-field scans were performed, each with a collection time of 3 min. An accelerating voltage of 15 kV was used with a working distance of 9 mm and 300× magnification. A sample EDS spectrum is shown in Figure S7. The following elements were identified using elemental analysis: Na, Mg, Al, Si, K, Ca, Ti, Fe, Cu, and Mo (the latter two elements were present at unexpectedly high levels, and identification of them using this technique is therefore considered tentative at best). Representative elemental mapping results, which are also shown in Figure S7, highlight the compositional heterogeneity of the road dust sample.

1.4.5 X-ray diffraction (XRD) analysis. In order to verify the mineralogy of the natural Ti-containing minerals employed in this study, X-ray diffraction (XRD) patterns were collected using an Inel MPD Multi Purpose Diffractometer System equipped with a CPS 120 curved position sensitive X-ray detector and a Cu Kα1 radiation source. The instrument was operated at a beam intensity of 40 kV and 20 mA. Phase identification was accomplished using Jade software (Materials Data, Inc.) in conjunction with the ICDD-PDF2 and ICSD databases. Phase refinement was performed using the TOPAS Academic software package (Bruker AXS), and phase presence was confirmed using Pawley fitting. Refined parameters include scaling, 6-term polynomial background, and cell parameters of the refined structures. Residual difference lines were calculated as the difference between observed intensity and calculated intensity. As shown in Figure S8, the XRD patterns of the natural minerals were consistent with those of anatase, ilmenite, and mica (identified as phlogopite; K (Mg,Fe)3Si3AlO10(OH)2). We note that since Pawley fit refines only peak positions, intensity mismatch is possible. For mica, a strong preferred orientation along
the 0 0 2n direction was observed, which resulted in increased intensity of the corresponding peaks (Figure S8c). Figure S8 also shows that the road dust sample was more compositionally complex, with contributions from quartz, microcline, dolomite, albite, scawtite (tentative), and calcite.

1.5 Synthesis of calibration standards

Standards were synthesized according to established literature procedures, which are briefly summarized here. NMR spectra, high-resolution mass spectra, and product ion scans of the synthesized standards are presented in Figures S9–S12.

1.5.1 Potassium hydroxyacetone sulfate. 5.6 mL (0.08 mol) of hydroxyacetone was added to a round-bottom flask containing 15 mL of tetrahydrofuran (THF) under nitrogen; then, 14.01 g (0.088 mol) of pyridine sulfur trioxide was added. The resultant cloudy mixture was stirred for 8 hours to yield a clear solution. THF was removed via rotary evaporation to yield a clear light-yellow oil (the pyridinium salt of hydroxyacetone sulfate). Isolation of the potassium salt was accomplished by creating an aqueous slurry of the pyridinium salt with 80 equivalents of Dowex 50WX8-200 cation exchange resin that had been previously charged with potassium ions by passing a 1 M KOH solution through the protonated cation exchanger. The solution was then filtered and water was removed via rotary evaporation. The resultant white solid was recrystallized from boiling 80% ethanol solution; hot filtration under vacuum was used to remove a white precipitate that gave no \(^1\)H or \(^13\)C signal. The potassium salt of hydroxyacetone sulfate was formed as colourless needles (29% yield).

\[^1\text{H} \text{NMR}\, (400\,\text{MHz, D}_{2}\text{O}): \delta/\text{ppm}\, 2.23\, (s, 3\text{H});\, 4.474\, (s, 2\text{H})
\]

\[^{13}\text{C} \text{NMR}\, (400\,\text{MHz, D}_{2}\text{O}): \delta/\text{ppm}\, 26.67;\, 72.76;\, 208.79\]

1.5.2 Potassium propyl sulfate (adapted from a published synthesis of sodium ethyl sulfate\(^9\)). 5 mL of concentrated H\(_2\)SO\(_4\) was added dropwise to a round-bottom flask containing 20 mL of 1-propanol. The mixture was stirred under reflux for 2 h, cooled by pouring into 250 mL of cold water, and neutralized using calcium carbonate, which converted the sulfuric acid into insoluble calcium sulfate and the propyl hydrogen sulfate product into its soluble calcium salt. After removal of calcium sulfate via filtration, calcium
propyl sulfate was converted to potassium propyl sulfate via addition of 30 g of potassium carbonate. The solution was then filtered and water was removed via rotary evaporation. The resultant crude solid was recrystallized from methanol to produce the pure product as colourless needles (68% yield).

\[ \text{\(^1H\) NMR (400 MHz, D}_2\text{O): } \delta/\text{ppm} \ 0.94 \ (t, \ J=7.4 \ \text{Hz}, \ 3\text{H}); \ 1.68 \ (sx, \ J=7.9 \ \text{Hz}, \ 2\text{H}); \ 4.01 \ (t, \ J=6.4 \ \text{Hz}, \ 2\text{H}) \]

\[ \text{\(^{13}C\) NMR (400 MHz, D}_2\text{O): } \delta/\text{ppm} \ 9.26; \ 21.81; \ 71.01 \]

1.6 Chemicals. Ammonium sulfate (ACS, \(\geq 99.0\%\)), sodium sulfate (ACS, \(\geq 99.0\%\)), methacrolein (95%), TiO\(_2\) (99.8% trace metals basis), 2-nitrobenzaldehyde (\(\geq 99.9\%\)), and tetrahydrofuran (HPLC grade, \(> 99.9\%\) purity, inhibitor-free) were obtained from Sigma Aldrich. Hydroxyacetone (95%), sulfur trioxide–pyridine complex (98%, active SO\(_3\) ca. 48–50%), and 1-propanol (ACS, \(\geq 99.5\%\)) were obtained from Alfa Aesar. Acetonitrile (HPLC grade), calcium carbonate (certified ACS powder, 100%), potassium carbonate (certified ACS powder, 100%), formic acid (Optima grade, LC-MS), and methanol (Optima grade, 99.9%) were obtained from Fisher Chemical. Dowex 50WX8-200 ion exchange resin (100–200 mesh) was obtained from ACROS Organics. Concentrated H\(_2\)SO\(_4\) (reagent grade) was obtained from Caledon Laboratory Chemicals. 80% ethanol was prepared from ethyl alcohol (100% anhydrous; Commercial Alcohols).
2 Supplementary Figures and Tables

Figure S1
Schematic drawing of the photochemical reactor employed in these experiments. The reactor itself is constructed from a flat o-ring flange (5 cm ID × 3.8 cm height) equipped with a 6 mm ID sampling port. The top of the reactor is equipped with a quartz window (76 mm diameter × 6 mm thickness), which is held in place using a horseshoe clamp. Samples are stirred using a custom-built two-part modular stirring apparatus*, both parts of which are contained within aluminum housings. The exchangeable upper part of the apparatus comprises the stirring mechanism itself, which consists of a brass disc equipped with four rare earth magnets. A milled depression in the aluminum housing serves as a sample holder. The upper and lower parts of the apparatus are interfaced via a fixed socket, which protrudes upward from the bottom part of the apparatus. The fixed socket, in turn, is mounted to a motor beneath the apparatus, which drives the mechanism. The temperature of the samples is controlled using a custom-built digital Peltier temperature control system, in which cooling fluid is circulated through channels in the bottom part of the apparatus. Sample temperature input to the control system is provided by a probe inserted through the reactor sampling port.

*Note: The stirring apparatus also has four- and nine-sample configurations. In these configurations, the upper part of the apparatus is exchanged for versions containing four and nine brass gears, respectively.
**Figure S2**  
Spectral irradiance of the solar simulator employed in the present study at a working distance of 203 nm (solid line) as compared to the AM1.5 reference spectrum (dashed line). Data provided by the solar simulator manufacturer (Abet Technologies). In the present experiments, the working distance was 190 mm. In order to compare the photon flux in our experiments with those in the ambient environment, we used chemical actinometry (see Section 1.2).
**Figure S3**
Loss of the chemical actinometer 2-nitrobenzaldehyde (2-NB) in our photochemical reactor as a function of illumination time. Each data point represents the mean of three experimental trials, with 1-σ error bars (here, the error bars are too small to be seen). The dashed line is a linear fit to the experimental data.
Figure S4
Recovery of hydroxyacetone sulfate (HAS) and propyl sulfate (PpS) using the MeOH cleanup procedure described in the SI text. Each data point represents the mean of three experimental trials, with 1-σ error bars (here, the error bars are too small to be seen).
Figure S5
Representative chromatograms showing organosulfate products: a) 1M Na₂SO₄ (adjusted to pH 5 using 50 mM aqueous H₂SO₄), 10 mM methacrolein, 1 mg mL⁻¹ TiO₂, 30 min illumination; b) 1M Na₂SO₄ (adjusted to pH 5 using 50 mM aqueous H₂SO₄), 10 mM methacrolein, 0.5 mg mL⁻¹ mica, 30 min illumination. Samples were run in multiple reaction monitoring (MRM) mode; in all cases, the [M–H]⁻ → m/z 97 transition was employed for analysis and quantification.

a)

![Chromatogram a](image)

b)

![Chromatogram b](image)
**Figure S6**
External calibration curve for hydroxyacetone sulfate (HAS). All standards were run in selected reaction monitoring (SRM) mode; the [M–H]$^-$ $\rightarrow$ m/z 97 transition was employed for analysis and quantification. Each data point represents the mean of triplicate injections, with 1-σ error bars (here, the error bars are too small to be seen).
Figure S7
Analysis of Edmonton road dust using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) analysis: a) sample EDS spectrum and b) elemental mapping.

(a) sample EDS spectrum

(b) elemental mapping
Figure S8
XRD diffractograms of a) anatase, b) ilmenite, c) mica, and d) Edmonton road dust.

a)
Figure S8
XRD diffractograms of a) anatase, b) ilmenite, c) mica, and d) Edmonton road dust.

b)
Figure S8
XRD diffractograms of a) anatase, b) ilmenite, c) mica, and d) Edmonton road dust.

c)
Figure S8
XRD diffractograms of a) anatase, b) ilmenite, c) mica, and d) Edmonton road dust.
**Figure S9**

a) $^1$H and b) $^{13}$C NMR spectra of hydroxyacetone sulfate in D$_2$O.

a)

![1H NMR spectrum](image)

b)

![13C NMR spectrum](image)
Figure S10
a) $^1$H and b) $^{13}$C NMR spectra of propyl sulfate in D$_2$O.

a)

b)
Figure S11
High-resolution mass spectra of a) hydroxyacetone sulfate and b) propyl sulfate synthesized standards.

a)

![Mass spectra of hydroxyacetone sulfate](image1)

| Formula | Ion Species | Mass | Calc. Mass | m/z | Calc. m/z | Diff (mDa) | Diff (ppm) | DBE | Ion | Score |
|---------|-------------|------|------------|-----|-----------|------------|------------|-----|-----|-------|
| C3 H6 O5 S | C3 H5 O5 S | 153.9933 | 153.9938 | 152.9861 | 152.9863 | 0.28 | 1.69 | 11 | (M-H)+ | 91.64 |

b)

![Mass spectra of propyl sulfate](image2)

| Formula | Ion Species | Mass | Calc. Mass | m/z | Calc. m/z | Diff (mDa) | Diff (ppm) | DBE | Ion | Score |
|---------|-------------|------|------------|-----|-----------|------------|------------|-----|-----|-------|
| C3 H7 O4 S | C3 H6 O4 S | 140.0143 | 140.0143 | 139.007 | 139.0071 | 0.07 | 0.51 | 0 | (M-H)+ | 40.48 |
Figure S12
Product ion scans for a) hydroxyacetone sulfate, b) propyl sulfate, and c) the $m/z$ 253 organosulfate; all show $m/z$ 97 ($\text{HSO}_4^-$).
**Figure S13**

TiO$_2$-catalyzed (0.5 mg mL$^{-1}$) loss of hydroxyacetone sulfate (HAS; 7 ppm) in the presence and absence of methacrolein (10 mM) as a function of illumination time. Experiments were performed in the absence of sulfate salts. Each experiment was performed once; the solid lines are linear fits to the experimental data. No HAS loss was observed under dark conditions (*i.e.* HAS concentrations were identical after 30 min stirring; results not shown).
Figure S14
Formation of hydroxyacetone sulfate (m/z 153) upon 30 min illumination in 1 M Na$_2$SO$_4$ (adjusted to pH 5 using 50 mM aqueous H$_2$SO$_4$) or 1 M (NH$_4$)$_2$SO$_4$ in the presence of 0.5 mg mL$^{-1}$ TiO$_2$ as a function of methacrolein concentration. Each data point represents the mean of three experimental trials, with 1-σ error bars.
Figure S15
Time-dependent production of a set of organosulfates with m/z 253 from methacrolein (10 mM) in illuminated suspensions of TiO$_2$ in aqueous Na$_2$SO$_4$ (1 M; adjusted to pH 5). In all cases, data points represent the mean of three trials, with 1σ error bars. The dashed lines are linear fits to the experimental data.
**Table S1**  
Summary of mass spectrometric parameters.

| Parameter                  | Value     |
|----------------------------|-----------|
| **ESI voltages**           |           |
| Capillary                  | 2.8 kV    |
| Cone                       | 25 V      |
| Extractor                  | 1         |
| RF Lens                    | 0.9       |
| **Temperatures**           |           |
| Source                     | 120 °C    |
| Desolvation                | 275 °C    |
| **Gas flows**              |           |
| Desolvation                | 300 L h⁻¹ |
| Cone                       | 30 L h⁻¹  |
| **MRM method**             |           |
| Transition to product ion  | [M-H]⁻ → m/z 97 |
| Dwell time                 | 0.1 s     |
| Cone voltage               | 25 V      |
| Collision energy           | 20 eV     |
Table S2
Specific surface areas (BET; m² g⁻¹) of three of the samples employed in these experiments.

| Sample         | Specific surface area (BET; m² g⁻¹) |
|----------------|-------------------------------------|
| TiO₂ (commercial) | 11.22                               |
| anatase        | 5.172                               |
| ilmenite       | 2.152                               |
Table S3
Elemental composition of a) anatase, b) ilmenite, and c) mica samples obtained via electron microprobe analysis. The point numbers in the tables correspond to the points labelled in the back-scattered-electron images for each mineral sample provided below the tables. In all cases, results below the estimated limits of detection at 99% confidence have been set to zero.

a)

| Point # | Nb₂O₅ | SiO₂ | TiO₂ | ZnO | Al₂O₃ | V₂O₅ | Cr₂O₃ | Fe₂O₃total | MnO | MgO | CaO | Na₂O | K₂O | Total |
|-------|------|-----|-----|-----|-------|------|------|------------|-----|-----|-----|------|-----|-------|
| 193   | 0.09 | 0.00| 99.63| 0.00| 0.00  | 0.03 | 0.00 | 0.03       | 0.00| 0.00| 0.00| 0.00  | 0.00| 99.78 |
| 194   | 0.07 | 0.00| 100.12| 0.00| 0.00  | 0.08 | 0.00 | 0.00       | 0.00| 0.00| 0.00| 0.00  | 0.00| 100.27|
| 195   | 0.08 | 0.00| 99.19| 0.00| 0.00  | 0.10 | 0.00 | 0.09       | 0.00| 0.00| 0.00| 0.00  | 0.00| 99.46 |
| 196   | 0.07 | 0.00| 99.70| 0.00| 0.00  | 0.00 | 0.00 | 0.00       | 0.00| 0.00| 0.00| 0.00  | 0.00| 99.77 |
| 197   | 0.12 | 0.02| 99.51| 0.00| 0.00  | 0.04 | 0.00 | 0.03       | 0.00| 0.00| 0.00| 0.00  | 0.00| 99.72 |
| 198   | 0.00 | 0.00| 99.30| 0.00| 0.00  | 0.02 | 0.00 | 0.03       | 0.00| 0.00| 0.00| 0.00  | 0.00| 99.41 |
| 199   | 0.00 | 0.00| 99.14| 0.00| 0.00  | 0.11 | 0.00 | 0.03       | 0.00| 0.00| 0.00| 0.01  | 0.00| 99.29 |
| 200   | 0.10 | 0.00| 99.14| 0.00| 0.00  | 0.10 | 0.00 | 0.05       | 0.00| 0.00| 0.00| 0.00  | 0.00| 99.39 |

Average: 0.07, 0.00, 99.47, 0.00, 0.00, 0.07, 0.00, 0.03, 0.00, 0.00, 0.00, 0.00, 0.00, 99.64
Std Dev: 0.04, 0.01, 0.34, 0.00, 0.01, 0.04, 0.00, 0.03, 0.00, 0.00, 0.00, 0.00, 0.00, 0.32
Min: 0.00, 0.00, 99.14, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00, 99.29
Max: 0.12, 0.02, 100.12, 0.00, 0.02, 0.11, 0.00, 0.09, 0.00, 0.00, 0.00, 0.01, 0.00, 100.27
Table S3
Elemental composition of a) anatase, b) ilmenite, and c) mica samples obtained via electron microprobe analysis. The point numbers in the tables correspond to the points labelled in the back-scattered-electron images for each mineral sample provided below the tables. In all cases, results below the estimated limits of detection at 99% confidence have been set to zero.

| Point # | Nb2O5 | SiO2 | TiO2 | ZnO | Al2O3 | V2O5 | Cr2O3 | FeOtotal | MnO | MgO | CaO | Na2O | K2O | Total |
|---------|-------|------|------|-----|-------|------|-------|----------|-----|-----|-----|------|-----|-------|
| 209     | 0.00  | 0.02 | 50.01| 0.04| 0.00  | 0.00 | 0.00  | 46.09    | 0.66| 0.00| 0.00| 0.00 | 0.00| 96.02 |
| 210     | 0.00  | 0.00 | 50.73| 0.00| 0.00  | 0.00 | 0.00  | 46.03    | 0.71| 0.00| 0.00| 0.00 | 0.00| 97.47 |
| 211     | 0.00  | 0.00 | 50.94| 0.04| 0.00  | 0.00 | 0.00  | 45.86    | 0.69| 0.00| 0.00| 0.00 | 0.00| 97.53 |
| 212     | 0.00  | 0.01 | 50.10| 0.03| 0.00  | 0.00 | 0.00  | 46.43    | 0.69| 0.00| 0.00| 0.00 | 0.00| 97.26 |
| 214     | 0.47  | 0.00 | 51.44| 0.00| 0.00  | 0.00 | 0.00  | 44.53    | 0.71| 0.00| 0.00| 0.00 | 0.00| 97.15 |
| 215     | 0.00  | 0.00 | 50.49| 0.03| 0.00  | 0.00 | 0.00  | 45.87    | 0.71| 0.00| 0.00| 0.00 | 0.00| 97.10 |
| 216     | 4.48  | 0.00 | 53.50| 0.02| 0.00  | 0.06 | 0.00  | 38.96    | 0.60| 0.03| 0.00| 0.00 | 0.00| 97.65 |
| **Average** | 0.71  | 0.00 | 51.03| 0.02| 0.00  | 0.01 | 0.00  | 44.82    | 0.68| 0.00| 0.00| 0.00 | 0.00| 97.27 |
| **Std Dev** | 1.67  | 0.01 | 1.10 | 0.02| 0.01  | 0.02 | 0.00  | 2.65     | 0.04| 0.01| 0.00| 0.00 | 0.00| 97.65 |
| **Min** | 4.48  | 0.02 | 53.50| 0.04| 0.02  | 0.06 | 0.00  | 46.43    | 0.71| 0.03| 0.00| 0.00 | 0.00| 97.65 |

*Property in sample, not used in average*

| 213     | 0.00  | 347  | 14.82| 0.00| 1.53  | 0.04 | 0.00  | 66.95    | 0.79| 0.14| 0.00| 0.00 | 0.00| 87.34 |
Table S3
Elemental composition of a) anatase, b) ilmenite, and c) mica samples obtained via electron microprobe analysis. The point numbers in the tables correspond to the points labelled in the back-scattered-electron images for each mineral sample provided below the tables. In all cases, results below the estimated limits of detection at 99% confidence have been set to zero.

c)

| Mica | \((K_{2}O,Na_{2}O)_{2+x+y}[Mg_{2-x-y}Fe_{x+y}Ti_{y}(Al_{1-x-y}Mn_{x+y})_{2+y}O_{2+y}(Si_{1+y}Al_{2-x-y})_{2}O_{12}[OH]_{2}]\) |
|------|----------------------------------------------------------------------------------------------------------------------------------|
| point # | Nb₂O₅ | SiO₂ | TiO₂ | ZnO | Al₂O₃ | V₂O₅ | Cr₂O₃ | FeO_total | MnO | MgO | CaO | Na₂O | K₂O | Total |
| 377  | 0.00 | 42.02 | 0.92 | 0.00 | 11.08 | 0.00 | 0.00 | 6.66 | 0.13 | 22.43 | 0.00 | 0.43 | 10.07 | 94.62 |
| 379  | 0.00 | 42.00 | 0.98 | 0.00 | 11.02 | 0.00 | 0.00 | 6.60 | 0.13 | 22.23 | 0.00 | 0.18 | 10.51 | 94.53 |
| 380  | 0.00 | 42.05 | 1.05 | 0.07 | 11.20 | 0.00 | 0.00 | 6.80 | 0.13 | 22.05 | 0.00 | 0.25 | 10.31 | 94.71 |
| 381  | 0.00 | 42.53 | 1.02 | 0.09 | 11.19 | 0.00 | 0.00 | 5.79 | 0.12 | 22.26 | 0.00 | 0.34 | 10.17 | 94.51 |
| 382  | 0.00 | 42.83 | 1.04 | 0.07 | 11.10 | 0.00 | 0.00 | 5.68 | 0.12 | 22.33 | 0.00 | 0.25 | 10.39 | 94.61 |
| 383  | 0.00 | 42.68 | 1.05 | 0.08 | 10.95 | 0.00 | 0.00 | 5.79 | 0.12 | 22.05 | 0.00 | 0.33 | 10.25 | 94.30 |
| 384  | 0.00 | 42.23 | 1.07 | 0.06 | 11.17 | 0.00 | 0.00 | 5.88 | 0.14 | 22.15 | 0.00 | 0.36 | 10.17 | 94.23 |
| Average | 0.00 | 42.68 | 1.02 | 0.08 | 11.10 | 0.00 | 0.00 | 5.74 | 0.13 | 22.39 | 0.00 | 0.31 | 10.27 | 94.52 |
| Std Dev | 0.00 | 0.23 | 0.05 | 0.01 | 0.09 | 0.00 | 0.00 | 0.10 | 0.01 | 0.13 | 0.00 | 0.08 | 0.15 | 0.10 |
| Min   | 0.00 | 42.23 | 0.92 | 0.06 | 10.95 | 0.00 | 0.00 | 5.60 | 0.12 | 22.05 | 0.00 | 0.10 | 10.07 | 94.23 |
| Max   | 0.00 | 42.85 | 1.07 | 0.09 | 11.20 | 0.00 | 0.00 | 6.88 | 0.14 | 22.43 | 0.00 | 0.43 | 10.51 | 94.71 |
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