

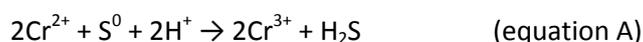
Supplementary Material (A)

A.1 Whole-rock chemical sulphur extraction: detailed methodology

Powdered rock samples were loaded into a flat-bottomed glass reaction vessel, with a large magnetic stirrer. A five-leg lid was used to seal the vessel, and clamped in position. The vessel was installed on a magnetic hotplate. A nitrogen gas line was fitted into the vessel lid. In addition, a rubber septum was fitted to one of the other legs, and a condenser clamped and installed vertically from the leg at the top of the vessel. The remaining two legs were blocked off. A Nalgene pipe fitting was connected from the top of the condenser to a gas bell jar, with a glass tube (no gas disperser) feeding down into 100ml of 0.1M AgNO₃ solution. The whole apparatus was constructed and operated in a fume cupboard.

At the start of the experiment, the nitrogen gas was turned on and allowed to circulate and equilibrate through the apparatus for a minimum of 20 minutes (at a rate of two or three gas bubbles a second bubbling into the gas bell jar). Once the apparatus was purged and under a N₂ atmosphere, the hotplate and stirrer were set to approximately 150°C, and a 1M solution of chromous chloride (CrCl₂) injected through the septum so that the entire powdered sample was submerged (approximately 80-100ml). The condenser was turned on to cool the sulphurous gases (mostly H₂S) produced by the reaction. The reaction was allowed to equilibrate for 3 hours.

During the reaction, chromous chloride solution reduces sulphur in the sample by the following reaction:



This process leads to the complete breakdown of elemental and reduced sulphur species into H₂S, including in the presence of Fe³⁺. During the reaction, H₂S was continually removed by the stream of N₂ gas and bubbled through the condenser and into the 0.1M AgNO₃ solution in the gas bell jar. Reaction with AgNO₃ produced a black precipitate of Ag₂S. At the end of the 3 hour period, the hotplate and nitrogen gas line were turned off. The contents of the gas bell jar (Ag₂S precipitate suspended in AgNO₃ solution) were filtered under a vacuum through a 0.45µm Millipore® cellulose filter paper. The filtrate was washed twice (still under vacuum) using 100ml of 18.2MΩ deionised water. The paper was collected and freeze dried overnight (or for a minimum of 4 hours). The dry Ag₂S was scraped off the filter papers using a spatula and collected and sealed in a clean sample bottle, ready for conventional sulphur isotope analysis.

A.2 Whole-rock chemical sulphur extraction: apparatus diagram

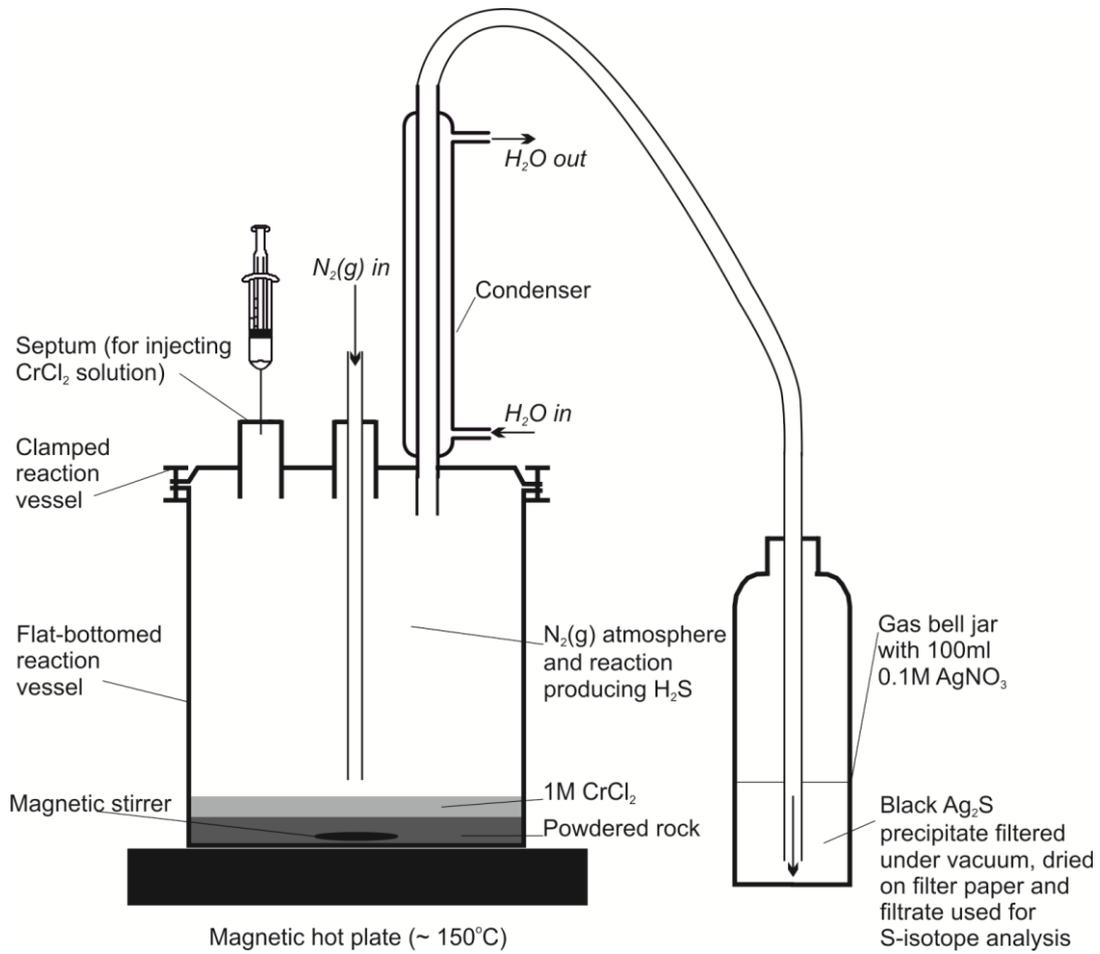
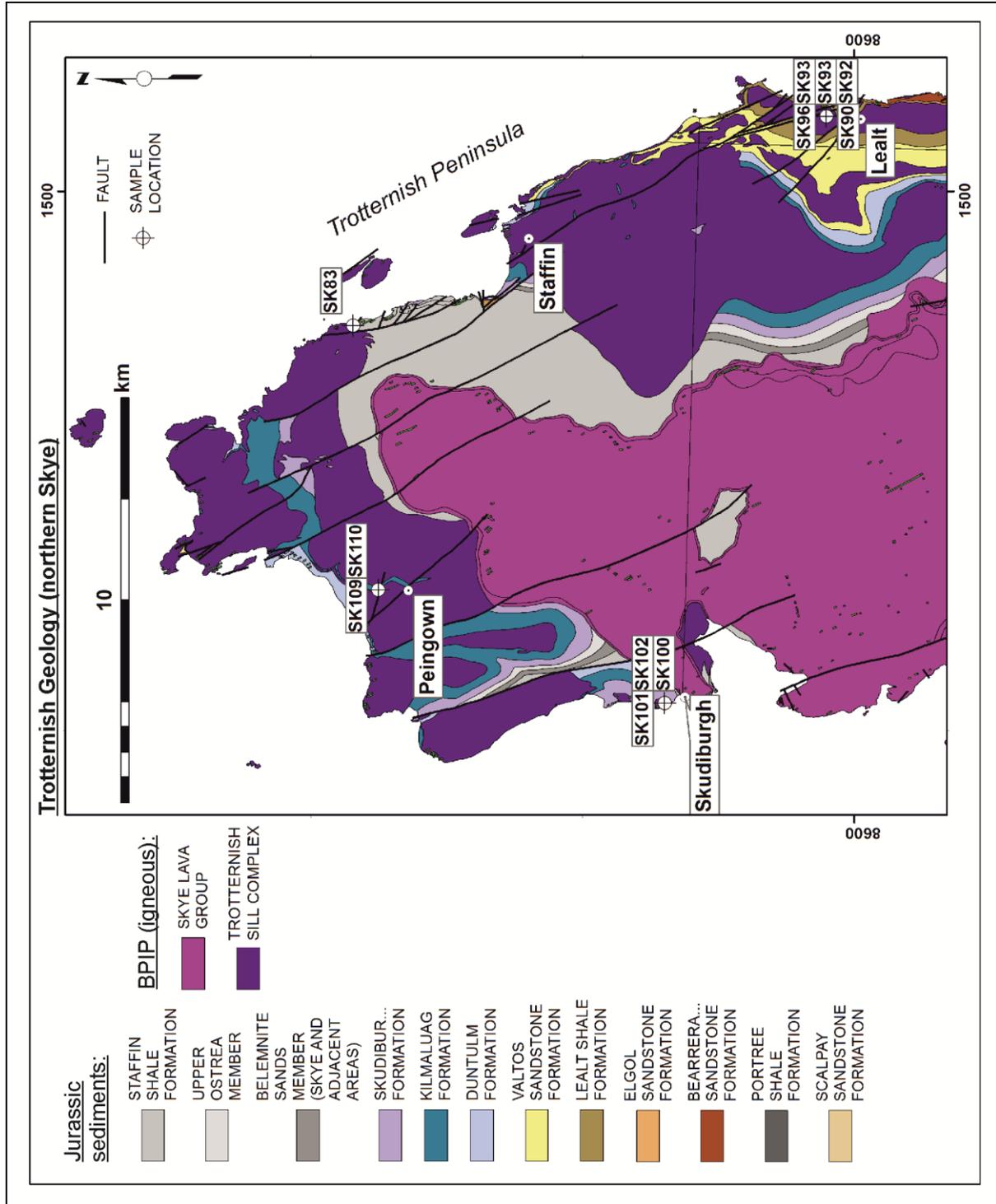


Figure A: Apparatus set-up and procedure for whole-rock S-extraction, as described in Supplementary Material section A.

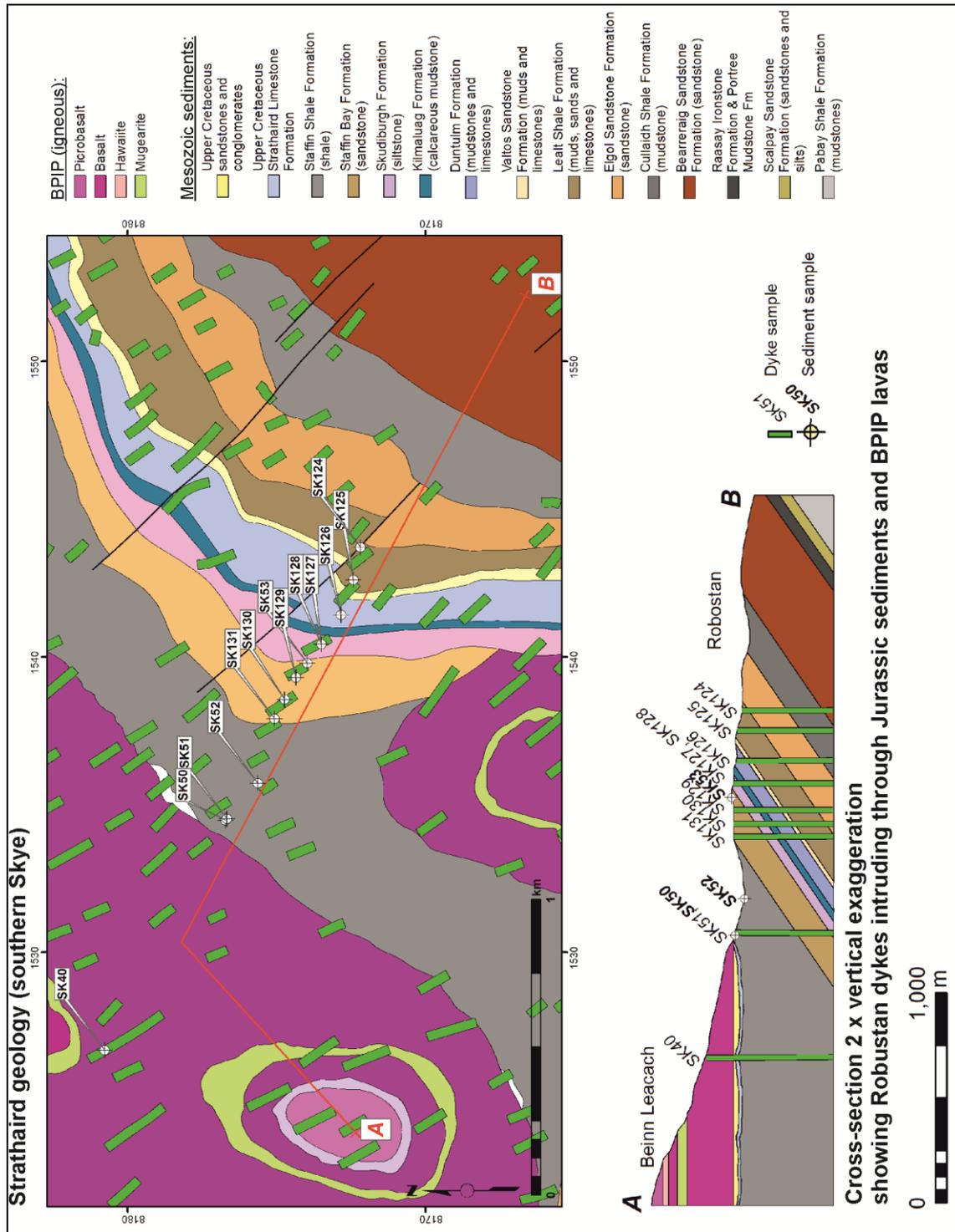
Supplementary Material (B)

B.1 Supplementary northern Skye map: Simplified geology of the Trotternish Sill Complex on the Trotternish Peninsula, showing sample locations



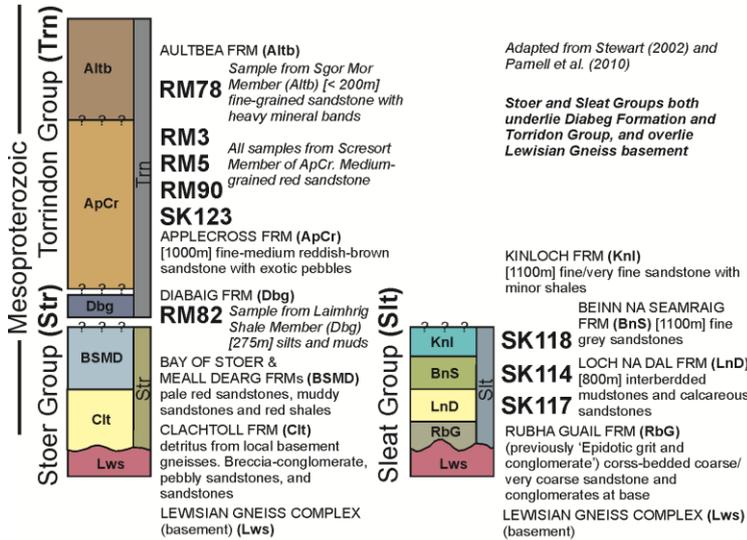
B.2 Supplementary southern Skye map: Strathaird Peninsula and Robustan-Kirkibost area.

Simplified geological map and sample locations. Line of cross-section displays position of the dyke samples as projected parallel to the strike of the sediment bedding planes, with the exception of sample SK40, which has been projected onto the cross-section along the strike of the dyke itself. Dykes drawn assuming vertical dip. Sediments dip approximately 10° dip NNW below the sediment-lava contact at Scaladal Burn (note cross-section shows 2 x vertical exaggeration). Extent of dyke structure under the current surface level is unknown – cross-section projects dykes for display purposes only.

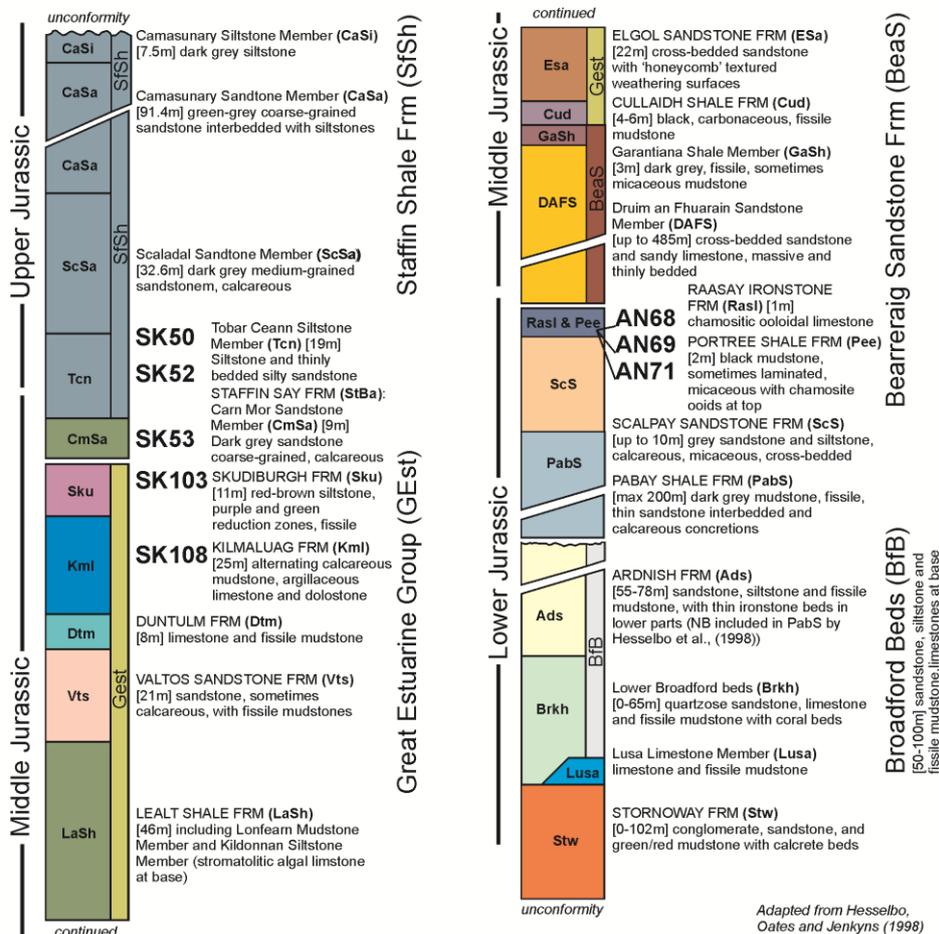


B.3 Supplementary stratigraphic section: (a) Simplified Mesoproterozoic sedimentary log, based on Stewart (2002) and Parnell *et al.*, (2010). (b).Simplified Hebrides Basin Jurassic sedimentary log, based on and adapted from Hesselbo *et al.*, (1998).

(a) Simplified stratigraphic column for Mesoproterozoic rocks exposed in the Hebrides

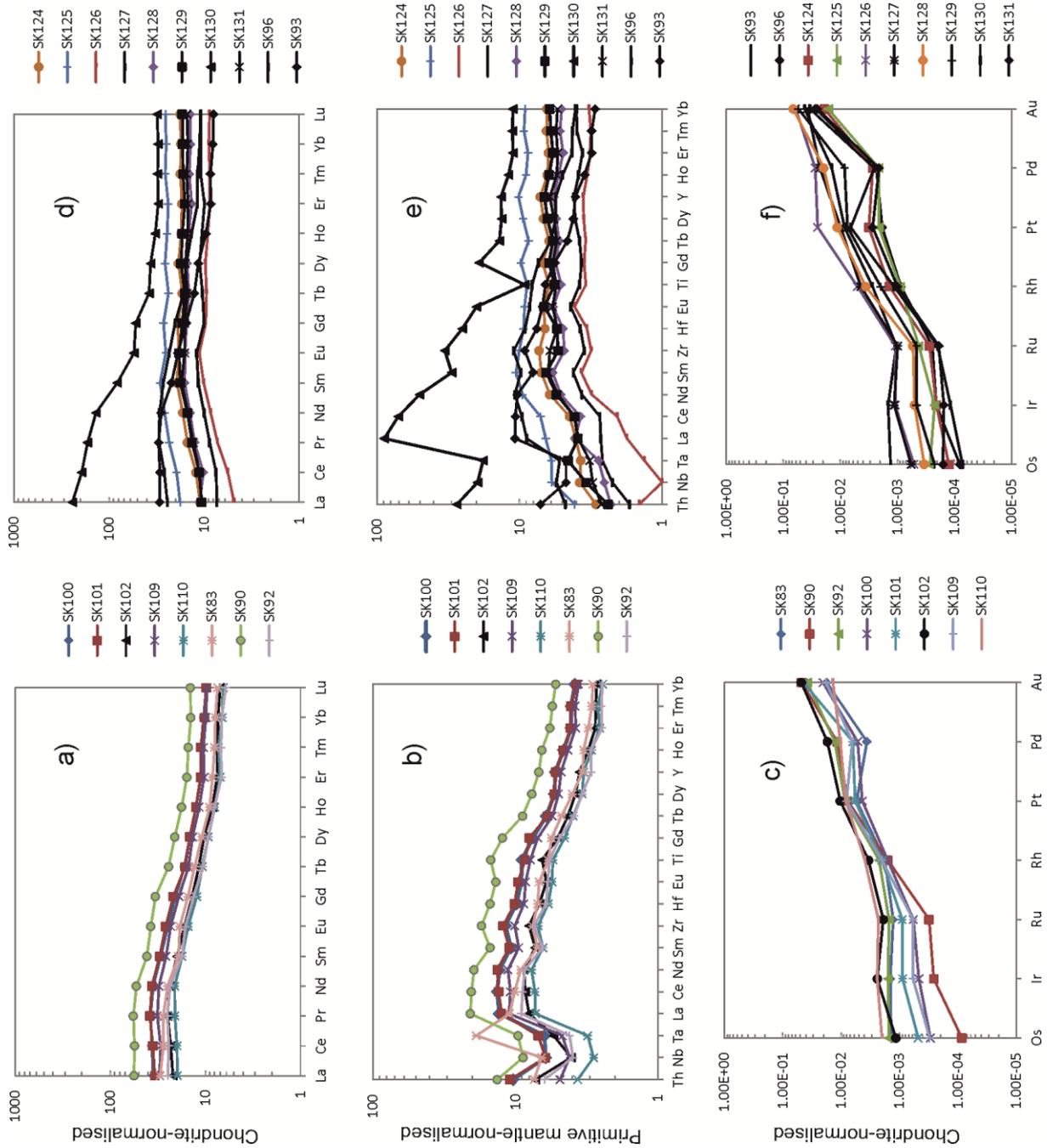


(b) Simplified stratigraphic column for Jurassic rocks of the Mesozoic Hebrides Basin

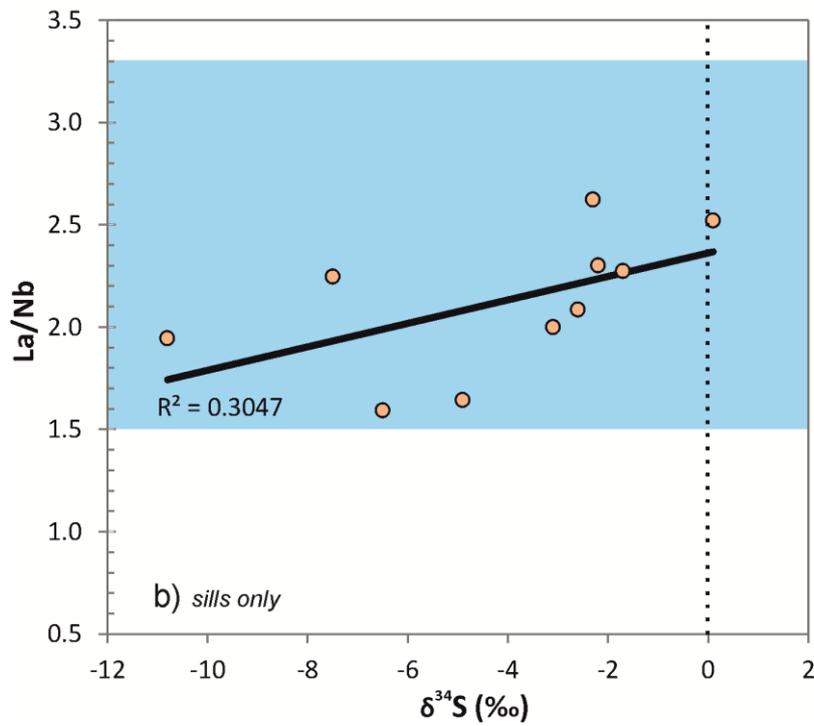
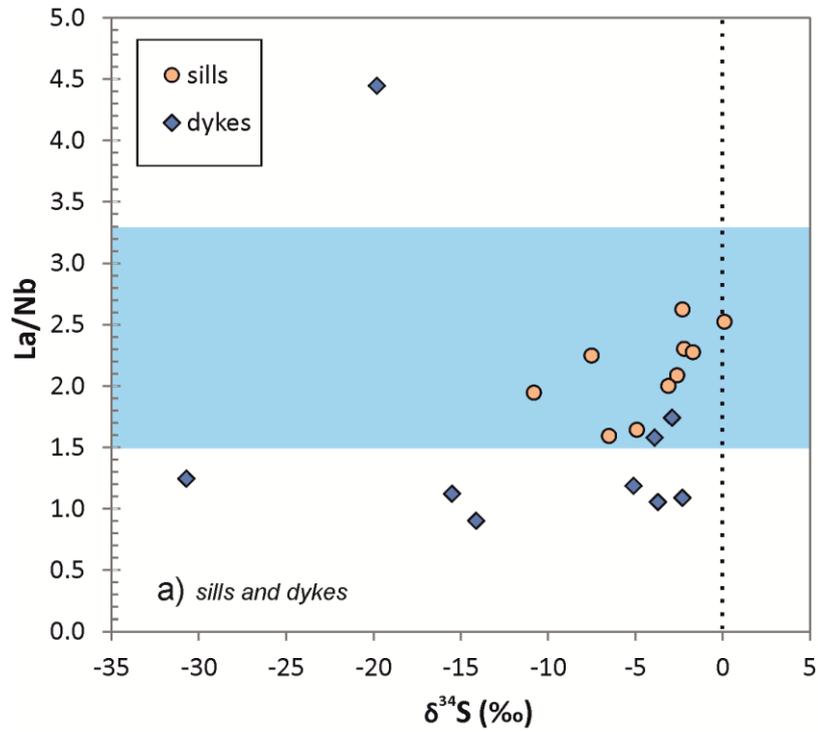


Supplementary Material (C)

C.1 Trace element diagrams sills and dykes: Multi-element normalised diagrams for dykes (a-c) and sills (d-f). Normalisation values from McDonough & Sun (1995). Samples in black highlight those with $\delta^{34}\text{S} < -5\text{‰}$.



C.2 La/Nb ratio of dykes and sills vs. $\delta^{34}\text{S}$: Blue shaded area denotes range of La/Nb ratios in Gibson (1990). Dashed line highlights 0‰ $\delta^{34}\text{S}$. (a) All sills and dykes. (b) sills only – with linear trend line displayed with calculated regression.



Supplementary Material (D)

D.1 Sulphur isotope results: sulphur extraction and conventional analysis vs. laser combustion

Conventional analyses of Ag₂S precipitates from our whole-rock sulphur extraction method were checked and cross-referenced with laser combustion analyses for sulphide minerals from corresponding samples. A maximum variance of $\pm 1.4\text{‰}$ was found between laser and precipitated samples for three sets of corresponding samples (SK127, SK129 and SK130). This variation was not systematic (i.e. neither a positive or negative shift in $\delta^{34}\text{S}$), but results from the laser combustion method usually had lighter $\delta^{34}\text{S}$ than the Ag₂S precipitates. This variation is likely the result of slightly differing $\delta^{34}\text{S}$ of elemental S, sulphide and sulphate species and within various silicate phases of the rock vs. sulphide minerals (normally pyrite), which would be averaged out during whole-rock sulphur extraction. In addition, a repeated sulphur extraction was run for a duplicate sample (SK52 – Jurassic siltstone). $\delta^{34}\text{S}$ results for this duplicate extraction varied only $\pm 0.2\text{‰}$.

Sample	SK127	SK127	SK127	SK127	SK129	SK129	SK129	SK130	SK130	SK130
Method	WRS/C	WRS/C	Py/L	Py/L	WRS/C	Py/L	Py/L	WRS/C	Py/L	Py/L
$\delta^{34}\text{S}$ (‰)	-6.6	-6.3	-3.9	-3.6	-15.5	-15.2	-15.7	-21.3	-17.9	-18.4

Table D.1: $\delta^{34}\text{S}$ results for three dykes comparing whole-rock S-extraction methodology followed by conventional analysis (WRS/C) vs. laser combustion of pyrite (Py/L).

D.2 Sulphur isotope sample duplicates

Conventional method:

SK127	SK127	SK131	SK131	SK52	SK52	SK52(2)	SK51	SK51
-6.6‰	-6.3‰	-30.7‰	-30.7‰	-29.2‰	-29.6‰	-29.0‰	-13.9‰	-14.2‰

Laser combustion:

SK50	SK50	SK50	SK93b	SK93b	SK127	SK127	SK129	SK129	SK130	SK130
-33.1‰	-33.2‰	-31.6‰	-8.0‰	-6.9‰	-3.9‰	-3.6‰	-15.2‰	-15.7‰	-17.9‰	-18.9‰

Table D2: Duplicate $\delta^{34}\text{S}$ results for rock samples (conventional analysis) and pyrite-bearing samples (laser combustion). Note that SK52(2) was re-run through the whole S-extraction procedure and conventional analysis to check the consistency of the S-extraction reaction.