

**Phantom zircons provide new insight to the evolution of one of the oldest
Banded Iron Formations on Earth (Isua Greenstone Belt, Greenland)**

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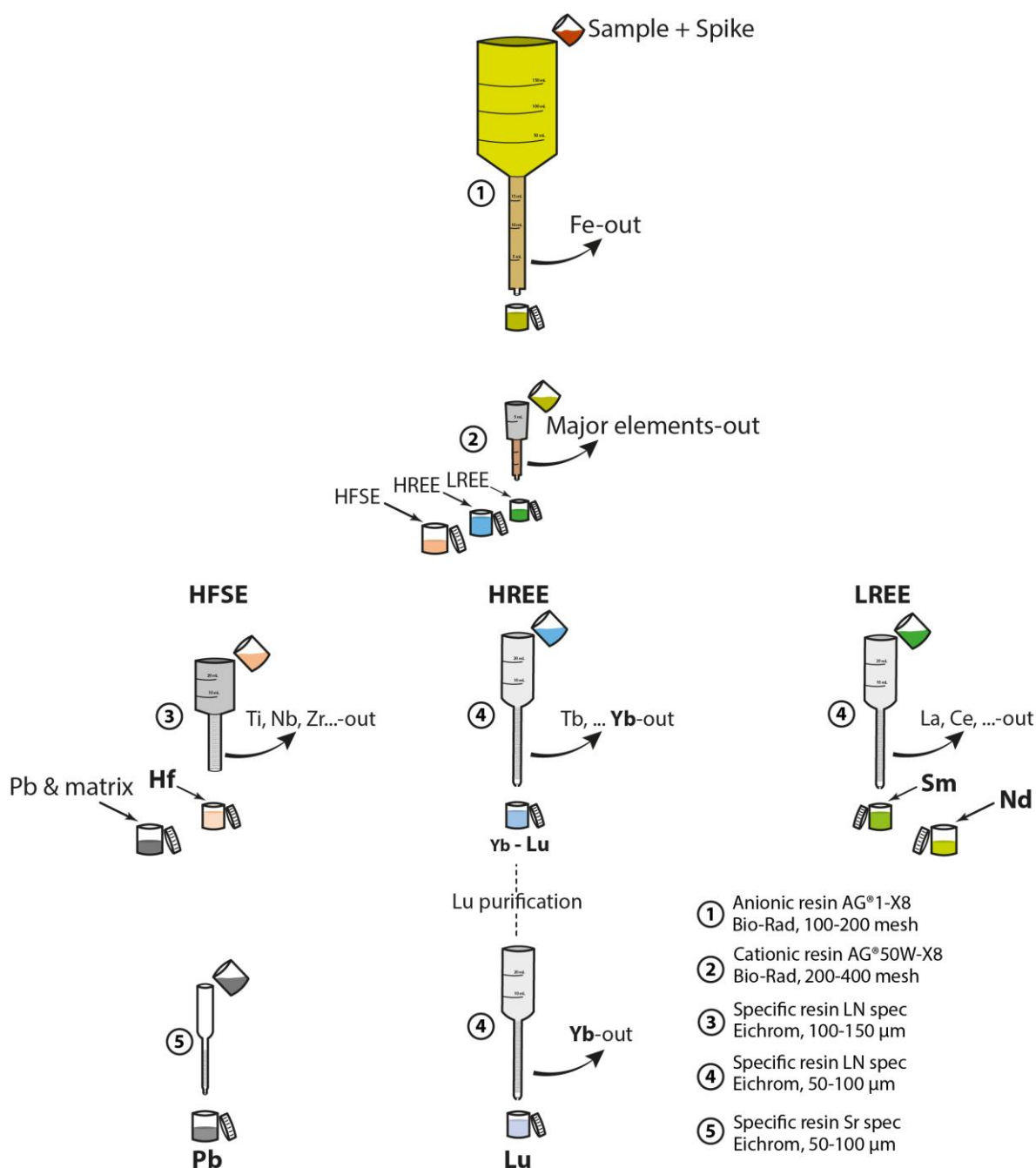
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Supplementary File A

A.1. Separation protocol of Lu, Hf, Sm, Nd and Pb by ion chromatography.

The procedure of separation and purification of elements of interest is schematically presented below:

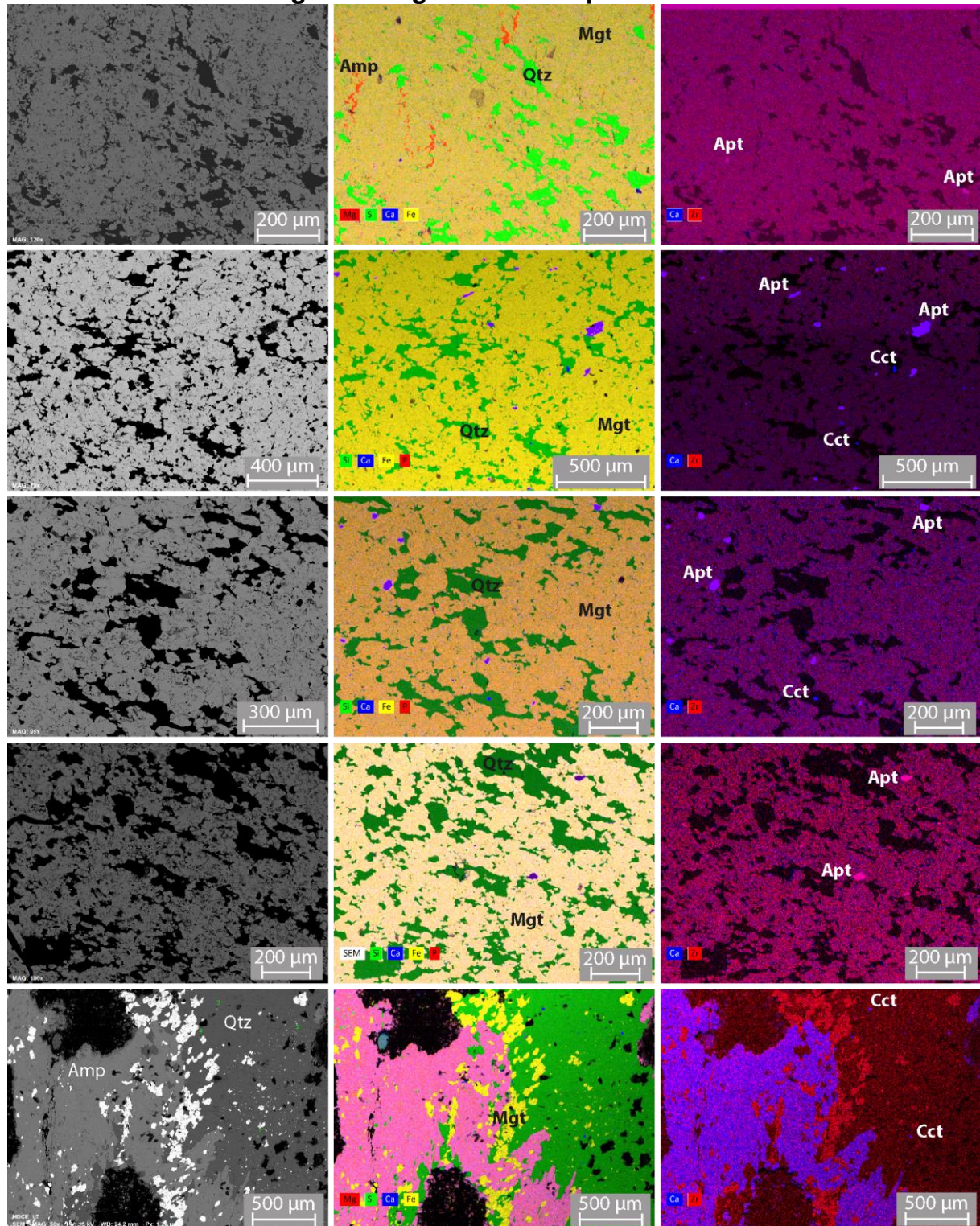


After complete dissolution of BIFs, the sample are loaded to remove the main Fe-matrix component using a 20 mL anionic resin (chloride form). Then, the separation is divided in three main fractions (HFSE, HREE and LREE) with a 2mL-column filled with cationic resin. The Hf, Lu, and Sm-Nd fractions are further purified using specific resin (Ln-spec). Lead is separated at the first step of the Hf purification column and then purified using a specific resin (Sr-spec). The Lu fraction is purified twice to remove a maximum of neighboring Yb interfering on Lu (^{176}Yb - ^{176}Lu) during MC-ICP-MS measurements.

A.2. Lu and Sm measurements.

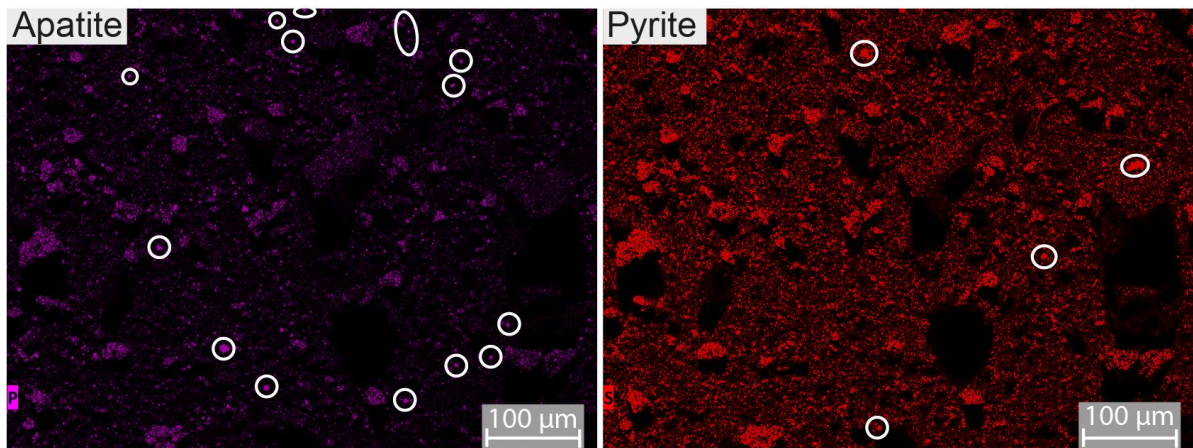
For Lu isotopic compositions, both instrumental mass fractionation and analytical drift during the measurement sequence were corrected by sample-standard bracketing using the Alfa Aesar Lu reference standard and a reference value of 0.02655 for $^{176}\text{Lu}/^{175}\text{Lu}$ (Lapen et al., 2004). The NIST Lu standard was analyzed as a quality standard and yielded an average $^{176}\text{Lu}/^{175}\text{Lu}$ ratio of 0.026553 ± 0.000010 ($n = 4$, 2SD) during the first sequence at 7,5 ppb and 0.026550 ± 0.000007 ($n = 4$, 2SD) during a second sequence at 10 ppb, which is similar to the value known for the Alfa Aesar Lu standard. For Sm isotopic compositions, the instrumental mass fractionation was corrected following the exponential law and a $^{147}\text{Sm}/^{152}\text{Sm}$ ratio of 0.56081.

A.3. Chemical SEM images of magnetite bands performed on IF-G thin section.



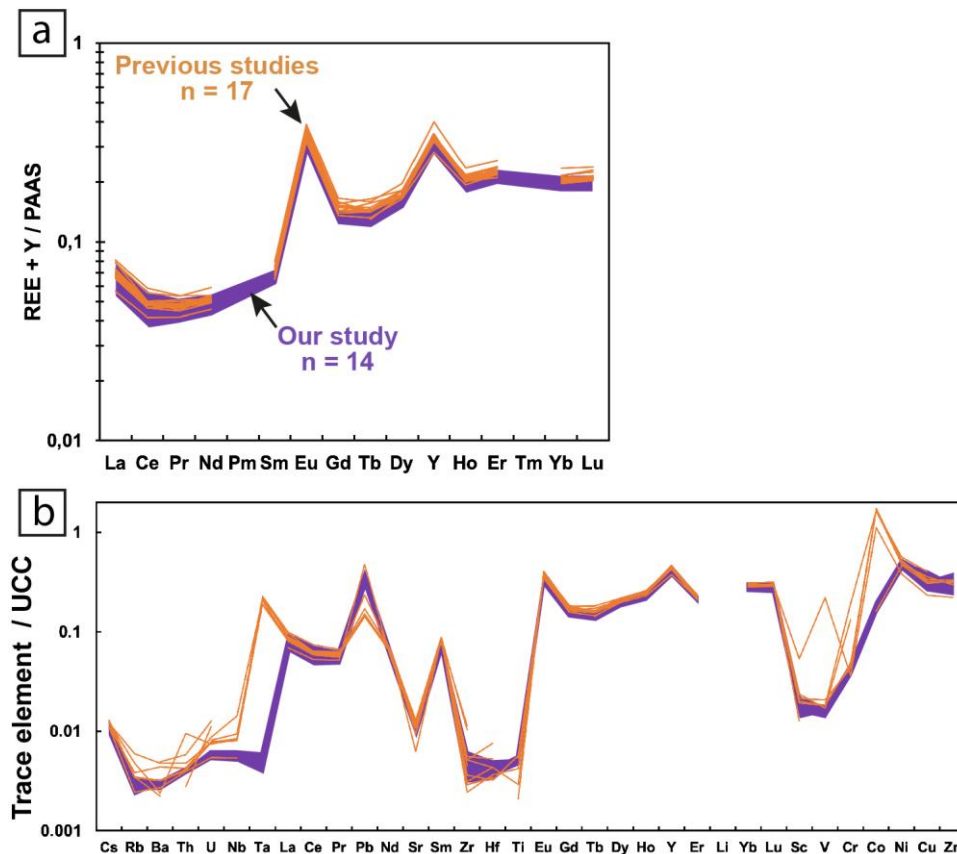
As magnetite is opaque in natural light, a reconnaissance phase has been performed on magnetite bands of the IF-G standard to check if zircon grains could be found. The chemical mapping did not find zircon with grain size larger than 10 μm . Chemical acquisition was performed at 15 kV and 73 μA in backscattered electron mode. Amp: amphibole (actinolite); Qtz: quartz; Apt: apatite; Mgt: magnetite; Cct: calcite.

A.4. Chemical SEM imaging of phosphorus and sulfur in the IF-G powder.



Apatite and pyrite mineral are visible with phosphorus (P) and sulfur (S) chemical SEM mapping, respectively. Apatite content in the powder has been estimated based on the surface area with high P signal to be around 1 to 2 %, whereas pyrite content is less than 1 %. Chemical acquisition performed at 15 kV in backscattered electron mode.

A.5. IF-G Trace element patterns - Comparison between literature data and our study.



Comparison of the trace element patterns from the literature and our study. (a) Literature REE+Y pattern agree with our IF-G pattern and highlight similar variability in Light Rare Earth Elements. (b) Multi-element patterns compiled from the literature

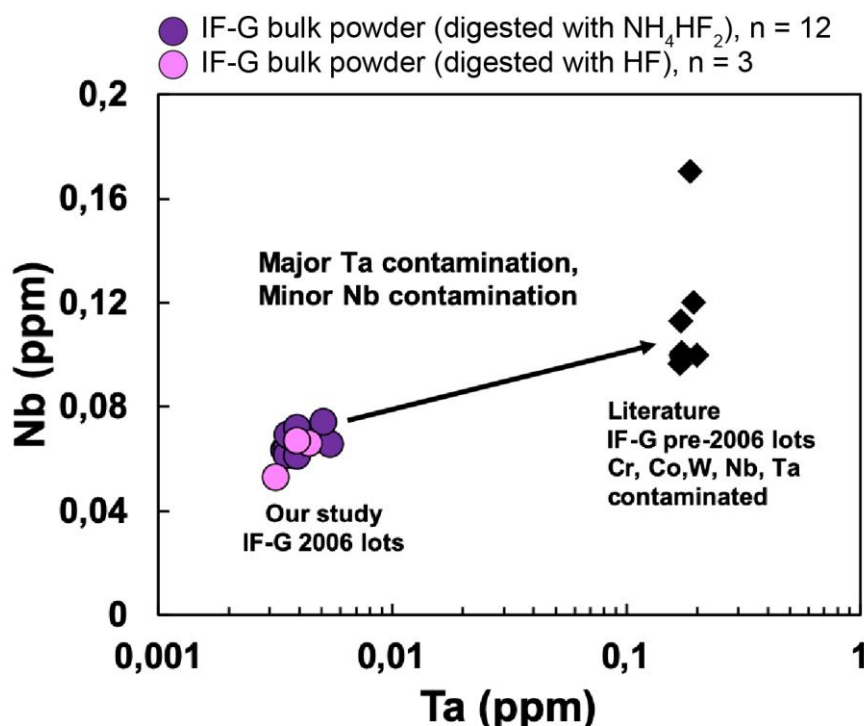
disagree with our data for various elements, reflecting contamination of elements in the bulk IF-G reference standard powder in pre-2006 lots analyzed by previous studies.

A.6. Nb, Ta contamination in the pre-2006 IF-G lot.

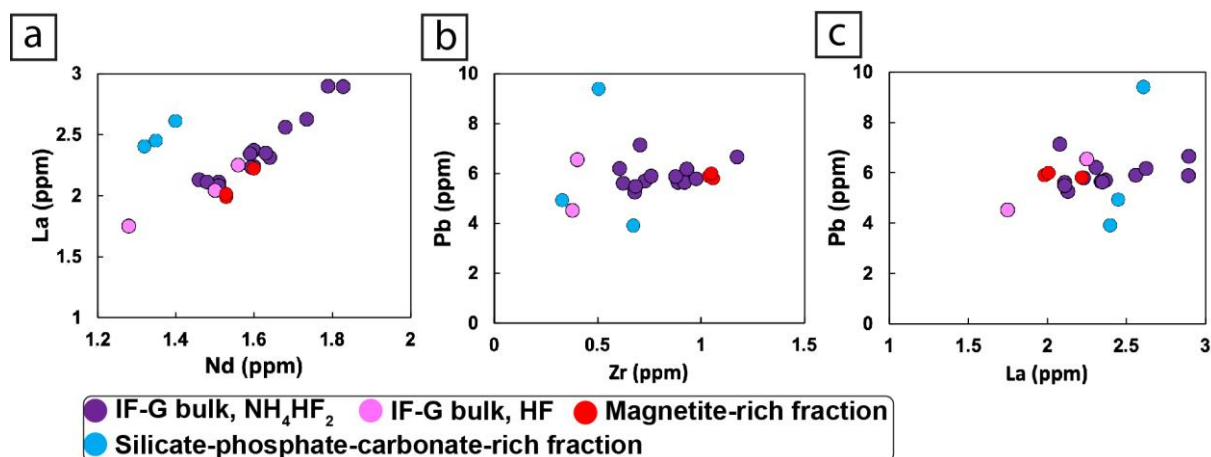
Previous studies have mainly analyzed pre-2006 IF-G reference material lots. They show drastic differences with our 2006 IF-G reference material that have been preserved of the crusher contamination such as Nb, Ta. These elements present differences with our average composition of respectively $+60 \pm 84 \%$ (2SD, $n = 9$) and $+4378 \pm 609 \%$ (2SD, $n = 9$).

Previous studies on pre-2006 IF-G lots measured $(\text{Nb}/\text{Ta})_{\text{N,UCC}}$ ratios of 0.0470 ± 0.0186 (2SD, $n = 8$) whereas our study provide $(\text{Nb}/\text{Ta})_{\text{N,UCC}}$ ratios very similar to the upper continental crust (UCC; Rudnick and Gao, 2014): $(\text{Nb}/\text{Ta})_{\text{N,UCC}} = 1.26 \pm 0.32$ (2SD, $n = 12$) in the IF-G bulk digested in NH_4HF_2 and 1.21 ± 0.16 (2SD, $n = 3$) for those digested with HF.

This decoupling of Nb/Ta ratio from literature when normalized to the average UCC (Rudnick and Gao, 2014) is not expected for elements with similar chemical properties such as Nb and Ta. In conjunction with previous observed contaminations of Cr, Co and W presented in the certificate of analysis, we suggest that the pre-2006 lots of IF-G standard powder was also contaminated in Nb and more importantly in Ta. This contamination may arise from the material used before 2006 for standard preparation (crusher) and not from an analytical issue when these lots were analyzed.



A.7. Correlations between REEs, Pb, and Zr in the IF-G powder and mineral fractions.



The diagram (a) shows that La is correlated with Nd as expected because LREE have similar electronic configuration and typically show similar geochemical behavior. If apatite is responsible for a nugget effect on LREE, it is highly probable that Nd isotopic composition would be at least partially controlled by apatite. (b) and (c) show that there is no correlation between Pb and Zr or La implying that the Pb budget of the bulk IF-G powder is not controlled by zircon or apatite, though isotopic data suggests that zircon exerts a strong control on Pb isotopic compositions.

A.8. Leaching test to highlight the presence of zircon in the IF-G bulk powder

Below is a description of the weak-dissolution protocol followed to confirm the presence of zircon in the IF-G reference material.

Dissolution protocol:

0.8513 g of IF-G reference material powder was weighed and digested in

i) - 3 mL 2M HF + 1 mL 7M HNO_3 at 90 °C during 24-hours

This step should have dissolved most of the silicates by breaking the Si-O bonds in silicates. However, at such concentration and temperature, zircon should have been preserved from total dissolution. Then, the sample was evaporated at 80 °C.

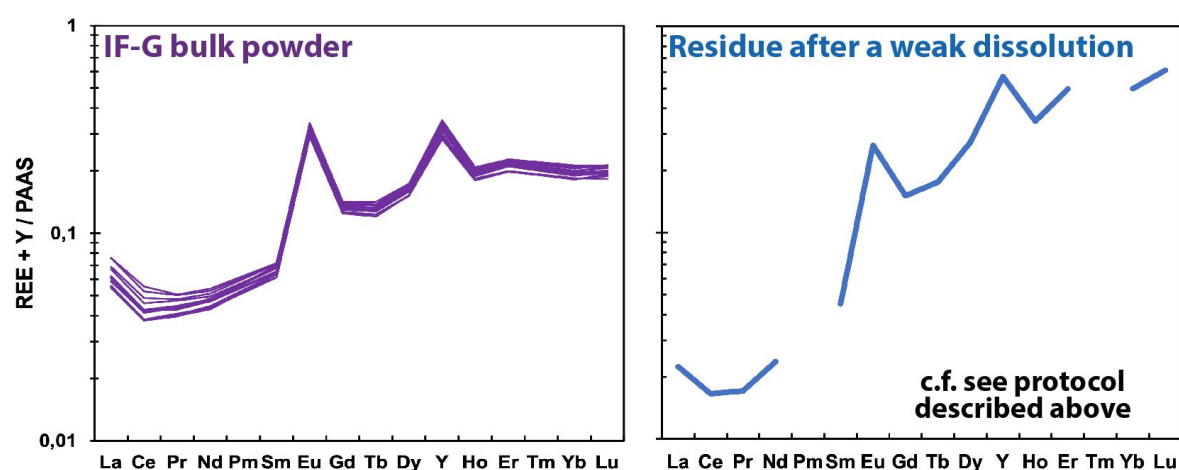
ii) – 3 cycles of addition-evaporation of 10 mL HCl at 80°C during 12-hours. This step should have dissolved magnetite, phosphate and carbonate. Ultrasonic bath during 30 min was used after each new addition of HCl.

iii) For the last step in HCl, the 10 mL-solution was centrifuged. The supernatant was separated from the residue. Several water cleaning by water addition, centrifugation and removal of the supernatant were done to clean as much as possible the residue.

iv) The residue - potentially containing zircons - was then dissolved using 205 mg of NH_4HF_2 at 220°C during 24-hours in an oven. It was converted in nitrate using 3 mL of 14N HNO_3 during 48-hours, then evaporated at 85°C.

v) After evaporation, the residue was dissolved in a solution of 5 mL of 7N HNO₃. Then an aliquot of 10 % was taken and diluted in 5 mL of 0.4N HNO₃ +0.05N HF for ICP-MS analysis on a 8900 Agilent-QQQ-ICPMS.

As the mass of the residue is unknown, results are semi-quantitative and only elemental ratios can be interpreted. For this reason, we do not show number of the y axis. The REE+Y concentrations were multiplied by 5 to adjust the pattern at similar level than IF-G bulk to help the comparison of their pattern. Elemental ratios clearly demonstrate the typical signature of zircon in the residue.



	¹⁷⁶ Lu/ ¹⁷⁷ Hf*	Th/U	Zr/Th	Zr/Hf	Y/Ho	(La/Yb) _{PAAS}
IF-G bulk n = 14	0.56 ± 0.11 (2SD)	2.78 ± 0.31 (2SD)	19.2 ± 7.8 (2SD)	37.5 ± 6.9 (2SD)	45.4 ± 3.6 (2SD)	0.31 ± 0.06 (2SD)
Residue (zircon)	0.035	1.57	1210	37.6	46.5	0.045

*Estimate based on Lu and Hf concentrations measured by ICP-MS and natural abundances of ¹⁷⁶Lu and ¹⁷⁷Hf; the average ¹⁷⁶Lu/¹⁷⁷Hf obtained by the ID-MC-ICP-MS method based on 11 analyses of the bulk IF-G powders is 0.620 ± 0.097 (2SD).