Supplementary Material for:

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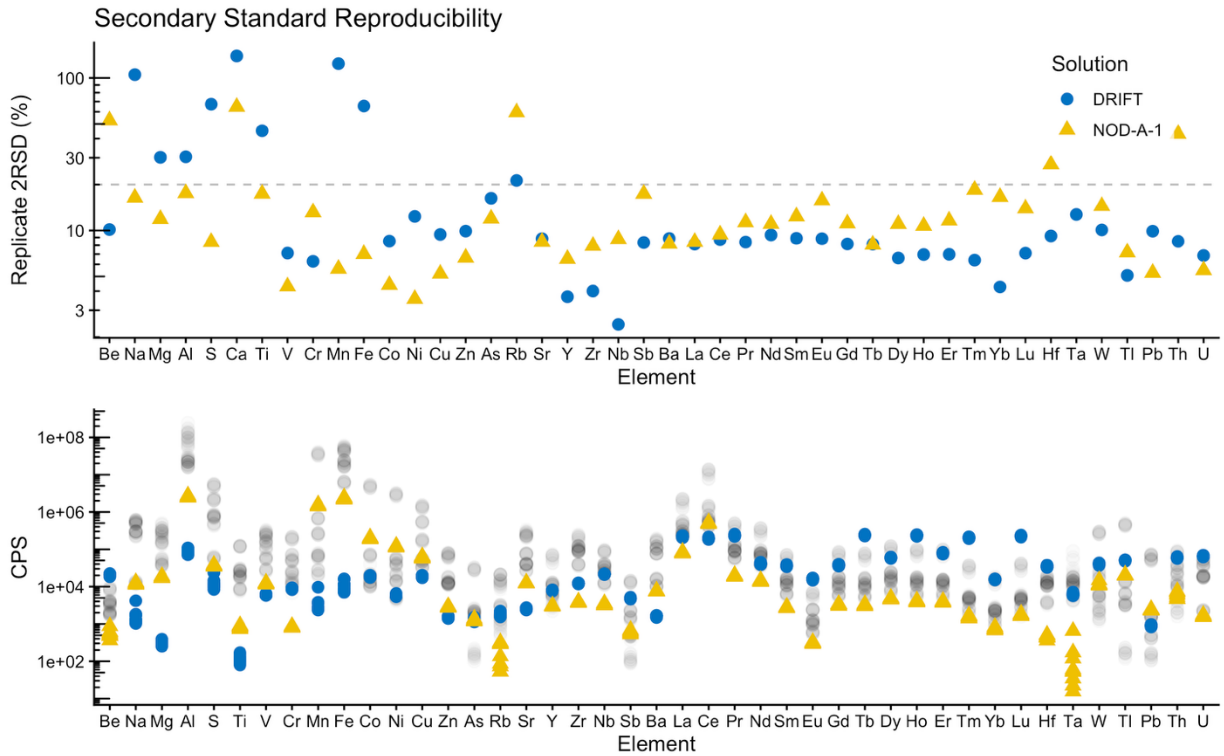
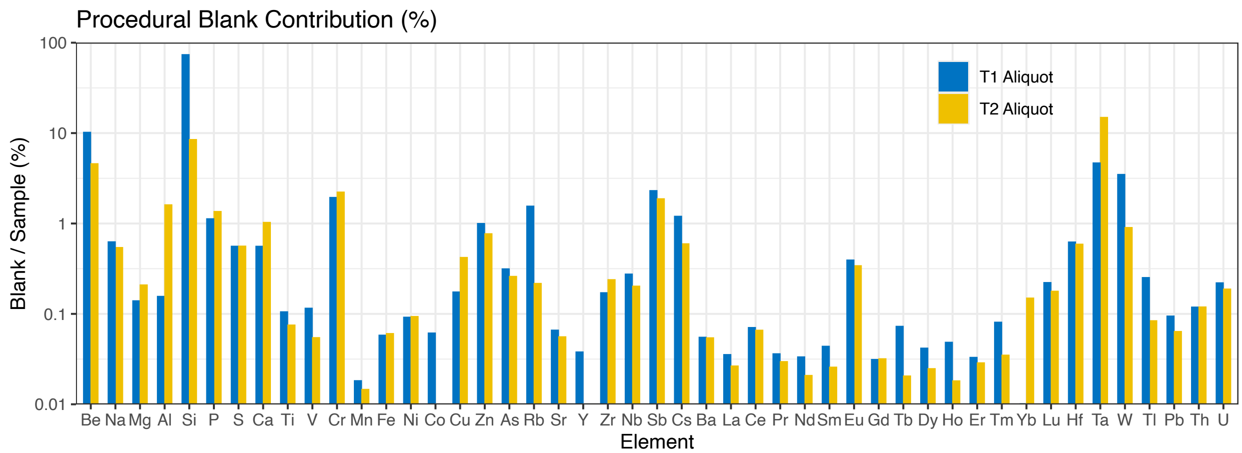
Supplementary Figures S1 to S6

Additional Supporting Information

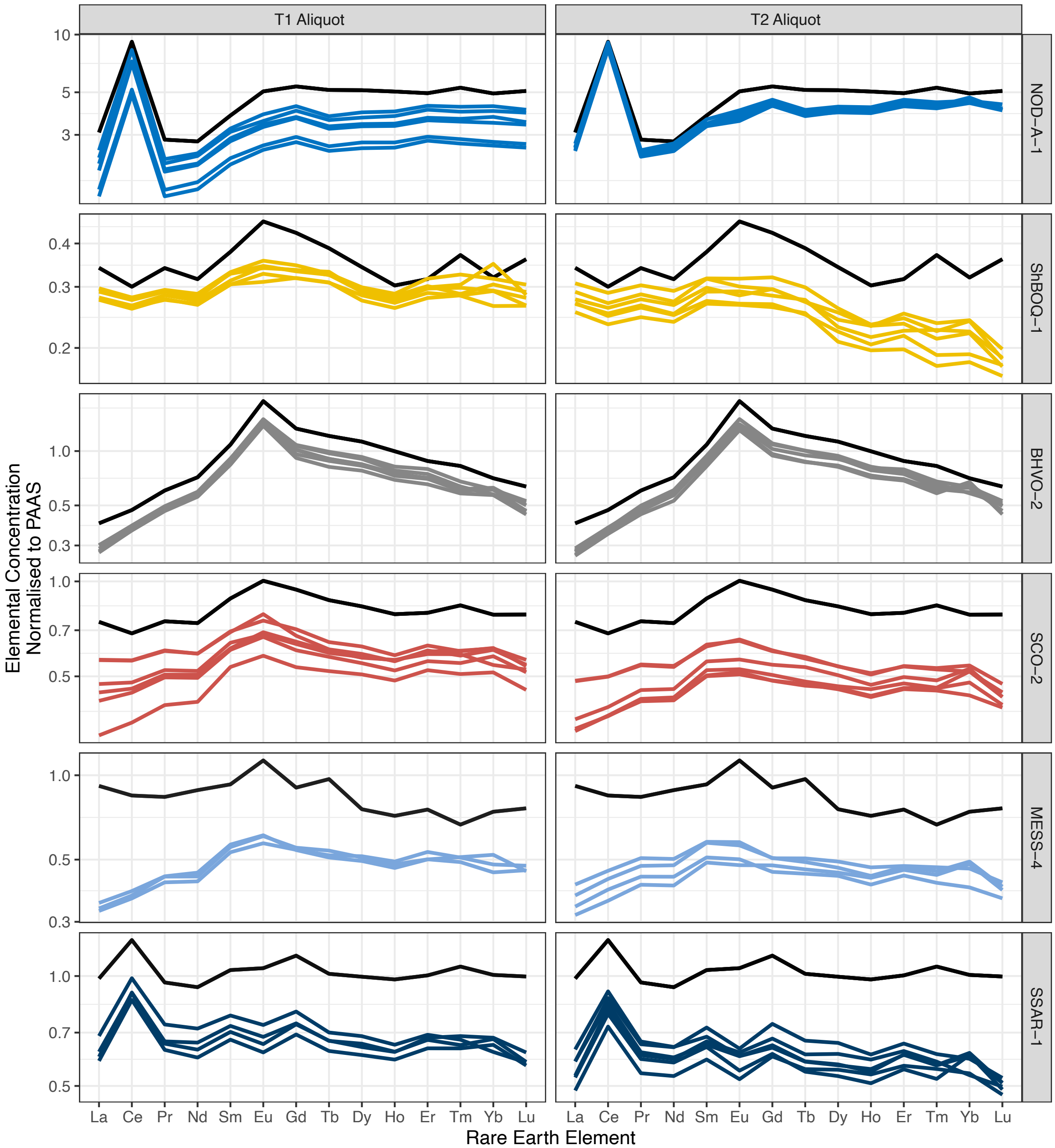
Supplementary Data Tables are available at https://doi.org/10.57744/LDLDB1186369



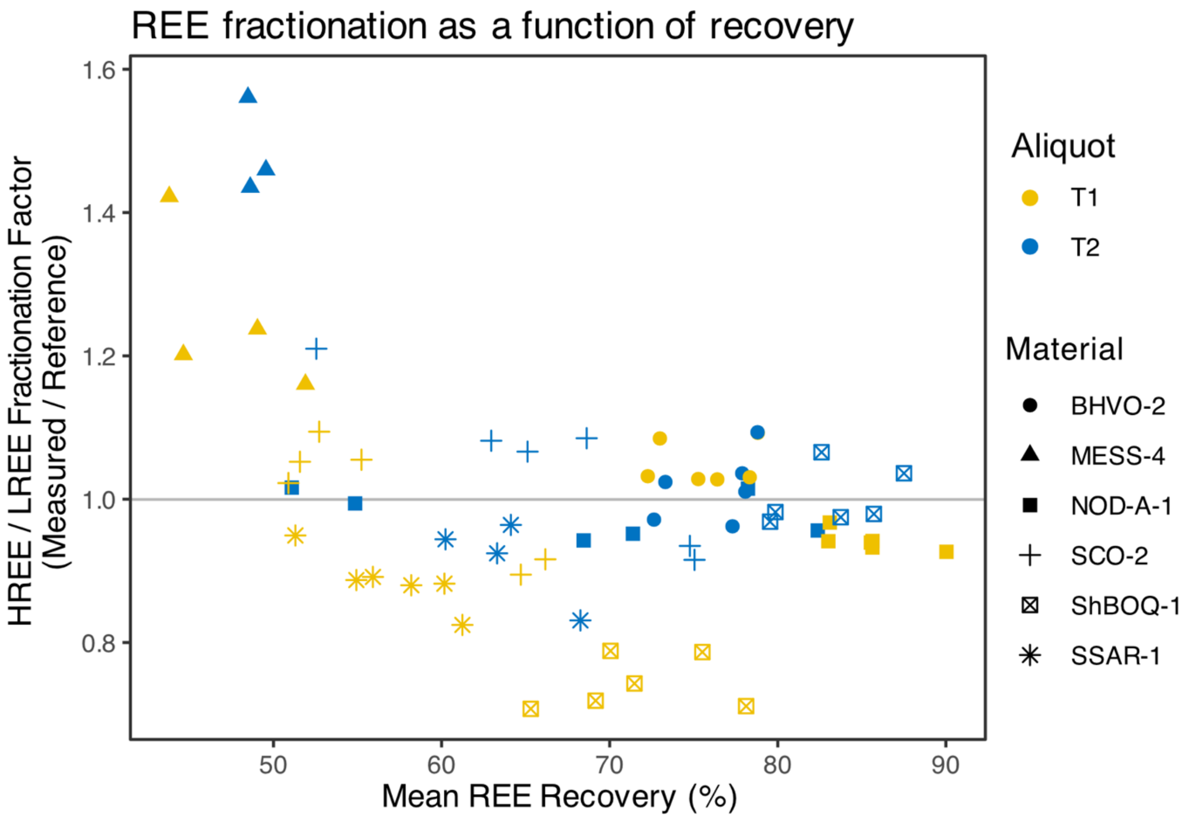
Supplementary Figure S1: Measurement reproducibility (upper) and count intensity (lower; counts per second; CPS) for NOD-A-1 (n = 9) and DRIFT (n = 10) reference solutions. The typical count intensity of digested samples is indicated by the grey circles in the lower panel, with each point marking an individual measurement. The DRIFT multi-element solution (1 ppb) better represents heavy element concentrations, whereas the NOD-A-1 solution more closely reflects light/major element concentrations. Across almost all reported elements, the uncertainty (2 relative standard deviations; 2RSD) was less than 20 % for the reference solution most representative of digested sample concentrations. There are two exceptions, Ca (2RSD = 64 %) and Rb (2RSD = 21 %), though the sample concentrations of Ca are at least an order of magnitude higher than in our reference solutions and therefore not reflective of typical sample measurement intensities.



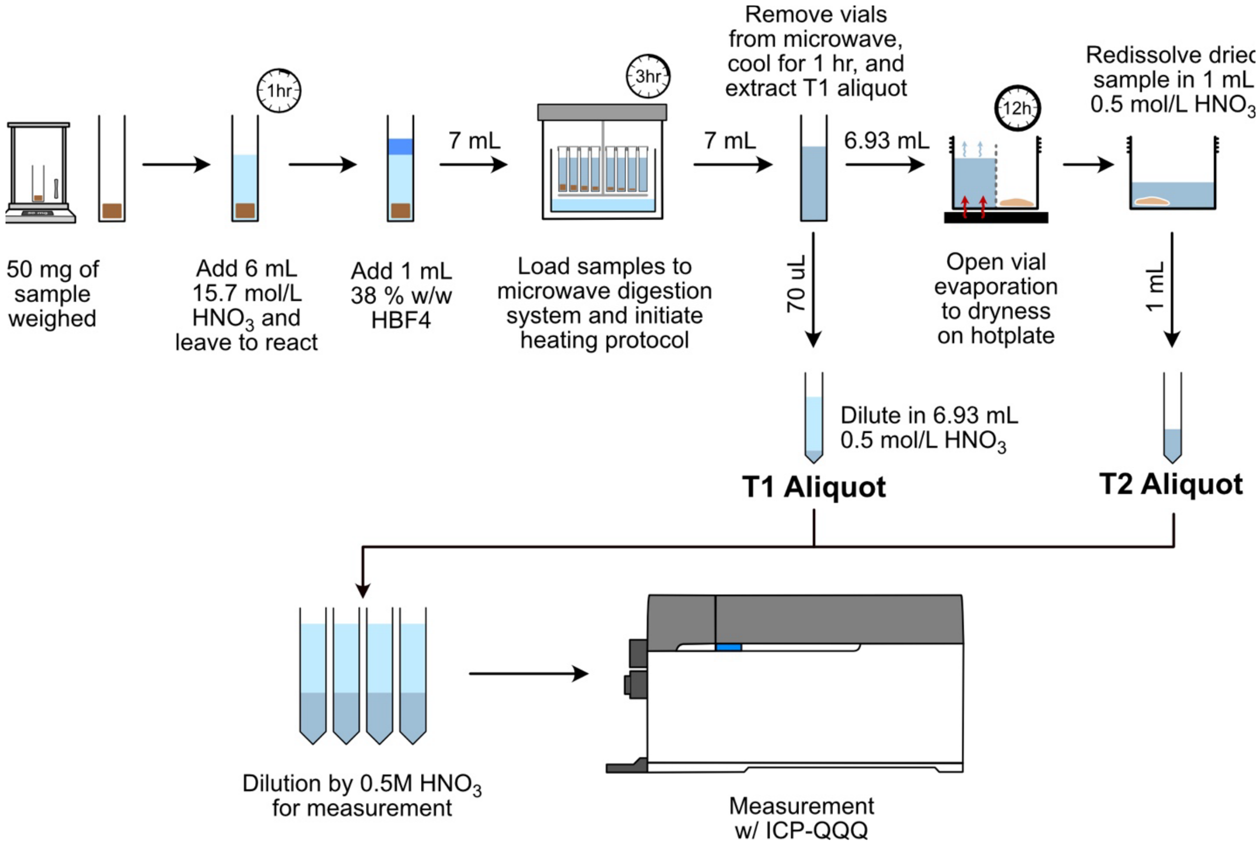
Supplementary Figure S2: Contribution of total procedural blanks compared to the lowest absolute concentration measurement from digested reference materials. Blank contribution is negligible for most elements, being typically less than 1 % and only exceeding 10 % in Si (T2) and Ta (T1). As blank contributions are significantly less than analytical uncertainty , procedural blank corrections were not applied.



Supplementary Figure S3: PAAS-normalised REE profiles measured from geological reference materials following HBF4 microwave digestion (coloured lines), compared to accepted values (black line). NOD-A-1, SSAR-1 and SCO-2 reference materials exhibit larger variability in their profiles due to matrix-dependent elemental reprecipitation insoluble fluorides and oxides, which affects the consistency of REE concentrations between replicate samples with different masses. To account for this variability, we secondarily normalised these values to the mean concentration of all REE in each measured sample, presented in Figure 3. This additional normalisation enables direct comparison of REE-only normalised values and resolves the matrix effect on REE recovery.



Supplementary Figure S4: Effect of absolute REE recovery on the fractionation of HREE / LREE across all measured samples. No systematic relationship is observed between absolute REE recovery and fractionation. Rather, fractionation appears mostly influenced by the chemical composition of reference materials, indicated by greater degrees of fractionation observed in the Al-rich MESS-4 and Ca-rich ShBOQ-1 reference materials.



Supplementary Figure S5: Procedural flow chart detailing the method steps taken for the preparation and analysis of geological samples.

Elemental recovery (T1)
Elemental recovery (T2)
Effect of evaporation and redissolution on elemental recovery
BHVO-2
MESS-4
NOD-A-1
SCO-2
ShBOQ-1
SSAR-1
Recovery (%)
T2 / T1 (%)
Element
STD

Supplementary Figure S6: Elemental recovery for T1 aliquots (upper panel) and T2 aliquots (middle panel), reflecting the relative yield of the digestion protocol before and after evaporation to dryness and subsequent redissolution, respectively. The lower panel shows the relative change in recovery between the T1 and T2 aliquots, where a value of 100% indicates no change in elemental recovery, and values greater than 100% indicate a higher elemental yield in solution following drying and redissolution. Data are displayed as violin plots, illustrating the frequency distribution of elemental recovery across measured samples for each reference material, shown in separate columns.

Supplementary References

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