

Apatite inclusions in zircon reveal a crustal origin for HREE depletion in Archean granitoids

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C.A. designed the study and wrote the initial paper. The analytical work was performed by C.A., L.L., M.G. and J.B. All authors discussed the results, provided feedback, and contributed to the final paper. Funding was acquired by L.C. and N.G.

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Abstract

Reconstructing the geodynamic conditions of the Hadean and Archean is essential for understanding Earth's evolution and the conditions that ultimately enabled life to emerge. Archean tonalite–trondhjemite–granodiorite (TTG) suites have been studied extensively because their evolved compositions provide clues to the processes that formed the early continental crust. Their trace-element signatures, particularly heavy rare earth element (HREE) depletion, have traditionally been attributed to melting of hydrous basaltic crust under pressure-temperature conditions within the garnet stability field. However, TTG compositional diversity may also arise during magmatic differentiation within the crust, rather than from differences in melting conditions alone. Distinguishing these mechanisms requires constraints on both primitive melt compositions and their evolution during differentiation. Whole-rock analyses provide only snapshots of this evolution and may be modified by alteration. Here, we use apatite inclusions in zircon to reconstruct the chemical evolution of TTG and related granitoid magmas. We first present a four-criterion protocol for distinguishing primary from secondary apatite inclusions and apply it to inclusions from five cratons, identifying 92 of 153 analysed grains as primary. Melt compositions reconstructed from

these primary apatites show little or no HREE depletion in many samples, whereas HREE depletion increases with the inferred degree of melt fractionation. We therefore propose that the HREE-depleted signature of many TTGs can develop through amphibole-bearing crystallization in the crust, without requiring garnet in the source in every case. These findings have implications for models of early continental-crust formation and Archean geodynamics.

Introduction

Tonalite-trondhjemite-granodiorite (TTG) suites constitute much of the preserved Archean continental crust, and understanding their petrogenesis is central to reconstructing early geodynamics^{1,2}. The conventional model proposes that TTGs formed by partial melting of hydrated metabasalt. In this model, their HREE-depleted patterns, high La/Yb ratios and high Sr/Y ratios reflect equilibration with a garnet-bearing, plagioclase-poor residue at pressures of approximately 1.5-2.0 GPa or higher^{1, 3}. Because the source must have been hydrated at or near the surface, this model has been interpreted as evidence for the downward transport of hydrated basalt, potentially through sagduction or subduction, before 3 Ga^{4,5}.

This framework assumes that TTG whole-rock compositions approximate melt compositions and that their trace-element signatures primarily record partial melting and/or magmatic fractionation. However, alternative models challenge aspects of the conventional interpretation^{6,7}. Liou and Guo⁸, for example, reproduced TTG-like compositional trends through amphibole-dominated fractionation without requiring deep melting. Smit⁹ argued that La/Sm, Sm/Yb and Sr/Y may reflect the combined effects of melting and fractional crystallization rather than pressure alone, and proposed that TTG precursors may have left plagioclase-rich cumulates rather than garnet-bearing residues. Phase-equilibrium modelling has also questioned whether high-pressure melting is required to generate Archean TTG compositions; garnet-like La/Yb and Sr/Y signatures may be achievable at pressures near 1.4 GPa¹⁰. Moyen¹¹ likewise cautioned that the adakitic signature is not a unique indicator of depth.

To investigate TTG petrogenesis, we analysed trace elements in apatite inclusions hosted by zircon and used them to reconstruct melt compositions during Archean magmatic evolution. Previous work has shown that zircon-hosted apatite can preserve primary magmatic signatures even in polymetamorphic Archean terranes^{12,13}. Interpretation is challenging, however, because inclusions are typically only 5-10 μm across, limiting the number of analytical methods that can be applied. Their cathodoluminescence response may also be weak or absent, making primary and metamorphic populations difficult to distinguish.

We first establish a screening framework to distinguish primary from secondary apatite inclusions using four criteria that target distinct potential sources of alteration. We deliberately exclude La/Yb from the screening criteria because this ratio is central to the petrogenetic question addressed here. The screening identifies approximately one-third of the analysed apatites as secondary. These grains are characterised by lower REE concentrations, particularly light rare earth elements (LREE), and by less pronounced negative Eu anomalies.

Using the filtered dataset, we reconstruct apatite-hosted melt compositions and compare them with zircon-hosted melt estimates and whole-rock compositions. We test whether the HREE depletion observed

in TTG whole rocks was inherited from the source or developed during subsequent magmatic differentiation.

Samples, workflow and apatite screening procedure

The study examines zircon-hosted apatite inclusions from five cratonic regions, spanning 4.02–2.5 Ga: the Slave Craton, Wyoming Craton, Itsaq Gneiss Complex, North China Craton (NCC) and Karelia Craton (Fig. 1). Zircon is highly resistant to many forms of alteration and has a high U–Th–Pb closure temperature, commonly exceeding 900 °C¹⁴. It can therefore preserve inclusions through metamorphic events that modify whole-rock and matrix-mineral signatures, making zircon-hosted inclusions valuable archives in terranes with complex histories¹³. In the Slave Craton of the Northwest Territories, Canada, we sampled sand from the Acasta River (YK24-71) and a tonalite (YK24-61; dated at 3.6 Ga) in the Acasta Gneiss Complex. In the Yellowknife area, we sampled lake sediments (YK24-54 and YK24-57) and a granite (YK24-06; U–Pb age of 2.6 Ga), two tonalites YK24-33 and -38 dated at 2.7 Ga and 2.65 Ga respectively. In the Wyoming Craton, Montana and Wyoming, USA, samples MT24-06 dated at 3.01 Ga (granite), MT24-15 dated at 2.7 Ga (Tonalite), MT24-18 dated at 3.54 Ga (Tonalite), MT24-29 dated at 2.7 Ga (Tonalite), from the Beartooth Mountains; sample MT24-32 is a 2.6 Ga gneiss from the Grand Teton Range. Sample GL25-23 is a 3.8 Ga tonalite from the internal tonalite complex of the Isua supracrustal belt, within the Itsaq Gneiss Complex of western Greenland. Sample 08XW501 is a 2.51 Ga tonalitic orthogneiss from the Miyun Complex of the North China Craton¹⁵. Finally, sample H405 comes from the non-migmatitic part of the Kuusamonkylä grey gneisses in Finnish Karelia, within the Baltic Shield; this unit belongs to the region's Archean granite–greenstone association^{16, 17}.

Zircon grains were separated from all samples using standard procedures. Non-sedimentary rocks were crushed before separation by magnetic and heavy liquids and a Wilfley table. Selected zircon grains were mounted in epoxy, polished and examined by scanning electron microscopy to identify apatite inclusions. Zircons were dated by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Laboratoire Magmas et Volcans in Clermont-Ferrand, France, except for samples H405 and 08XW501 that were already dated in other studies. Major elements in apatite inclusions were measured by electron-probe microanalysis, and REE concentrations were measured by LA-ICP-MS at the University of Geneva, Switzerland. Whole-rock (WR) compositions were determined on glass-fused disks by X-ray fluorescence spectrometry at the University of Lausanne, Switzerland. Further analytical details are provided in the Methods section.

We screened apatite analyses using four criteria designed to identify distinct problems. Criterion 1 identifies analyses contaminated by the host zircon; criteria 2–4 target possible redistribution of REE during secondary alteration, growth of metamorphic phases and overall metamorphism. An analysis was classified as secondary if it failed criterion 1, or if it failed all three of criteria 2–4. We then inspected the data using a ternary discrimination diagram to check for potentially misclassified grains. Grains classified as secondary were excluded from subsequent interpretation.

Criterion 1: Host-zircon contamination. Zircon contains approximately 500,000 ppm zirconium (Zr), compared with only a few ppm in apatite. Analyses containing more than 50 ppm Zr were therefore interpreted as sampling both the inclusion and its zircon host. This criterion excluded 28 grains, the largest number removed by any single criterion.

Criterion 2: $\text{Th}/\text{U} < 0.1$. Low Th/U may indicate Th loss during metamorphic reactions. Th is generally less mobile in fluids than U and can be incorporated into metamorphic monazite (Mnz) and allanite (Aln). This criterion excluded 11 grains. However, a low ratio can also result from high U concentrations rather than Th redistribution. Because Th concentrations in apatite from granitoids are commonly below 16 ppm, we interpret this criterion cautiously and do not use it in isolation.

Criterion 3: $\text{Nd} < 50$ ppm. This criterion targets strong LREE depletion that may result from preferential removal of LREE by monazite or allanite during prograde metamorphism or redistribution by fluids. It identifies grains that may retain unremarkable Th/U ratios and Eu anomalies despite substantial LREE redistribution. It excluded five grains.

Criterion 4: $\text{Eu}/\text{Eu}^* \geq 0.8$. Primary magmatic apatite commonly displays a negative Europium anomaly (Eu/Eu^*), in part because apatite crystallises after plagioclase has fractionated Eu. Re-equilibration may weaken this anomaly through changes in the feldspar assemblage or the oxidation state of Eu, which controls the relative behaviour of Eu and the other REE. This criterion excluded 15 grains.

In contrast to previous studies [¹³; ¹⁸], we deliberately did not use La/Yb as a screening criterion because we use this ratio to investigate magmatic processes. Sr has also been proposed as a discriminator between primary and secondary apatite. However, depending on fluid chemistry and host-rock buffering, metamorphic apatite may become strongly enriched in Sr or depleted to a small fraction of its original concentration through thermally driven diffusion^{19, 20}. We therefore excluded Sr from the screening criteria.

We performed an additional visual check to identify secondary apatites that may have passed the initial screening. We plotted the data on a $\text{La}/\text{Sm}_\text{N}$ -(HREE+Y)- Eu/Eu^* ternary diagram (Fig. 2). The diagram helps distinguish grains affected by fluid-driven alteration or recrystallisation, which may show low $\text{La}/\text{Sm}_\text{N}$ and a subdued Eu anomaly, from grains with relatively HREE-rich, flat patterns or stronger LREE enrichment. It also highlights anomalous LREE slopes ($\text{La}/\text{Sm}_\text{N}$) that may indicate LREE loss rather than primary fractionation between LREE and HREE.

This inspection identified three additional misclassified analyses: two from Karelia and one from Wyoming. Re-examination showed evidence of LREE re-equilibration that was apparent only when the grains were compared with other apatites from the same sample; the changes were not sufficiently pronounced to be detected by the initial criteria.

Results

Of the 153 successfully analysed apatite grains (Supplementary Table 1), 92 were classified as primary (Fig. 2). Most primary apatites from the Wyoming Craton show the relatively flat REE patterns commonly

reported for Archean apatite (Fig. 3a). An exception is sample MT24-29, whose apatites are enriched in LREE relative to HREE. In the Itsaq Gneiss Complex (Greenland; Fig. 3b), one sample contains apatites with a bell-shaped LREE segment enriched relative to HREE. REE concentrations vary by approximately one order of magnitude between the lowest- and highest-concentration patterns. The Slave Craton samples show the greatest diversity in REE-pattern shape (Fig. 3c), in part because YK24-21, YK24-71, YK24-54 and YK24-57 are detrital grains recovered from river or lake sediments. Most grains display negative Eu anomalies and variable LREE enrichment relative to HREE. Exceptions include one HREE-enriched grain from YK24-54 and the flat REE patterns of apatites from YK24-61. Apatites from the North China Craton show the strongest LREE enrichment relative to HREE, with comparatively little variation in total REE concentration (Fig. 3d). Sample H405 from Karelia contains two distinct apatite populations: one has higher SiO₂ and is relatively HREE-enriched (Fig. 3), whereas the other has lower SiO₂ and is relatively LREE-enriched (Fig. 3). The two populations occur in the same rock sample and show no resolvable difference in U-Pb age.

Across the sampled interval, whole-sample La/Yb_N values increase from approximately 4.0 to 2.5 Ga (Fig. 4). Data from the Wyoming and Slave cratons also show substantial variation in La/Yb_N within individual cratons.

Whole-rock REE patterns from all cratons are depleted in HREE relative to LREE and mostly display small negative Eu anomalies (Fig. 5). Two Wyoming samples have positive Eu anomalies (Fig. 5a), as do all samples from the Slave Craton analysed in this study (Fig. 5b). The whole-rock REE patterns differ from those of the zircon-hosted apatite inclusions, despite apatite being used here to reconstruct melt compositions (Figs. 3 and 5).

Discussion

Apatites from the same craton share some broad REE-pattern characteristics, such as their La/Yb ratios, but their absolute REE concentrations vary substantially. LREE concentrations vary by nearly three orders of magnitude within individual cratons. HREE concentrations vary less, although their variation remains significant (Fig. 3). Most of the variation within a craton occurs between samples rather than within a single sample. An exception is sample H405 from Karelia, which contains two distinct compositional groups. These differences suggest that apatite inclusions preserve a range of Archean melt compositions rather than recording a single melting regime.

Because the reconstructed melt compositions differ from the whole-rock data, we used an inverse model to estimate the melts from which the apatites crystallised. The model samples combinations of temperature (T) and oxygen fugacity (log fO₂)²¹, calculates REE apatite-melt partition coefficients (D) for each combination (21, 22), and estimates the melt composition from each apatite analysis:

$$C_{\text{melt}} = C_{\text{apatite}} / D_{\text{calculated}}$$

The resulting melt estimates were pooled to obtain distributions of plausible compositions. The median and percentile ranges, together with whole-rock and zircon-inverted melt estimates, are reported in

Supplementary Table 2. The reconstructed melts are normalised to chondritic values from McDonough and Sun²² in Figure 6. The detailed model can be found in the Supplementary Material S3.

The reconstructed melt patterns do not match the whole-rock patterns. In many samples, HREE are only weakly depleted relative to LREE or are not depleted at all (Fig. 6). Some reconstructed melts, from two Slave Craton samples, one North China Craton sample, one Karelia group and one Wyoming Craton sample, show LREE enrichment relative to HREE, but this enrichment is substantially weaker than in the corresponding whole rocks (Fig. 5). These results challenge the interpretation that TTG melt REE patterns are controlled predominantly by melting of hydrated basalt in the garnet stability field. If garnet remained in the source, the earliest melt increments would generally be expected to show HREE depletion, which is absent from many reconstructed compositions. The HREE depletion in the whole rocks therefore appears to have developed, at least in many of our samples, through a process other than source-residue control during partial melting.

This raises the question of how melts with flat or HREE-enriched reconstructed patterns and negative Eu anomalies evolved into the compositions recorded by the whole rocks. The absence of pronounced HREE depletion in the reconstructed melts argues against a garnet-bearing source as the sole explanation for the whole-rock signature. This pattern occurs across several cratons and throughout the sampled time interval. Negative Eu anomalies in some reconstructed melts may indicate that plagioclase was present in the source during melting. However, Eu anomalies alone cannot uniquely distinguish source-related effects from later magmatic differentiation or crystal accumulation. In the absence of petrographic information, these alternative explanations cannot be unambiguously evaluated, and the source-related interpretation should therefore remain tentative.

Across the dataset, apatite inclusions span a wide range of $(La/Yb)_N$ values, with little overall correlation with $(Sr/Y)_N$ (Fig. 7). Sample H405 from Karelia (orange in Fig. 7) contains two groups, one with low and one with high $(La/Yb)_N$, creating an apparent positive trend. Sample 08XW501 from the North China Craton (brown in Fig. 7) shows a positive relationship between $(La/Yb)_N$ and $(Sr/Y)_N$, which may be consistent with a garnet-bearing residue. Garnet in the residue raises both $(La/Yb)_N$ and $(Sr/Y)_N$, because it retains Y and the HREE while plagioclase is absent^{5,11}. A residue of amphibole and plagioclase keeps Sr/Y low and raises La/Yb only moderately, and it lowers Dy/Yb ^{23, 3, 24}. The positive $(La/Yb)_N$ - $(Sr/Y)_N$ trend in 08XW501 is therefore consistent with a garnet-bearing residue. However, amphibole fractionation under conditions that suppress plagioclase could produce a similar trend²⁵, and the two can be distinguished using $(Dy/Yb)_N$ ^{26,27}. After inversion, the reconstructed melts have higher $(Sr/Y)_N$ values than the apatite inclusions and values closer to those of the corresponding whole rocks. However, their $(La/Yb)_N$ values remain lower than those of the whole rocks. This difference suggests that the Sr/Y signature may be inherited from the source, whereas the stronger La/Yb fractionation developed later during melt differentiation and crystallisation. Sample GL25-23 from Greenland is the only sample whose reconstructed melt has a higher $(Sr/Y)_N$ than its whole rock. Its ratio is mainly influenced by relatively high Y concentrations, while Lu/Yb remains low. Apatite inclusions with a positive La-to-Nd slope also have high Lu concentrations. We hypothesise that these features may reflect apatite replacing monazite; the inclusions have low Th, a bell-shaped LREE segment in chondrite-normalised patterns, and elevated Lu relative to the other HREE. This interpretation should be treated as provisional and tested against petrographic evidence.

Apatite inclusions enclosed in zircon must have crystallised before their zircon host. This textural relationship allows comparison of successive stages of magmatic evolution when REE data are available for apatite, zircon, and whole rock: an earlier melt recorded by apatite, a later melt estimated from zircon, and the final rock composition.

We identified two Wyoming Craton samples with REE data for apatite, zircon and whole rock: MT24-06 (3.01 Ga) and MT24-32 (2.6 Ga). Because zircon incorporates sufficient REE primarily at the HREE end of the pattern, we focus on HREE when comparing these stages. Zircon-hosted melt compositions were reconstructed using the same inversion approach as for apatite, with partition coefficients calculated at temperatures estimated from Ti-in-zircon thermometry. Sample MT24-06 shows evidence consistent with mixing with a plagioclase cumulate, as its whole-rock composition has a positive Eu anomaly and high Sr concentrations. The three-stage reconstruction for this sample is provided in the Supplementary Information. Figure 8 compares the reconstructed apatite-hosted and zircon-hosted melts with the whole-rock composition of MT24-32, a 2.6 Ga Wyoming Craton gneiss.

In MT24-32, HREE concentrations decrease from the apatite-hosted melt estimate to the zircon-hosted melt estimate and then to the whole rock, with the clearest decrease occurring from Gd towards the heaviest REE. Gd is the only element whose concentration is similar in the reconstructed melts and the whole rock. The apatite- and zircon-hosted melt estimates are comparatively flat from Gd to Lu, whereas the whole rock is depleted in the heaviest REE. This pattern suggests that the HREE depletion developed during crystallisation, after the earliest stage recorded by the apatite inclusions, rather than being fully inherited from the source. A garnet-bearing residue would be expected to impart HREE depletion to the melt from the outset; that depletion is not apparent in the apatite-hosted melt estimate.

The whole rocks are also enriched in LREE relative to the reconstructed apatite-hosted melts. Apatite-melt partition coefficients are typically curved across the REE series, with relatively high partitioning of middle REE. The whole-rock LREE enrichment may therefore reflect the involvement of an earlier-crystallising LREE-rich phase, such as monazite or allanite, followed by dissolution or reaction. Allanite commonly occurs in granites and can crystallise early²⁸. This interpretation remains a hypothesis and requires textural and geochemical testing.

Mineral assemblages and whole-rock composition

Comparing reconstructed apatite-hosted melts with whole-rock compositions suggests that several processes contributed to the final TTG-like signatures. Although individual samples show local variation, the recurrence of HREE-depleted whole-rock patterns across cratons motivates testing whether a common differentiation process could generate this feature. For most samples in this dataset, apart from the North China Craton sample, the reconstructed melt compositions do not require a garnet-bearing source to explain the observed whole-rock HREE depletion. We therefore tested simple mineral-assemblage models to evaluate whether crystallisation and fractionation could reproduce the whole-rock patterns (Figs. 9 and 10). Because partition coefficients are unavailable for every mineral in the relevant melt-composition range, and because temperature and oxygen fugacity are not independently constrained, these models should be regarded as qualitative rather than quantitative. Mineral assemblages and partition coefficients were taken from the literature^{2, 8} and tested against our data.

The models yield three broad outcomes (Fig. 9). In the first, an assemblage of amphibole, apatite and zircon reproduces the whole-rock pattern (model A1). In the second, adding monazite improves the fit (model A2). The third requires a more complex history (model A3): to reproduce the whole-rock LREE concentrations, the system must either begin with an LREE-enriched source or receive LREE later. Because the reconstructed apatite-hosted melts do not show source-related LREE enrichment, we consider an alternative in which monazite crystallises early in a different environment and dissolves later. Dissolution and fluid contamination could return LREE to the melt without substantially changing its HREE budget. A similar texture was described in sample AG09009 by Antoine¹³, although those authors could not establish whether dissolution and recrystallisation occurred during emplacement or subsequent metamorphism. In many samples, early monazite may sequester LREE before apatite crystallises, while HREE remain available in the melt for incorporation into apatite before zircon saturation.

Except for two samples (one from the Itsaq Gneiss Complex and Slave Craton sample YK24-33), the observed HREE depletion can be approximated by a model dominated by amphibole, with apatite and zircon as accessory phases. The model reproduces the shape of the reconstructed melt pattern particularly well for Wyoming Craton sample MT24-29, although the predicted concentrations do not match all samples.

The best fits to the LREE data in some samples require early monazite crystallisation followed by dissolution and replacement by apatite, potentially after additional amphibole fractionation. A comparable texture was reported in sample AG09009 by Antoine¹³, although a post-emplacement metamorphic origin could not be ruled out. We tested the monazite hypothesis using the ratio of whole-rock Th to inclusion Th ($Th_{WR}/Th_{inclusion}$). Ratios greater than one may indicate retention of Th in monazite, whereas ratios below one may be consistent with Th loss during dissolution or fluid-mediated redistribution; this proxy is not uniquely diagnostic. Only three Wyoming samples have ratios above one: MT24-06 (1.43; $n = 3$), MT24-32 (2.34; $n = 5$) and MT24-15 (5.57; $n = 1$). The MT24-15 value should be treated cautiously because it is based on one inclusion with unusually high Th, and microscopic inclusions could not be ruled out. The model with persistent monazite best fits MT24-06. It does not fit MT24-15, although the single measurement prevents a firm conclusion. For MT24-32, monazite reproduces the pattern shape but not the absolute concentrations, potentially indicating that a larger monazite proportion would be required.

Three samples (MT24-06, MT24-18 and YK24-38; Fig. 10) have positive whole-rock Eu anomalies. For MT24-06, the best-fitting assemblage includes monazite and amphibole, with apatite and zircon as accessory phases. The same assemblage reproduces the LREE pattern of MT24-18 but fits its HREE pattern less well. The Slave Craton sample YK24-38 is better matched by a model in which early monazite dissolves and the subsequent fluid enriches the rock later on (model A3, Fig. 10). The positive Eu anomalies may reflect the accumulation or mixing of plagioclase, consistent with the negative Eu anomalies in the apatites and the modelled REE budgets. Differences in REE budgets and Eu-anomaly magnitude may reflect varying degrees of cumulate involvement and metamorphic recrystallisation.

Overall, the models show that the observed whole-rock fractionation between LREE and HREE can be reproduced from melt compositions recorded earlier by zircon-hosted apatite. The tested assemblages involve amphibole, apatite and zircon, with monazite either crystallising during an early stage or

contributing LREE through later dissolution and fluid contamination. Positive whole-rock Eu anomalies may reflect plagioclase accumulation or cumulate mixing. For most samples, the reconstructed melt compositions do not require a source that was already depleted in HREE by residual garnet.

Conclusion

We present a four-criterion screening framework for distinguishing primary apatite inclusions in zircon from inclusions affected by contamination or secondary modification. The screened population records heterogeneous reconstructed melt compositions, many of which show little HREE depletion. Comparisons between apatite-hosted melt estimates, zircon-hosted melt estimates and whole-rock compositions indicate that HREE depletion can develop during magmatic differentiation rather than being inherited entirely from a garnet-bearing source. Qualitative mineral-assemblage models suggest that amphibole, apatite and zircon can reproduce much of the observed HREE depletion, while monazite may explain LREE variations in some samples. Positive whole-rock Eu anomalies further indicate that some samples may contain a cumulate component and should not automatically be treated as liquid compositions. These results show that HREE depletion in TTG-like granitoids is not, by itself, definitive evidence for melting in the garnet stability field; source conditions must be assessed alongside subsequent crystallisation and differentiation.

Methods

Analytical work

Apatite inclusions were analysed for major elements (Ca, P, Cl and F) and selected trace elements by electron-probe microanalysis (EPMA) using a JEOL JXA-iHP200F at the University of Geneva. Analyses were performed at 15 kV with a defocused 10 nA beam (4–8 μm) to limit F migration and Na loss. Calibration used well-characterised in-house mineral and synthetic standards, including Durango apatite for Cl, Ca, F and P; albite for Na; fayalite for Si; sphalerite for S; MNTI for Mn; and olivine for Mg. Elements were measured on the following spectrometers: Cl, Ca, La and Ce on PETL; S and F on PETH; Fe on LIFL; Na, Si and Mn on TAPL; Mg on LIFH. REE concentrations were measured by LA-ICP-MS using an NWR-193 HE coupled to an Agilent 8900, at a fluence of 2.85 J cm^{-2} and 1 Hz. NIST 610 and GSE-1G were used as primary standards, Durango apatite as a secondary standard, and ^{43}Ca from Durango apatite as the internal standard. U-Pb dating was performed by LA-ICP-MS at the Laboratoire Magmas et Volcans in Clermont-Ferrand, using GJ-1 for external normalisation and Kara 18 and 91500 as quality-control materials.

For whole-rock analyses, samples were cleaned and cut, crushed using a hydraulic press, and powdered in an agate mill. Major and selected trace elements were measured on glass-fused disks using a Philips PW2400 X-ray fluorescence spectrometer at the University of Lausanne, Switzerland. Reference materials NIM-N, NIM-G, BHVO-1/2 and SY-2 were used for quality control.

Data reduction

Of the 709 apatite grains examined, 153 yielded successful analyses. Three sampling biases should be considered when interpreting population-level patterns. First, apatite abundance varies with whole-rock

silica content, so low-silica rocks may contribute more inclusions. Second, inclusions smaller than approximately 5 μm could not be analysed. Third, older zircons are more susceptible to metamictisation and isotopic resetting and may therefore be more likely to be excluded during screening. Trace-element data were further filtered using Zr concentrations. Analyses with Zr signals exceeding those of P or Ca were discarded as potentially contaminated by the host. Analyses lacking a complete REE dataset were also excluded. Data reduction was performed using Iolite for U-Pb data²⁹ and ICP-BASE³⁰ for trace-element data.

Data availability

All data and models discussed in this paper is available either in the text, tables, and figures or in the Supplementary materials.

References

- 1 Moyen, J.-F. The composite Archaean grey gneisses: petrological significance, and evidence for a non-unique tectonic setting for Archaean crustal growth. *Lithos* **123**, 21-36 (2011).
- 2 Moyen, J.-F. & Martin, H. Forty years of TTG research. *Lithos* **148**, 312-336 (2012).
- 3 Rapp, R. P. & Watson, E. B. Dehydration melting of metabasalt at 8–32 kbar: implications for continental growth and crust-mantle recycling. *Journal of petrology* **36**, 891-931 (1995).
- 4 Foley, S., Tiepolo, M. & Vannucci, R. Growth of early continental crust controlled by melting of amphibolite in subduction zones. *Nature* **417**, 837-840 (2002).
- 5 Martin, H., Smithies, R., Rapp, R., Moyen, J.-F. & Champion, D. An overview of adakite, tonalite–trondhjemite–granodiorite (TTG), and sanukitoid: relationships and some implications for crustal evolution. *Lithos* **79**, 1-24 (2005).
- 6 Laurent, O. *et al.* Earth's earliest granitoids are crystal-rich magma reservoirs tapped by silicic eruptions. *Nature Geoscience* **13**, 163-169 (2020).
- 7 Ding, N., Wang, X.-L., Du, D.-H., Wang, D. & Anhaeusser, C. Compositional diversity of TTGs controlled by heterogeneous accumulation of accessory minerals. *Lithos* **482**, 107718 (2024).
- 8 Liou, P. & Guo, J. Generation of Archaean TTG gneisses through amphibole-dominated fractionation. *Journal of Geophysical Research: Solid Earth* **124**, 3605-3619 (2019).
- 9 Smit, M. A., Musiyachenko, K. A. & Goumans, J. Archaean continental crust formed from mafic cumulates. *nature communications* **15**, 692 (2024).
- 10 Johnson, N. M. & de Oliveira, M. R. R. Venus Atmospheric Composition In Situ Data: A Compilation. *Earth and Space Science* **6**, 1299-1318, doi:<https://doi.org/10.1029/2018EA000536> (2019).
- 11 Moyen, J.-F. High Sr/Y and La/Yb ratios: the meaning of the “adakitic signature”. *Lithos* **112**, 556-574 (2009).
- 12 Bruand, E., Storey, C. & Fowler, M. An apatite for progress: Inclusions in zircon and titanite constrain petrogenesis and provenance. *Geology* **44**, 91-94 (2016).
- 13 Antoine, C., Bruand, E., Guitreau, M. & Devidal, J. L. Understanding Preservation of Primary Signatures in Apatite by Comparing Matrix and Zircon-Hosted Crystals From the Eoarchean Acasta Gneiss Complex (Canada). *Geochemistry, Geophysics, Geosystems* **21**, doi:10.1029/2020gc008923 (2020).
- 14 Lee, J. K., Williams, I. S. & Ellis, D. J. Pb, U and Th diffusion in natural zircon. *Nature* **390**, 159-162 (1997).
- 15 Guitreau, M. *Les isotopes de l'hafnium dans les TTG et leurs zircons : témoins de la croissance des premiers continents*, (2012).

- 16 Martin, H. Archaean chronology in the eastern part of the Baltic Shield: a synthesis. *Precambrian research* **43**, 63-77 (1989).
- 17 <Germa_2008_these martinique.pdf>.
- 18 Kieffer, M. A., Dare, S. A. & Gendron, M. Trace element discrimination diagrams to identify igneous apatite from I-, S-and A-type granites and mafic intrusions: Implications for provenance studies and mineral exploration. *Chemical Geology* **649**, 121965 (2024).
- 19 Piccoli, P. M. & Candela, P. A. Apatite in igneous systems. *Reviews in Mineralogy and Geochemistry* **48**, 255-292 (2002).
- 20 Cherniak, D. & Ryerson, F. A study of strontium diffusion in apatite using Rutherford backscattering spectroscopy and ion implantation. *Geochimica et Cosmochimica Acta* **57**, 4653-4662 (1993).
- 21 Schreiber, H. D. An electrochemical series of redox couples in silicate melts: a review and applications to geochemistry. *Journal of Geophysical Research: Solid Earth* **92**, 9225-9232 (1987).
- 22 McDonough, W. F. & Sun, S.-S. The composition of the Earth. *Chemical geology* **120**, 223-253 (1995).
- 23 Rapp, R. P., Watson, E. B. & Miller, C. F. Partial melting of amphibolite/eclogite and the origin of Archean trondhjemites and tonalites. *Precambrian Research* **51**, 1-25 (1991).
- 24 Moyen, J. & Stevens, G. Experimental constraints on TTG petrogenesis: implications for Archean geodynamics. *Geophysical Monograph-American Geophysical Union* **164**, 149 (2006).
- 25 Castillo, P. R. An overview of adakite petrogenesis. *Chinese science bulletin* **51**, 257-268 (2006).
- 26 Davidson, J., Turner, S., Handley, H., Macpherson, C. & Dosseto, A. Amphibole “sponge” in arc crust? *Geology* **35**, 787-790 (2007).
- 27 Davidson, J., Turner, S. & Plank, T. Dy/Dy*: variations arising from mantle sources and petrogenetic processes. *Journal of Petrology* **54**, 525-537 (2013).
- 28 Gieré, R. & Sorensen, S. S. Allanite and other REE-rich epidote-group minerals. *Reviews in mineralogy and geochemistry* **56**, 431-493 (2004).
- 29 Paton, C., Hellstrom, J., Paul, B., Woodhead, J. & Hergt, J. Lolite: Freeware for the visualisation and processing of mass spectrometric data. *Journal of Analytical Atomic Spectrometry* **26**, 2508-2518 (2011).
- 30 Stumpf, S., Gies, N., Pettke, T. & Guillong, M. in *Goldschmidt 2025 Conference*. (GOLDSCHMIDT).
- 31 Hasterok, D. *et al.* New Maps of Global Geological Provinces and Tectonic Plates. *Earth-Science Reviews* **231**, 104069, doi:<https://doi.org/10.1016/j.earscirev.2022.104069> (2022).

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Conflict of interest

The authors declare no competing interests.

Figure legends

Figure 1 | Geological map showing the distribution of Precambrian shields and the locations of the sampled sites across the five cratonic regions. Modified from ³¹.

Figure 2 | $\text{La}/\text{Sm}_\text{N}$ -(HREE+Y)- Eu/Eu^* ternary diagram used to distinguish primary from secondary apatite inclusions. Purple curves illustrate representative REE patterns for the two end-member groups.

Figure 3 | Chondrite-normalised trace-element patterns of primary apatite inclusions, using the values of McDonough and Sun (1995). The colour gradient indicates the SiO_2 content (wt%) of the associated melt. In panel e, a narrower SiO_2 range is used to highlight the two apatite populations.

Figure 4 | Whisker plot showing variation in $\text{La}/\text{Yb}_\text{N}$ across cratons and geological ages.

Figure 5 | Chondrite-normalised whole-rock REE patterns for all cratons, including data from Antoine et al. (2020).

Figure 6 | Median reconstructed melt compositions for apatite inclusions from each craton.

Figure 7 | $\text{La}/\text{Yb}_\text{N}$ versus $\text{Sr}/\text{Y}_\text{N}$ for apatite inclusions, reconstructed melts and whole-rock compositions. Apatite-inclusion data are shaded because the inclusions are mineral compositions rather than melt compositions.

Figure 8 | Reconstructed melts from apatite inclusions and their host zircons compared with the whole-rock composition of the same sample. All patterns are normalised to the chondrite values of McDonough and Sun (1995).

Figure 9 | Mineral-assemblage models used to test whether the whole-rock REE patterns can be reproduced by fractional crystallisation. A1: 96.8% amphibole + 3.0% apatite + 0.2% zircon. A2: A1 assemblage plus 0.25% monazite. A3: A1 with early monazite crystallisation followed by dissolution and replacement by apatite by an external fluid. Dashed lines indicate overlapping patterns.

Figure 10 | Mineral-assemblage models for samples with positive whole-rock Eu anomalies.

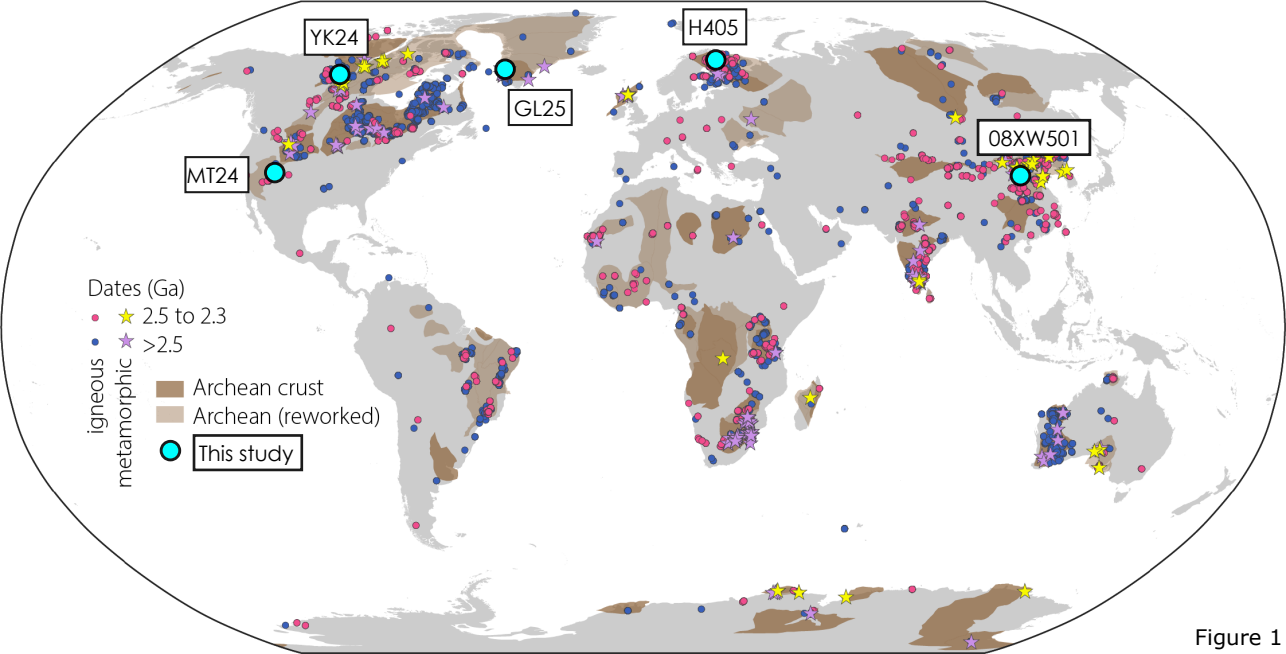


Figure 1

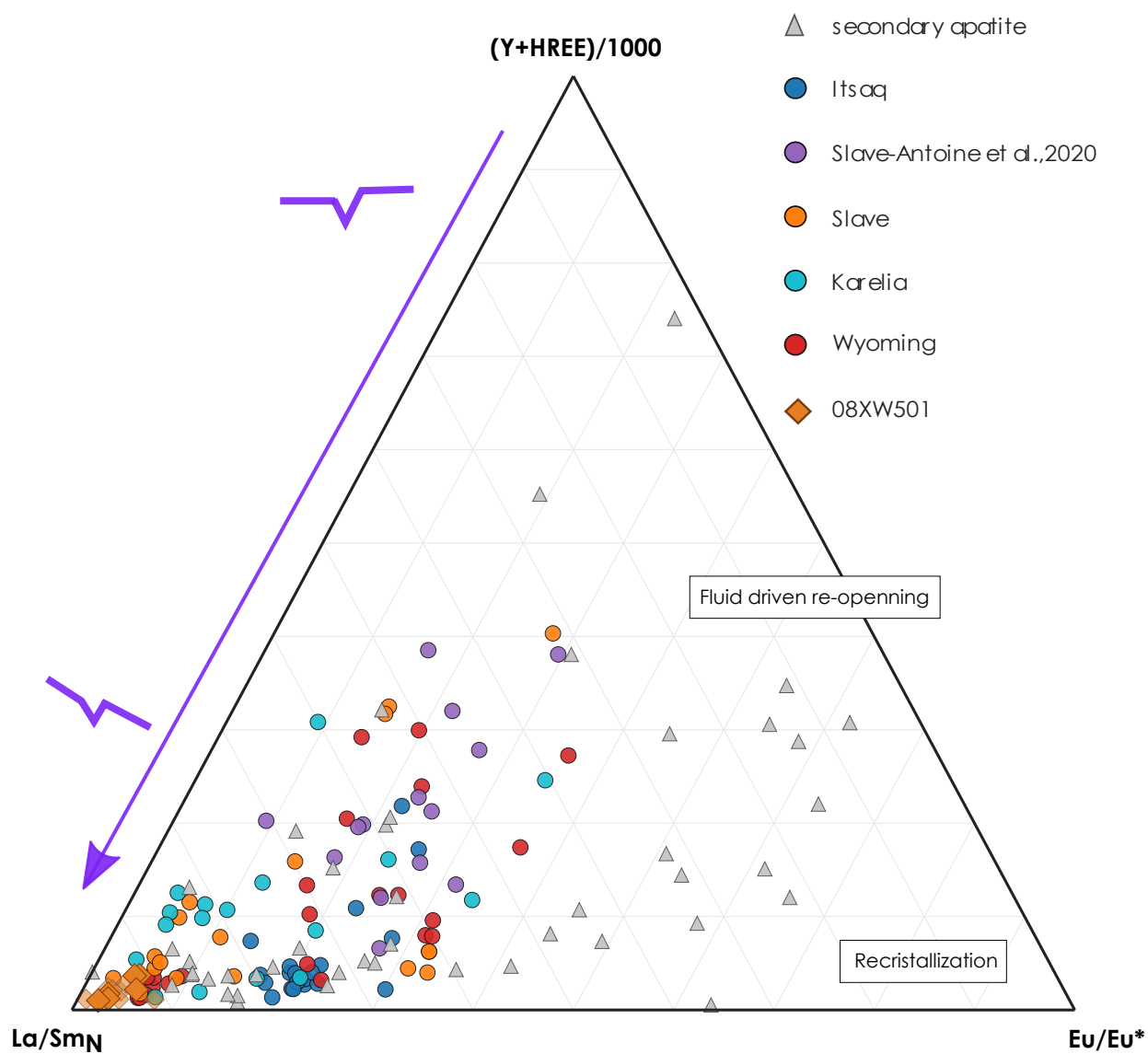


Figure 2

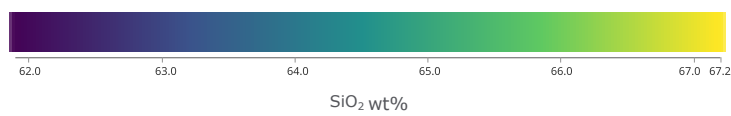
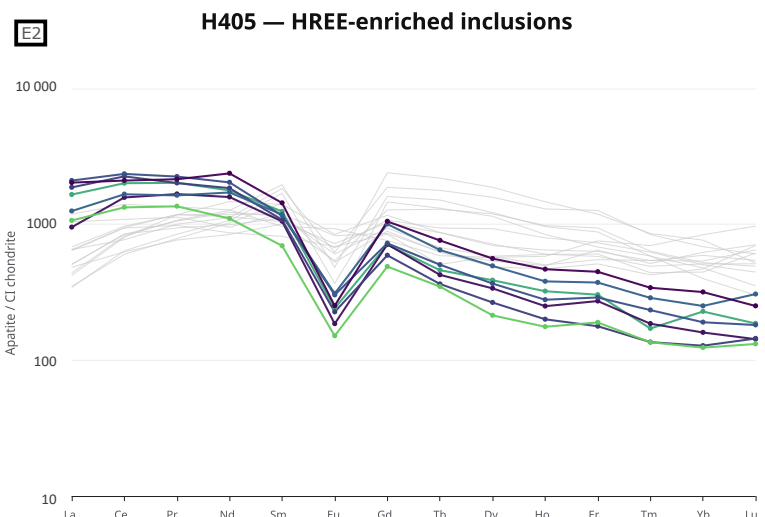
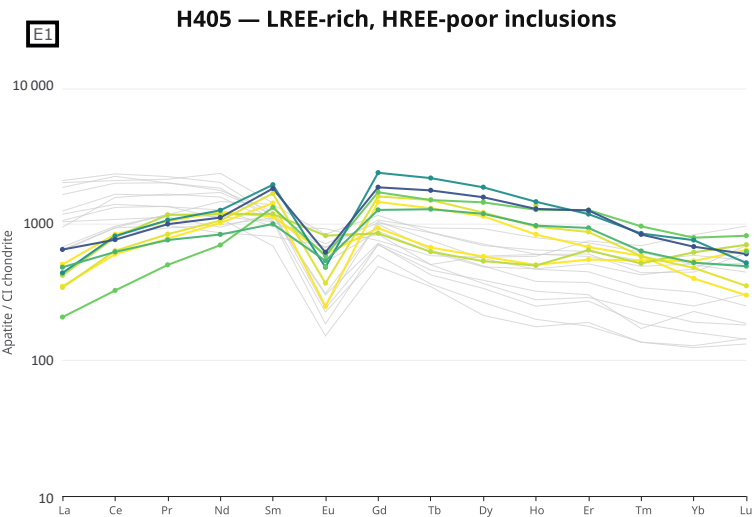
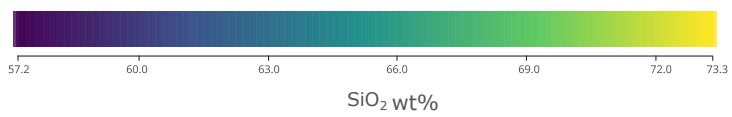
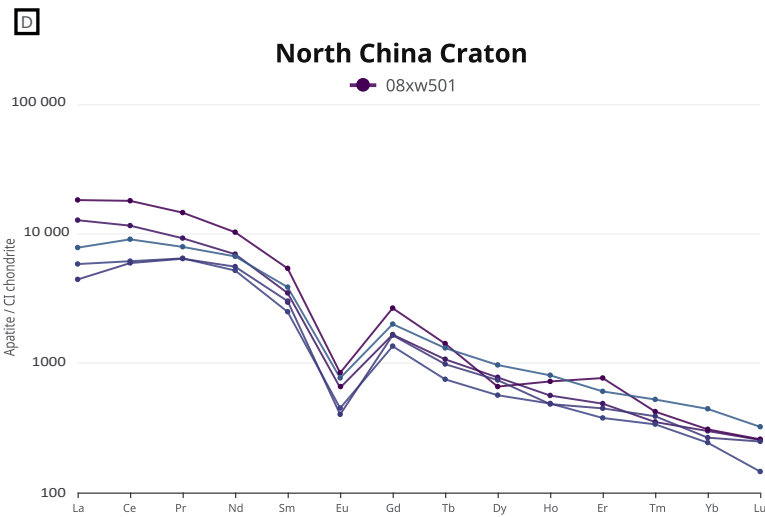
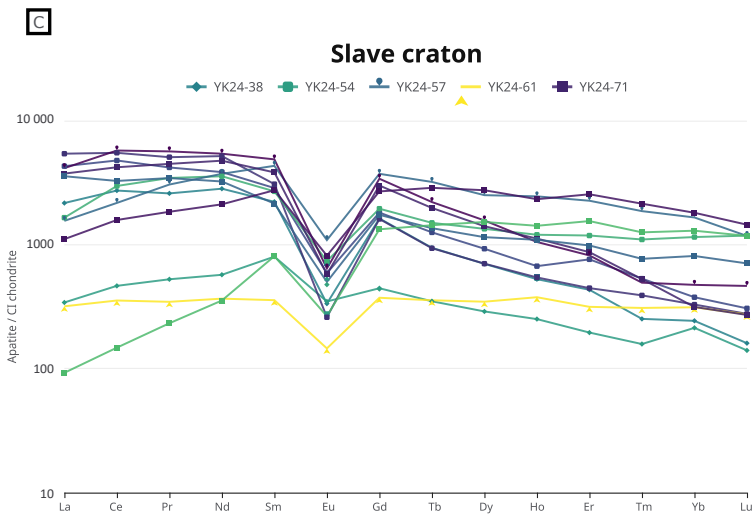
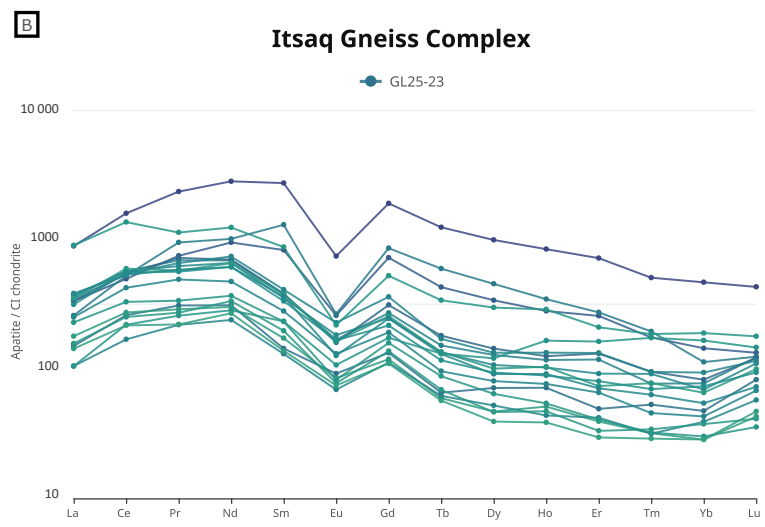
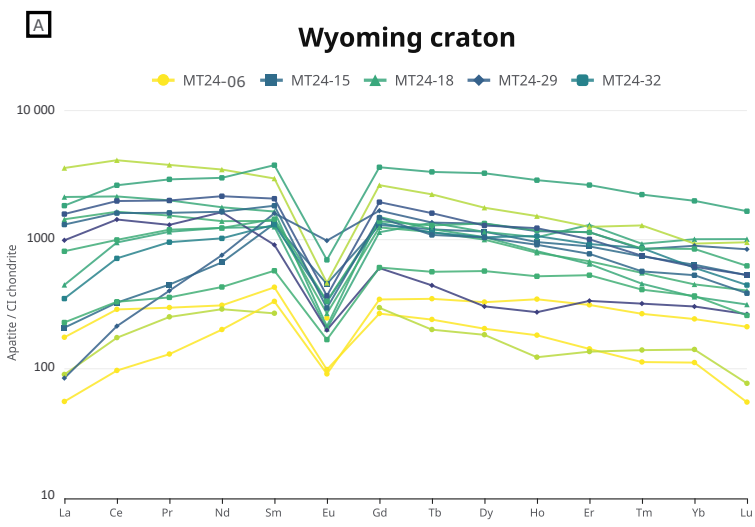


FIGURE 3

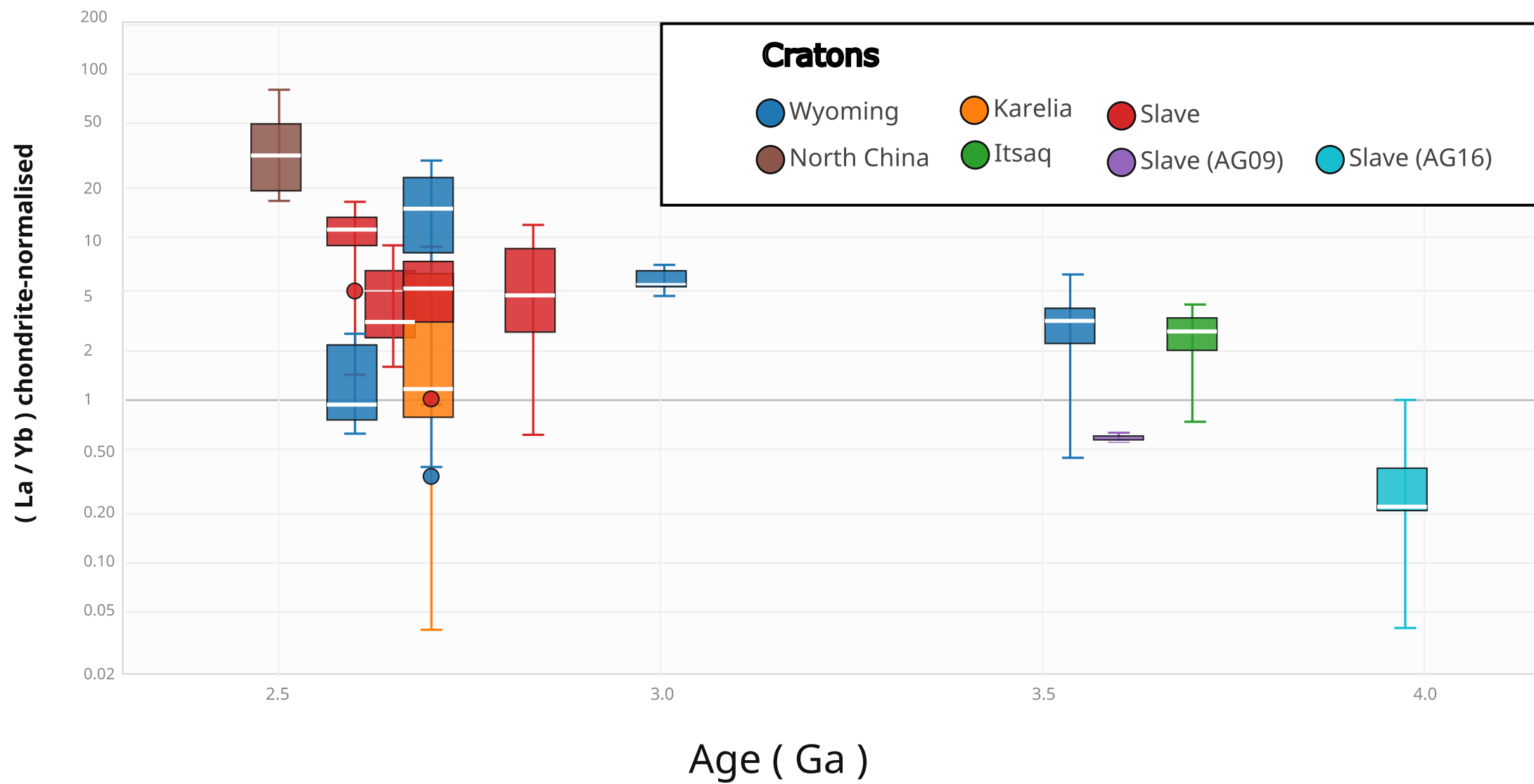
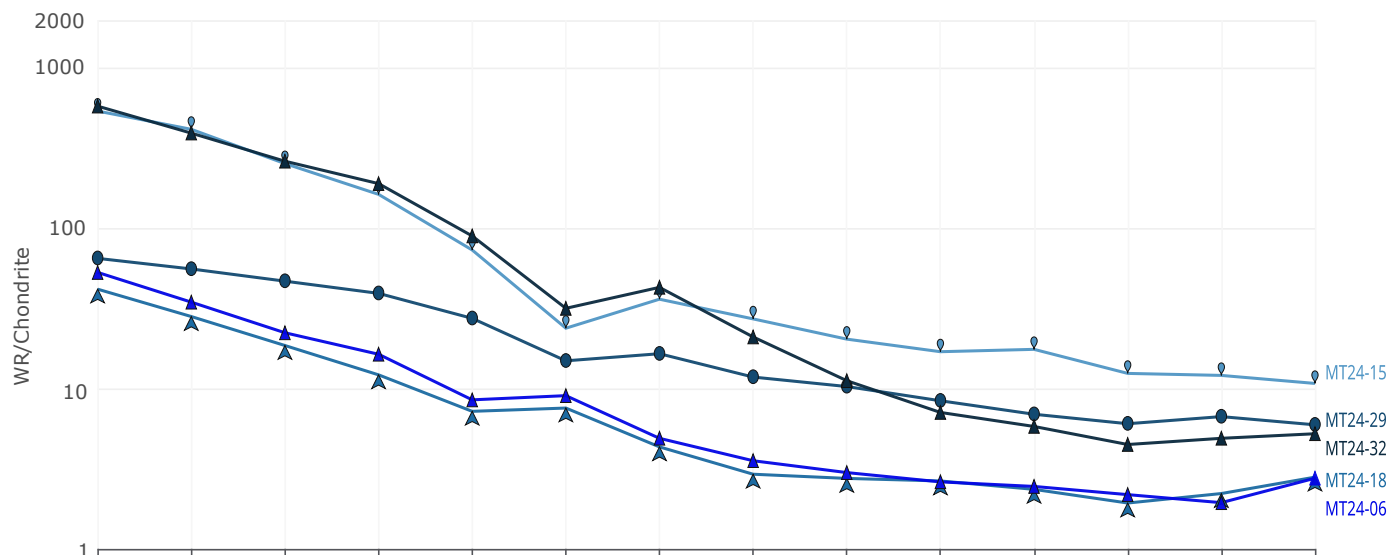


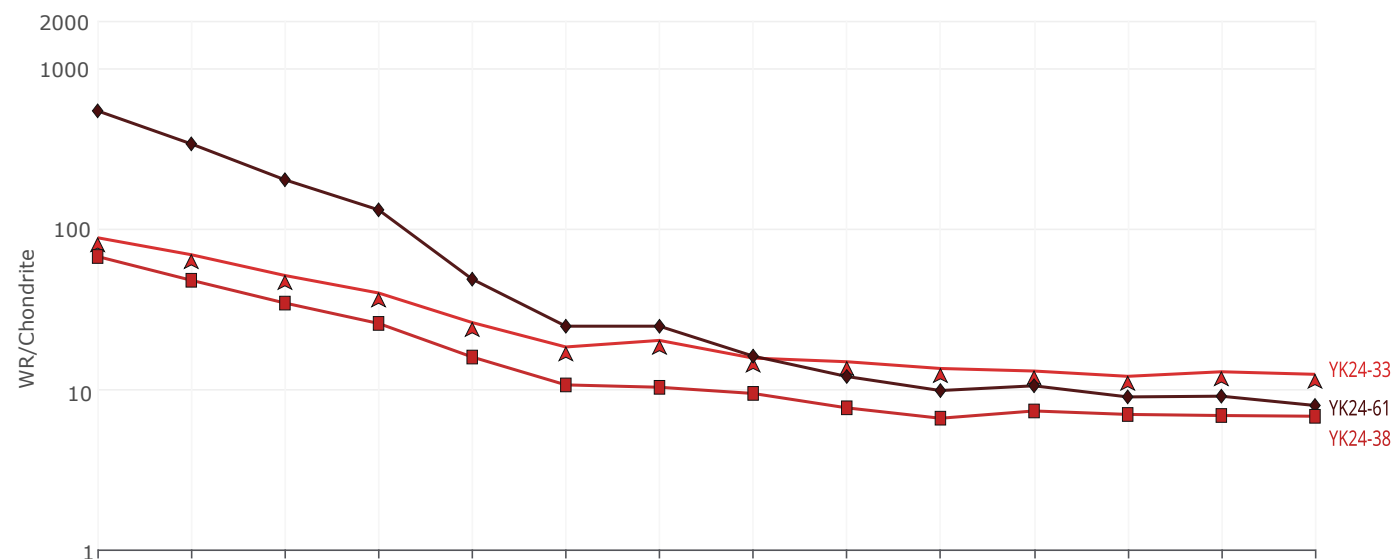
Figure 4

Wyoming Craton

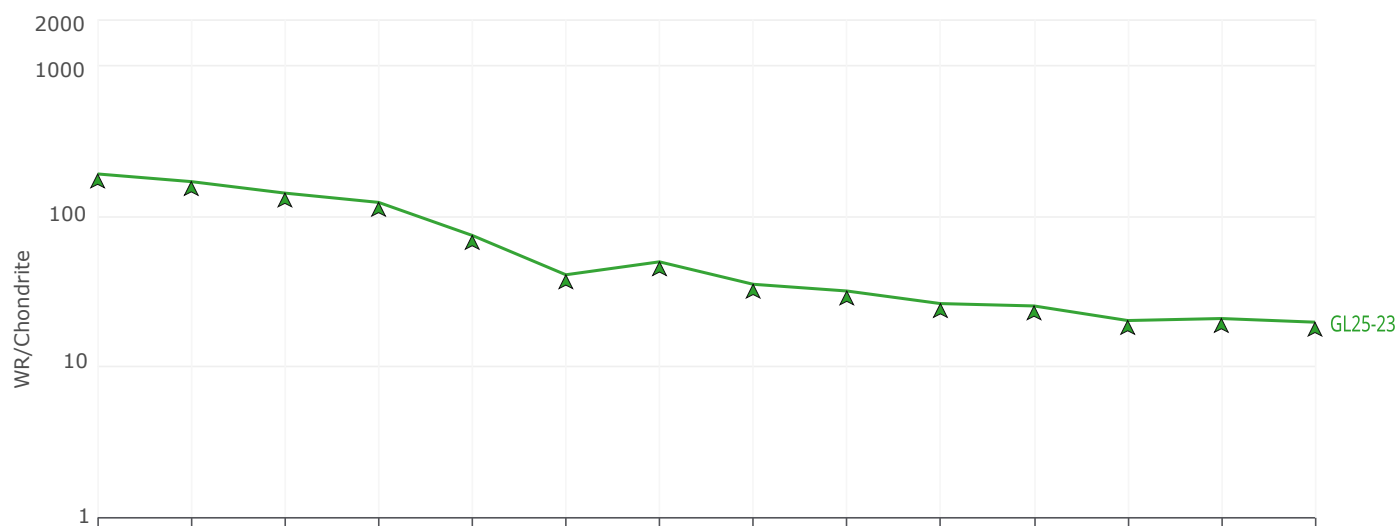
FIGURE 5



Slave Craton



Itsaq Craton



Slave Antoine et al., 2020

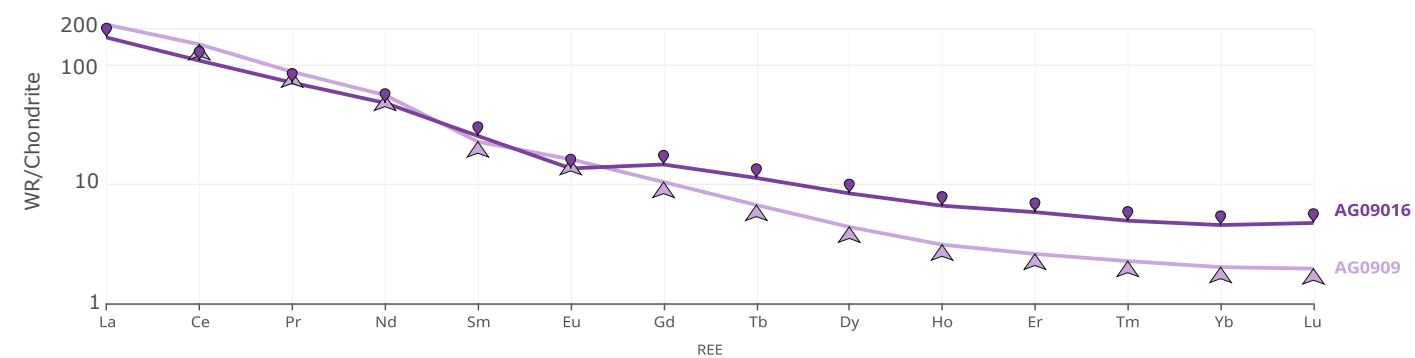
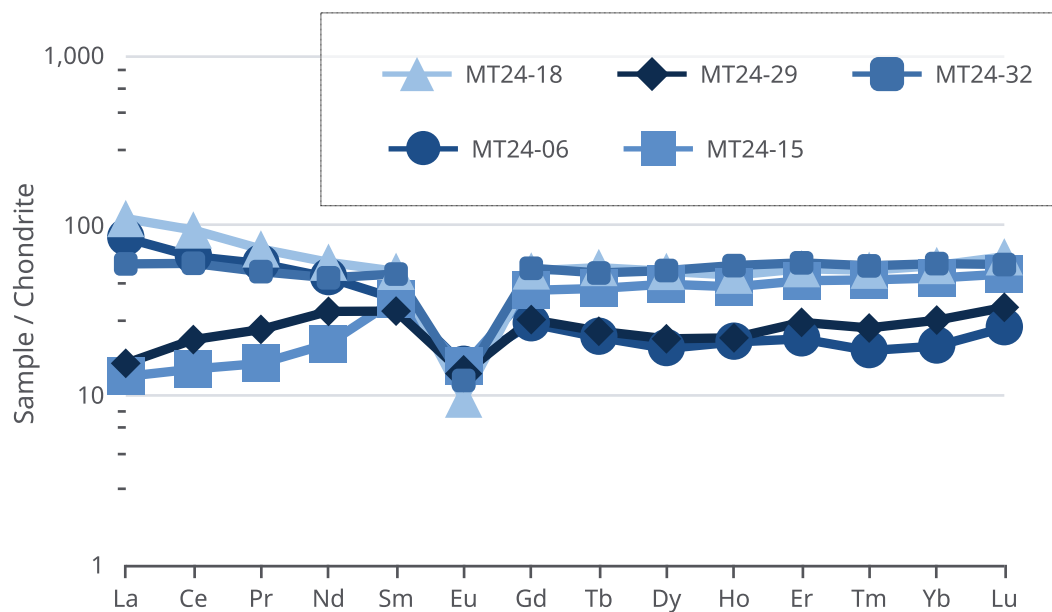
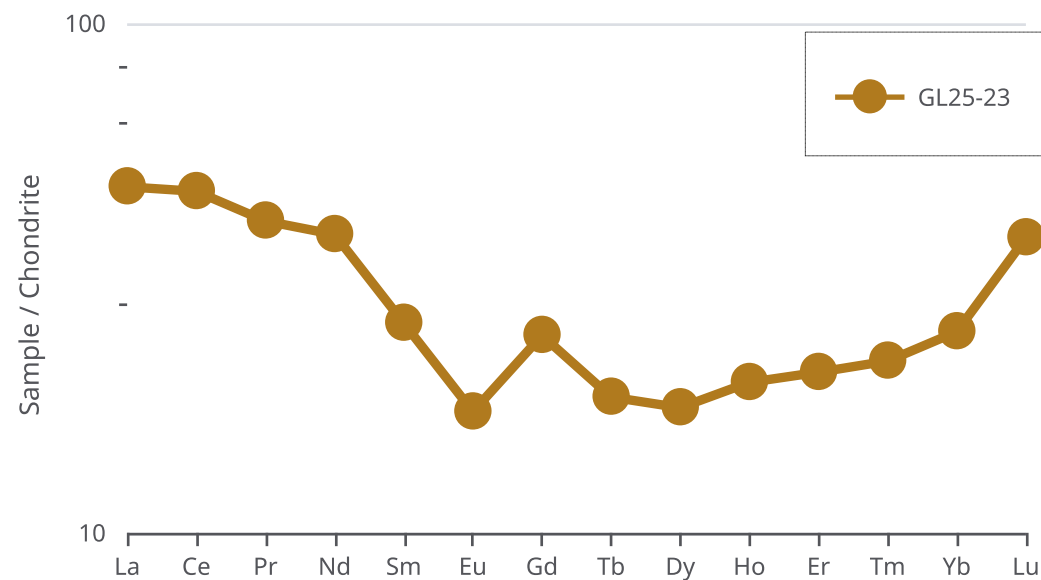


FIGURE 6

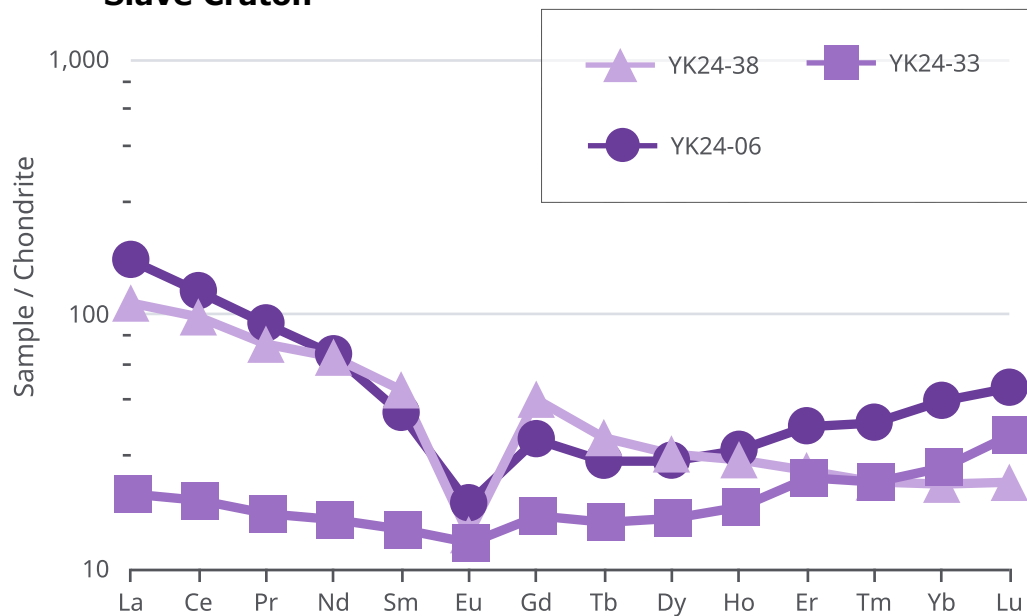
Wyoming Craton



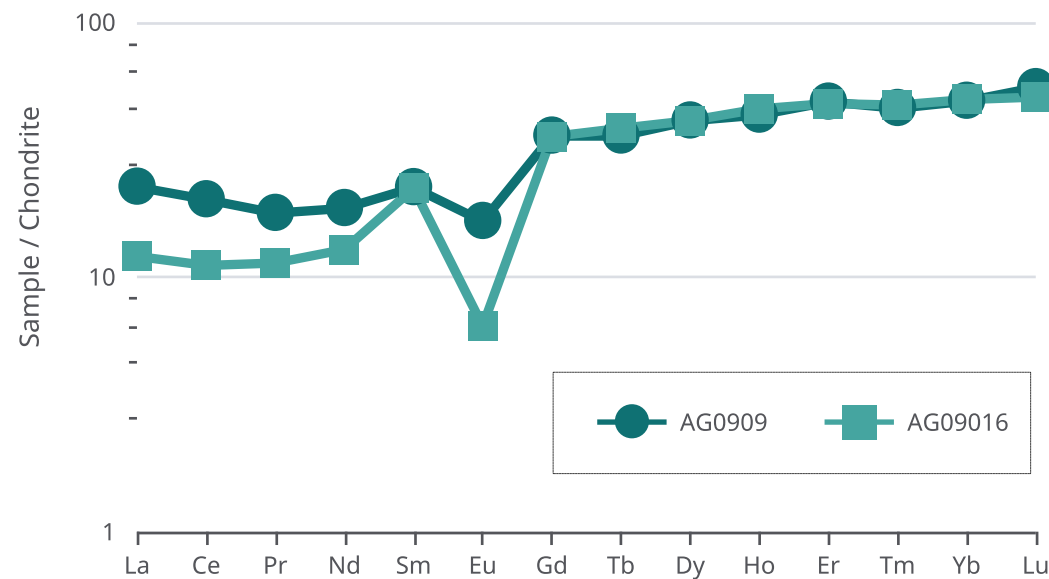
Itsaq Craton



Slave Craton



Slave Craton - Antoine et al., 2020



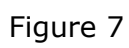


Figure 7

MT24-32

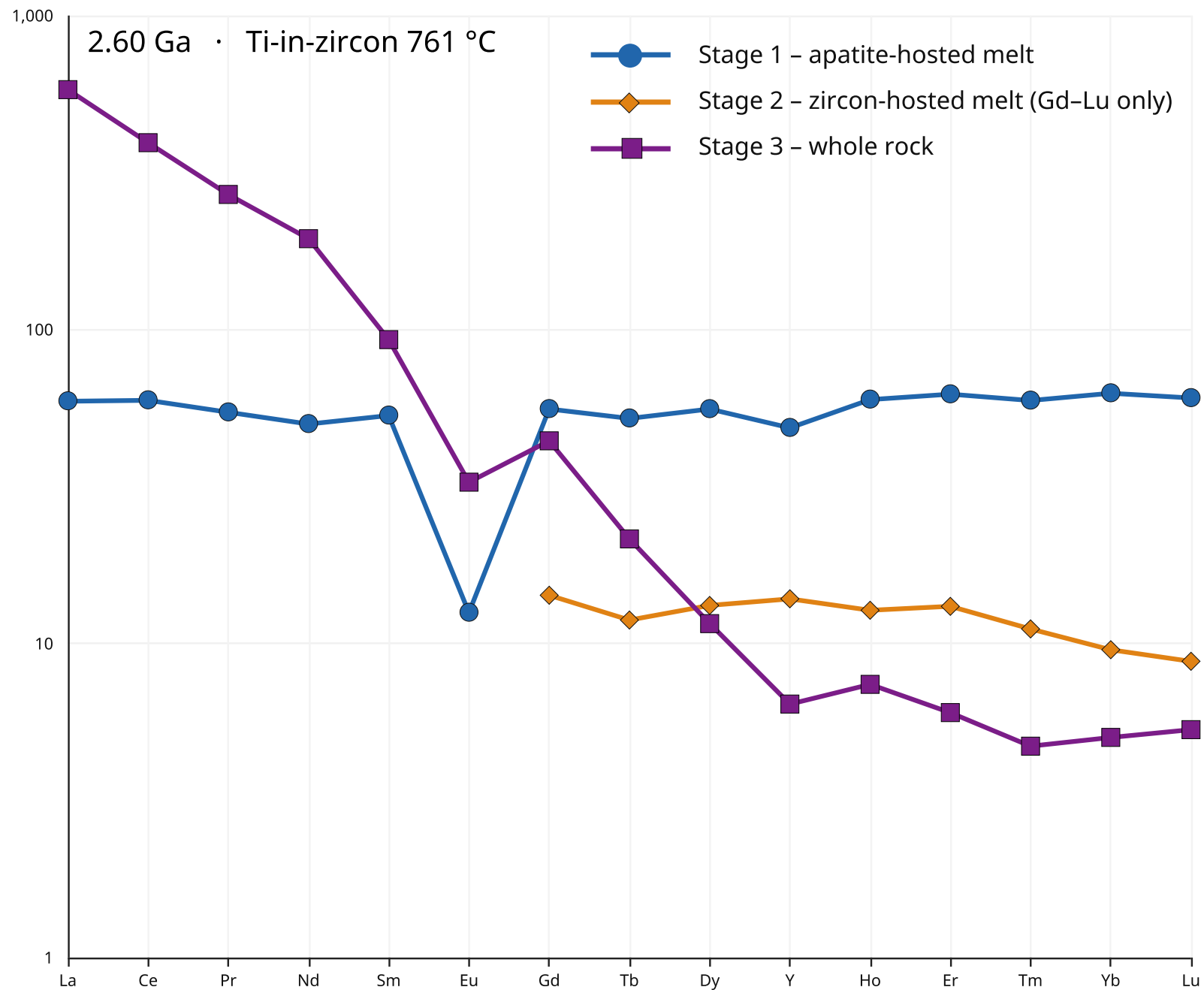


FIGURE 9

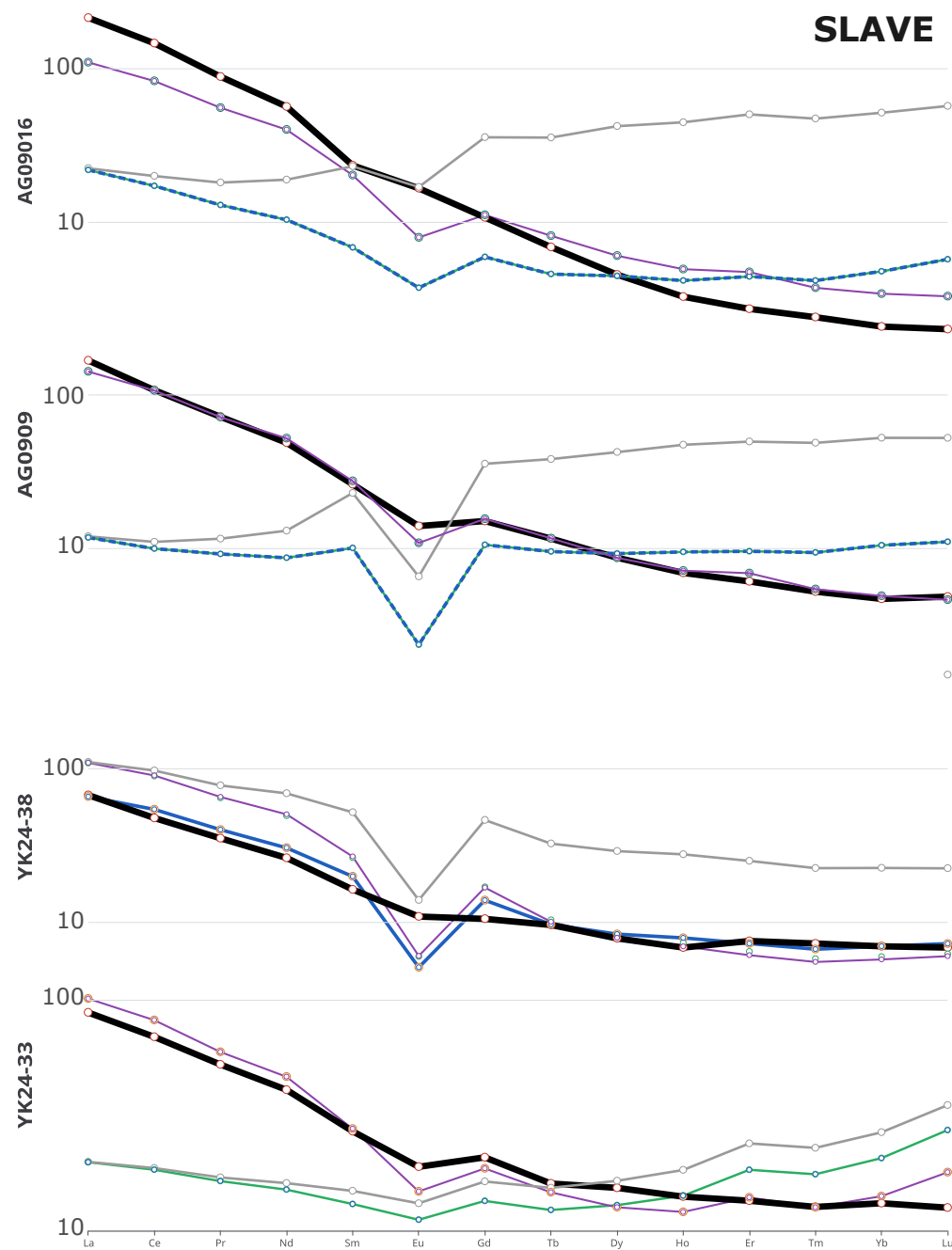
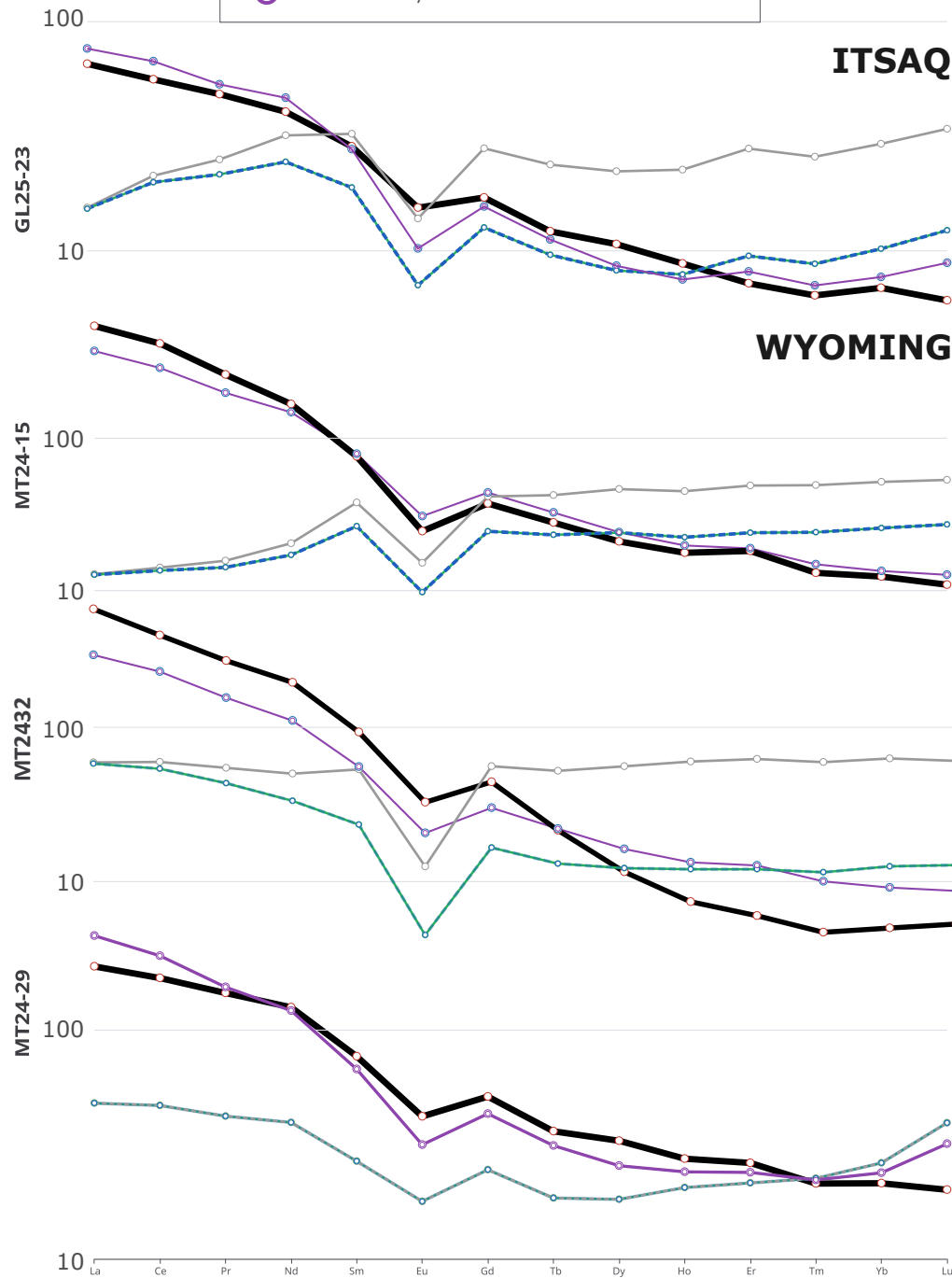
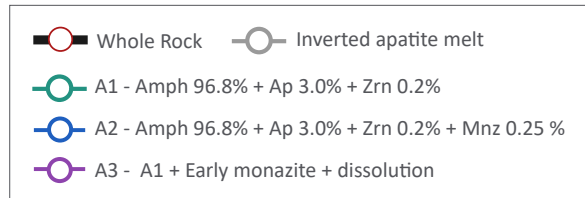
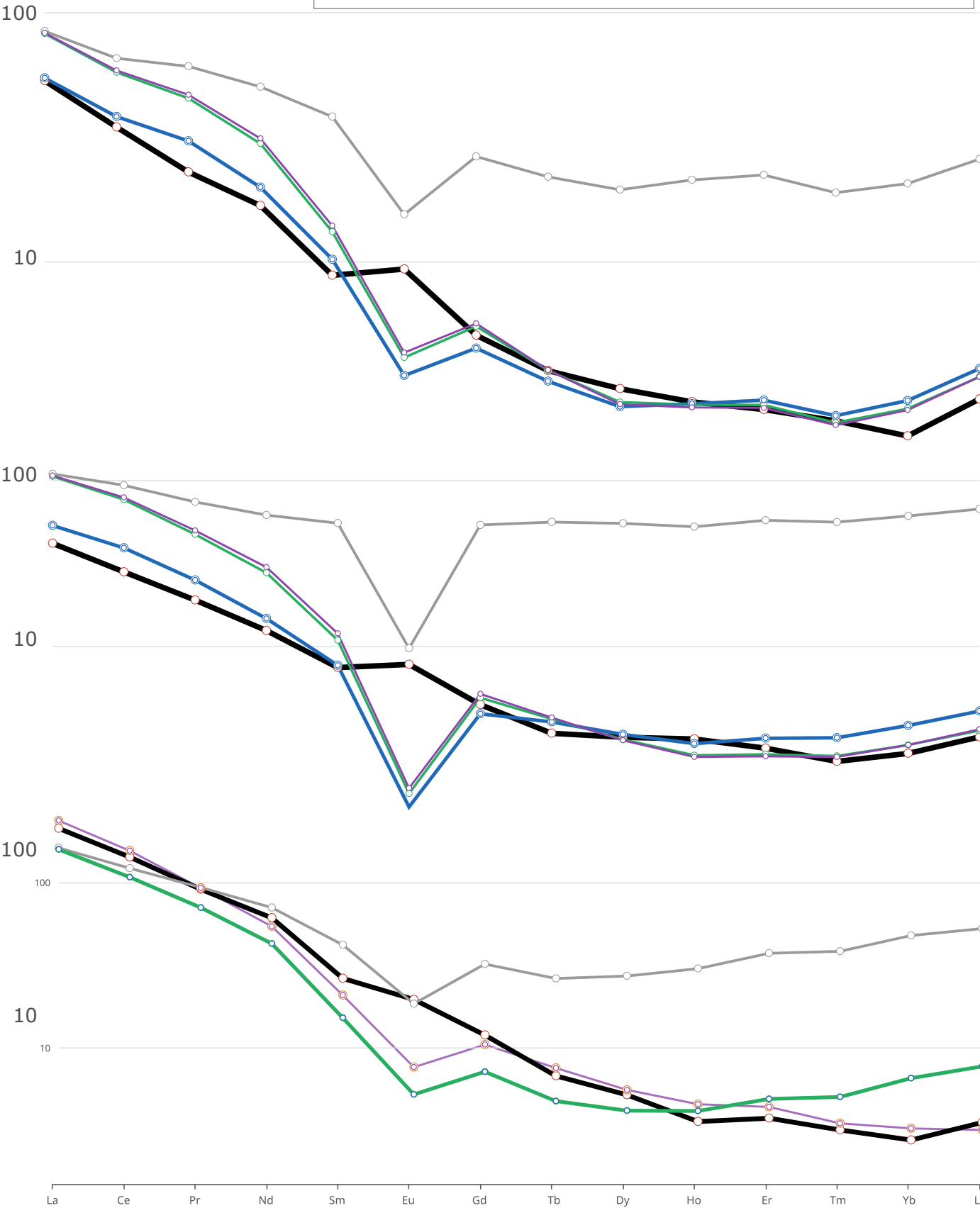
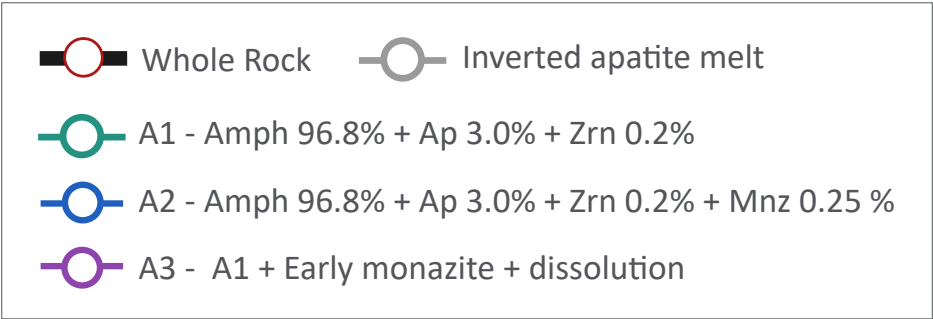


FIGURE 10

MT24-06

MT24-18

YK24-06



Sample	Spot Name
08xw501	Zr12 inc14
08xw501	Zr21 inc 24
08xw501	Zr20 inc23
08xw501	Zr26 inc28
08xw501	Zr34 inc 39
08xw501	Zr35 inc 40
08xw501	Zr13 inc15 bis
08xw501	Zr16 inc 19
08xw501	Zr15 inc17
08xw501	Zr26 inc30
08xw501	Zr26 inc 28
08xw501	Zr27 inc 31
08xw501	Zr33 inc 38
AG09016	AG16-11(1)
AG09016	AG16g100
AG09016	AG16g14
AG09016	AG16g15
AG09016	AG16g15(1-4)
AG09016	AG16g15(2-3)
AG09016	AG16g62
AG09016	AG16g88
AG09016	AG16g90
AG09016	AG16g108
AG09016	AG16g4(5)
AG09016	AG16g62(9-10)
AG0909	AG09 36
AG0909	AG09 42
AG0909	AG09 86
AG0909	AG0942
GL25-23	GL25-23 zr42
GL25-23	GL25-23 zr39
GL25-23	GL25-23 zr39
GL25-23	GL25-23 zr38
GL25-23	GL25-23-zr36
GL25-23	GL25-23-zr35
GL25-23	GL25-23 zr30
GL25-23	GL25-23 zr29
GL25-23	GL25-23 zr23
GL25-23	GL25-23 zr24
GL25-23	GL25-23 zr24
GL25-23	GL25-23 zr24
GL25-23	GL25-23 zr22
GL25-23	GL25-23 zr19
GL25-23	GL25-23 zr17
GL25-23	GL25-23 zr16

GL25-23	GL25-23 zr15
GL25-23	GL25-23 zr13
GL25-23	GL25-23 zr12
GL25-23	GL25-23 zr9
GL25-23	GL25-23 zr8
H405	Zr03 inc4
H405	Zr04 inc 07
H405	Zr07 inc 11
H405	Zr13 inc 19
H405	Zr14 inc22
H405	Zr17 inc26
H405	Zr20 inc32
H405	Zr21 inc33
H405	Zr24 inc36
H405	Zr28 inc42
H405	Zr30 inc 45
H405	Zr31 inc 30
H405	Zr31 inc46
H405	Zr44 inc68
H405	Zr48 inc75
H405	Zr51 inc79
H405	Zr53 inc82
H405	Zr54 inc83
H405	Zr56 inc87
H405	Zr57 inc89
H405	Zr57 inc92
H405	Zr59 inc95
H405	Zr62 inc 101
H405	Zr74 inc 118
H405	Zr75 inc 119
H405	Zr79 inc 126
H405	Zr03 inc5
H405	Zr06 inc09
H405	Zr11 inc16
H405	Zr14 inc20
H405	Zr16 inc24
H405	Zr29 inc 43
H405	Zr33 inc 49
H405	Zr34 inc51
H405	Zr38 inc56
H405	Zr55 inc85
H405	Zr56 inc 88
H405	Zr56 inc86
H405	Zr71 inc 113
H405	Zr71 inc 114
H405	Zr73 inc 117

MT24-06	MT24-06-1-zr2-inc2
MT24-06	MT24-06-1-zr3-inc3
MT24-06	MT24-06-1-zr6-inc6
MT24-15	MT24-15 zr5
MT24-18	MT24-18-zr4
MT24-18	MT24-18-zr5
MT24-18	MT24-18-zr8
MT24-18	MT24-18-zr8
MT24-18	MT24-18-zr3
MT24-18	MT24-18-zr6
MT24-18	MT24-18-zr7
MT24-29	MT24-29 zr4
MT24-29	MT24-29 zr4
MT24-29	MT24-29 zr1
MT24-29	MT24-29 zr3
MT24-29	MT24-29 zr6
MT24-29	MT24-29 zr9
MT24-32	MT24-32-2-zr2-inc3
MT24-32	MT24-32-2-zr2-inc2-1
MT24-32	MT24-32-2-zr2-inc2-2
MT24-32	MT24-32-2-zr2-inc4
MT24-32	MT24-32-2-zr5-inc9
MT24-32	MT24-32-2-zr5-inc8
MT24-32	MT24-32-2-zr1-inc1
YK24-06	YK24-06-01-zr7-inc10
YK24-06	YK24-06-01-zr3-inc3
YK24-06	YK24-06-01-zr4-inc5
YK24-06	YK24-06-01-zr4-inc4
YK24-33	YK24-33 zr2
YK24-33	YK24-33 zr4
YK24-38	YK24-38 Zr1
YK24-38	YK24-38 Zr3
YK24-38	YK24-38 Zr5
YK24-38	YK24-38 Zr1
YK24-38	YK24-38 Zr4
YK24-38	YK24-38 Zr6
YK24-54	YK24-54-zr3-inc4
YK24-54	YK24-54-zr11-inc13
YK24-54	YK24-54-zr08-inc10
YK24-54	YK24-54-zr06-inc7
YK24-54	YK24-54-zr2-inc3
YK24-57	YK24-57-zr03-inc4
YK24-57	YK24-57-zr05-inc7
YK24-61	YK24-61-62-1 10 7
YK24-61	Zr3-YK24-61-0
YK24-71	YK24-71-zr3-inc4

YK24-71	YK24-71-zr5-inc6
YK24-71	YK24-71-zr6-inc7
YK24-71	YK24-71_zr12_inc11
YK24-71	YK24-71_zr14_inc13

Craton	Coordinates	Age (Ga)	flag	zr_status
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North China Craton (NCC)	Martin 1982	2.4	primary	below detection
North China Craton (NCC)	Martin 1982	2.4	primary	passes cut
North China Craton (NCC)	Martin 1982	2.4	primary	passes cut
North China Craton (NCC)	Martin 1982	2.4	primary	passes cut
North China Craton (NCC)	Martin 1982	2.4	primary	passes cut
North China Craton (NCC)	Martin 1982	2.4	secondary	fails cut
North China Craton (NCC)	Martin 1982	2.4	secondary	fails cut
North China Craton (NCC)	Martin 1982	2.4	secondary	fails cut
North China Craton (NCC)	Martin 1982	2.4	secondary	fails cut
North China Craton (NCC)	Martin 1982	2.4	secondary	fails cut
North China Craton (NCC)	Martin 1982	2.4	secondary	fails cut
North China Craton (NCC)	Martin 1982	2.4	secondary	fails cut
Slave-Antoine et al.,2020	Antoine et al., 2020	3.975	primary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.975	primary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.975	primary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.975	primary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.975	primary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.975	primary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.975	primary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.975	primary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.975	secondary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.975	secondary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.975	secondary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.6	primary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.6	primary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.6	primary	below detection
Slave-Antoine et al.,2020	Antoine et al., 2020	3.6	primary	below detection
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Itsaq	64.01489, -51,36290	3.7	primary	passes cut
Itsaq	64.01489, -51,36291	3.7	primary	passes cut
Itsaq	64.01489, -51,36292	3.7	primary	passes cut
Itsaq	64.01489, -51,36293	3.7	primary	passes cut
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Itsaq	64.01489, -51,36304	3.7	primary	passes cut

[illegible]

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Wyoming	45.035655, -109.411847	3.54 primary	passes cut
Wyoming	45.035655, -109.411847	3.54 primary	passes cut
Wyoming	45.035655, -109.411847	3.54 primary	below detection
Wyoming	45.035655, -109.411847	3.54 primary	passes cut
Wyoming	45.035655, -109.411847	3.54 secondary	fails cut
Wyoming	45.035655, -109.411847	3.54 secondary	fails cut
Wyoming	45.035655, -109.411847	3.54 secondary	passes cut
Wyoming	45.083569, -109.955869	2.7 primary	below detection
Wyoming	45.083569, -109.955869	2.7 primary	passes cut
Wyoming	45.083569, -109.955869	2.7 secondary	passes cut
Wyoming	45.083569, -109.955869	2.7 secondary	fails cut
Wyoming	45.083569, -109.955869	2.7 secondary	fails cut
Wyoming	45.083569, -109.955869	2.7 secondary	passes cut
Wyoming	43.7593150, -110.74427	2.6 primary	passes cut
Wyoming	43.7593150, -110.74427	2.6 primary	below detection
Wyoming	43.7593150, -110.74427	2.6 primary	passes cut
Wyoming	43.7593150, -110.74427	2.6 primary	below detection
Wyoming	43.7593150, -110.74427	2.6 primary	passes cut
Wyoming	43.7593150, -110.74427	2.6 primary	passes cut
Wyoming	43.7593150, -110.74427	2.6 secondary	fails cut
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Slave	62.452208, -114.310548	2.7 secondary	passes cut
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Slave	62.55279, -114.026873	2.7 secondary	passes cut
Slave	61.244947, -117.48214	2.7 primary	passes cut
Slave	61.244947, -117.48214	2.7 primary	passes cut
Slave	65.173875, -115.553639	3.629 primary	below detection
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Slave	65.166573,-115.561883	3.2 primary	passes cut
Slave	65.166573,-115.561883	2.9 secondary	passes cut

Zr	Th	U	thyU	Nd	La	Ce	Sm
1.94617	81.8289	3.3506	24.422163	3171.38	3011.24	7065.08	515.121
	5.99029	5.18841	1.1545522	3047.91	1848.09	5544.49	571.422
8.5898	5.94927	2.40094	2.477892	2541.38	1049.85	3636.59	445.432
1.38252	54.3521	3.56808	15.23287	2463.47	2335.68	5714.54	391.156
19.6313	9.16622	1.93913	4.7269755	1454.83	962.515	2573.4	299.247
18.2808	35.5855	2.31888	15.345986	2502.34	2554.6	5647.08	376.49
568.644				879.07	1577.69	2788.95	437.663
3576.45	76.318	12.5846	6.0643962	4686.53	4311.28	10999.8	797.326
599.416	0.431176	1.59464	0.2703908	2373.89	1379.55	3755.77	368.623
100.559	51.4498	1.0924	47.097949	3511.54	2363.53	5843.05	394.862
222.651	19.8903	1.43008	13.908523	4263.37	4462.32	9909.55	482.317
1690.08	44.1033	4.06684	10.844612	2503.26	1412.84	4005.86	451.458
1162.97	108.264	7.00613	15.452754	3571.42	3352.93	8140.84	632.269
	1.09	10.34	0.1054159	198.96	40.44	129.47	155.58
	1.55	3.95	0.3924051	474.61	81.6	402.58	201.9
		3.01		206.93	82.37	222.68	104.98
	12.02	21.63	0.5557097	209.06	72.25	161.92	128.87
		5.61		85.17	24.35	79.16	63.05
	5.89	19.22	0.3064516	166.45	39.82	126.87	102.09
	2.05	15.25	0.1344262	58.96	9.1	37.12	59.51
	2.27	9.98	0.2274549	226.98	38.38	167.85	149.33
	5.16	15.67	0.3292916	210.51	53.57	147.97	123.78
	4.02	7.79	0.5160462	16.09	1.38	6.12	19.59
	3.19	6.02	0.5299003	43.16	0.73	2.51	90.53
	1.81	11.62	0.1557659	44.9	1.35	13.8	36.42
	33.37	18.74	1.780683	698.74	204.93	721.14	274.67
	3.3	2.62	1.259542	142.74	45.9	139.37	59.45
	5.78	5.97	0.9681742	281.07	76.72	267.48	129.32
	9.28	7.91	1.1731985	279.99	94.78	299.95	121.12
39.354494	2.9378903	5.1157897	0.5742789	451.4009	144.35632	537.74487	87.499396
2.1469174	3.7110376	5.1421912	0.7216841	950.00658	245.66556	827.08954	281.31443
2.9607653	17.057072	22.032657	0.7741722	1960.5768	472.15732	1799.8061	622.00989
3.3527239	2.3085978	5.0593268	0.4563053	767.8494	262.84456	906.25935	166.03715
2.0678978	8.2067789	12.920937	0.6351535	990.81059	207.04039	859.97123	379.70606
9.7163238	1.7181634	4.3561737	0.3944203	775.47935	246.4476	875.96458	167.85023
3.4861732	2.1656401	5.7449223	0.3769659	804.88673	252.64291	874.58726	175.76935
2.4084409	1.8847219	4.1012544	0.4595477	744.90893	260.66389	906.28056	159.4345
1.0713413	0.5212231	0.947544	0.550078	161.64623	38.088218	152.83939	44.790585
2.0450214	0.1922672	0.8259372	0.2327867	275.1185	85.228511	298.09531	50.400035
0.8546839	0.8122668	1.4621208	0.5555401	442.15869	162.08435	555.31576	98.886911
2.1402753	1.3199165	3.1196936	0.4230917	597.54653	202.97651	744.32967	136.36771
2.1318847	1.8697145	4.7592845	0.3928562	743.58553	253.98543	934.19186	167.10736
2.2686391	1.2951515	1.1932863	1.0853653	379.34176	113.74734	403.9401	82.118852
3.1114695	9.3912998	8.624761	1.0888765	710.49458	269.09513	868.67589	162.10869
14.172315	4.591726	3.5809645	1.2822596	425.08001	113.63943	480.43533	120.74866

9.6674779	10.591066	13.290114	0.7969131	1134.8135	476.05327	1622.324	291.26533
49.541583	1.3885313	1.9259213	0.7209699	505.03601	190.76781	629.94407	120.42814
3.3042711	1.3232723	2.5533791	0.5182436	473.96538	148.53845	526.41668	107.92124
3.6489644	2.0792618	4.8633021	0.4275412	711.01704	236.06981	892.55088	153.52896
1.6222231	1.0447496	1.8060583	0.5784694	410.14501	139.78768	476.47555	85.116172
3.2106987	29.489193	39.127742	0.7536646	561.81375	120.16076	516.92104	169.03116
39.516456	17.053303	28.8466	0.591172	812.17004	392.33258	1229.8807	183.96968
1.5102166	10.883911	18.636877	0.5839987	467.84032	82.813165	369.36772	211.91621
13.639574	4.8497588	10.461433	0.4635846	725.6552	225.74898	966.44257	155.91723
8.3707467	10.600896	24.276652	0.4366704	844.8805	443.32505	1382.0856	159.71014
20.177542	26.603766	57.115339	0.4657902	454.17361	119.91297	520.24501	164.46542
12.660594	16.262344	20.6225	0.7885729	931.08202	497.59934	1440.9085	172.16797
	10.07222	39.961136	0.2520504	141.04542	10.014027	54.051462	142.66526
	24.912471	34.396105	0.7242817	486.92863	81.184443	391.30785	249.67061
5.048078	23.124483	49.503276	0.4671304	321.13409	49.145775	199.55622	197.11951
	12.292373	43.929717	0.2798191	784.69045	296.71893	1021.2493	174.50564
15.627798	7.3241986	17.757476	0.4124572	504.25368	252.8919	817.78062	102.82547
	18.397901	29.516812	0.6233024	579.05924	103.92477	502.63732	289.30515
4.8901502	3.1603379	12.702982	0.2487871	384.68681	114.44257	384.0072	148.83999
11.400528	9.6019211	28.675921	0.3348426	120.67949	8.2048309	46.942474	93.57839
9.1474808	18.454703	19.237487	0.9593094	1084.7448	480.70625	1288.645	212.67838
4.3560641	17.308103	70.087512	0.2469499	673.01674	161.78825	594.1276	207.59833
2.9561649	4.2136082	38.148757	0.110452	482.7481	124.79313	454.06061	123.88443
17.70883	2.9900837	8.1775809	0.365644	509.08975	93.783576	373.60541	249.82761
4.7536212	25.606719	51.077602	0.5013297	1272.326	463.68999	1481.4003	231.15496
29.188066	38.490488	28.069326	1.3712652	757.64738	130.34322	651.68476	209.12206
2.8678735	39.371782	54.278899	0.7253607	645.782	228.84589	803.87901	145.29114
2.2079045	77.077224	97.165096	0.7932604	715.29335	183.28274	714.86759	216.63786
4.1854523	21.259687	31.824496	0.668029	567.87389	152.46367	555.95426	186.94637
9.4236877	13.006508	22.612506	0.5751909	276.05843	36.429329	144.51709	131.25747
8.7834418	24.650865	22.936844	1.0747278	1044.9189	463.72035	1304.8948	204.91666
10.164255	93.605245	113.94771	0.8214754	753.38685	356.73738	1191.3443	191.76347
10.675033	4.7054352	20.042344	0.2347747	44.485314	8.3434947	30.316792	43.930675
678.88651	27.69478	81.545249	0.3396247	396.30887	151.91583	576.23228	120.68769
1.1432484	42.469807	58.399783	0.7272254	541.57485	99.768369	492.35055	176.36711
326.15069	61.884829	157.71253	0.3923901	435.43605	247.75195	665.56952	177.41573
	55.717328	160.2473	0.3476959	583.69709	281.31355	860.41082	142.80872
643.21179	14.202995	34.029936	0.4173677	512.06991	154.50882	472.52761	271.54705
411.19177	35.150975	151.62556	0.2318275	519.98173	154.65084	579.61539	154.74135
662.56539	4.9303409	24.892553	0.1980649	63.105369	12.782415	50.918367	54.512751
148.26865	9.71931	10.0726	0.9649256	852.95171	215.59621	970.11203	180.6452
915.80764	36.415712	59.999555	0.606933	646.2797	120.31418	476.50245	308.41811
596.29599	22.002079	87.96583	0.2501207	634.96849	185.74802	674.79002	166.0983
637.13745	1.5170779	15.560184	0.0974974	347.19401	75.428023	318.65962	164.43039
89.474311	56.198662	157.61897	0.3565476	451.96772	152.20637	482.24874	132.09848
108.58092	10.094909	38.356004	0.2631898	219.72307	19.354866	97.789521	141.04297

177.12061	0.5122728	53.049999	0.0096564	671.7204	351.28833	962.01465	197.28897
18.162092	1.988546	67.036018	0.0296638	783.80176	294.08322	809.25323	195.1252
31.567144	2.0856173	55.540936	0.037551	823.91034	338.56732	1069.6436	208.60989
0.5223785	4.5840612	33.397278	0.1372585	303.63327	49.325318	199.25881	195.5513
6.4728871	10.386219	20.969716	0.4952961	1584.4218	844.73954	2509.2997	437.5647
14.745394	3.2456146	18.18938	0.1784346	810.27539	504.29447	1316.8523	243.122
	5.9934981	14.388871	0.4165371	1143.9667	606.80298	1721.9646	342.10761
1.6299185	8.5305746	44.239668	0.1928264	1356.1797	700.03498	1927.1981	401.87482
125.89596	10.299014	23.393266	0.4402555	561.79545	105.61185	580.45198	185.34458
58.955023	1.6849028	8.858335	0.1902054	632.55428	339.17242	1004.1771	205.90732
36.143965	2.4933525	27.232197	0.091559	1047.3295	540.33312	1520.9086	372.65037
	11.472595	3.843646	2.9848211	854.34476	476.54883	1335.5628	175.80733
1.2743717	4.0624848	35.613329	0.114072	581.20727	73.824227	457.11964	160.32591
0.6914636	4.2697528	96.729982	0.0441409	345.63157	20.131317	131.20408	235.76695
151.44114	13.131676	20.493697	0.6407666	741.82935	233.59547	874.30183	134.46618
180.22762	2.6361051	51.111209	0.0515759	270.37159	24.854436	114.73541	155.27352
19.32706	4.8074942	50.889953	0.0944684	354.87854	27.957263	163.55675	151.17036
3.7242391	13.714322	42.995422	0.3189717	560.90582	192.07339	608.19025	212.47623
	10.223771	40.106487	0.2549156	986.30963	372.33014	1214.9053	305.7265
0.7320827	4.4862847	22.808771	0.1966912	748.46002	308.90598	979.62988	269.74759
	7.2148914	19.961523	0.3614399	196.21677	54.106373	202.39279	84.870392
6.7756925	104.09792	202.8403	0.5132014	1367.7039	432.4202	1607.8701	554.78815
20.835848	8.5083075	28.57975	0.2977041	297.31757	108.68684	341.37506	121.97048
166.827	9.2951422	27.615303	0.3365939	465.97046	82.788071	437.97037	192.56117
2.0137641	25.321392	20.684893	1.2241491	1041.8254	623.98633	1704.1317	216.8951
	16.453503	23.484697	0.7006053	135.90088	58.276066	145.63792	75.184616
0.5354573	8.3161259	16.873732	0.4928445	206.68779	64.201378	208.13283	67.993721
1.1723031	25.071627	55.592453	0.4509898	95.942253	29.913614	95.032913	61.280151
1.0479694	32.967183	13.340694	2.4711745	240.0595	76.702387	266.38687	78.1439
3.1174598	70.010631	51.862247	1.3499344	277.3416	155.22918	447.16267	66.402783
2.4797828	19.874604	13.665613	1.4543515	1291.2225	513.20572	1674.4934	328.03218
13.745274	12.004783	18.810558	0.6381939	261.28259	80.934586	284.99374	118.45336
1.6902878	56.113547	26.792318	2.0943894	932.56785	441.689	1207.0025	293.57364
58.14556	19.585297	26.666289	0.734459	438.9518	286.59083	664.09381	99.241862
3.2304637	26.883366	26.620845	1.0098615	434.18329	311.72078	800.69091	102.21523
74.985649	12.790411	8.8519417	1.4449271	913.19022	336.6787	1266.4031	205.84591
12.729779	39.062824	22.112652	1.7665373	1759.0994	1017.8749	2924.3904	423.70288
22.099077	10.857666	11.322089	0.9589808	2367.0732	1282.8342	3376.0691	455.30478
5.6442304	147.53825	97.260513	1.5169389	1627.0045	391.31094	1821.2992	398.21228
1.3623759	52.418652	40.339161	1.2994482	816.01147	633.22675	1545.4741	177.71904
13.798199	15.126271	14.573396	1.0379373	297.75513	152.94199	493.95462	54.524597
37.963989	5.2416759	22.363028	0.2343903	1701.3856	368.24976	1329.7017	639.98865
14.324336	28.583776	24.750769	1.1548642	2472.4287	981.90814	3523.147	720.37268
	5.5630852	13.68798	0.4064212	167.64531	75.35666	217.01321	52.759034
56602.649	39.363938	82.22993	0.4787057	678.27418	285.15831	859.42055	249.06558
10.225378	95.330292	15.068777	6.3263456	2173.835	886.20923	2579.0103	566.26733

38.638947	44.595547	45.332157	0.9837508	1475.9969	844.7489	2003.1606	317.02975
	12.768393	31.182617	0.4094715	966.20978	262.51794	968.70703	406.16629
2.859339	78.721321	80.063873	0.9832315	161.84242	21.938852	90.49118	119.29805
1.3819661	0.696483	10.137486	0.0687037	270.92664	28.672369	141.537	203.22032

Eu	Gd	Yb	Y	Sr	Mn	REE	LREE
36.3544	330.248	48.1891	909.732	469.741	898.844	15386.976	14619.097
43.1924	398.053	71.3657	1145.26	349.13	295.693	12705.345	11746.156
22.6045	326.516	42.7256	783.018	416.195	485.178	8990.4432	8267.65
30.8249	253.357	32.3176	649.702	545.352	937.022	12128.439	11562.468
24.9664	221.19	31.1721	677.277	417.831	418.936	6171.8816	5637.021
24.2851	260.2	21.6135	590.769	337.386	354.642	12268.056	11729.166
40.4067	148.705	37.0718	349.173	619.143		6330.1994	5976.531
47.4346	528.873	49.5569	1131.11	776.504	1455.24	23160.943	22143.306
25.2836	269.097	39.1216	670.642	395.93	308.259	9074.5838	8476.309
39.9211	218.699	34.3393	588.61	501.734	740.864	13367.565	12789.907
15.0488	270.566	39.2713	960.161	402.598	218.811	20993.074	20222.927
24.2171	270.181	53.1249	907.147	571.777	947.214	9603.821	8968.346
43.9968	405.772	52.9846	1010	555.132	886.409	17553.307	16641.353
10.26	281.85	164.91	2318.65	241.52		1772.95	552.46
6.31	255.43	55.25	1117.41	199.79		1980.26	1243.67
16.82	211.65	124.19	2137.86	223.61		1634.76	656.2
16.59	253.35	133.94	1859.8	204.75		1654.61	602.35
9.42	157.6	82.3	1061.69	218.37		896.22	265.5
13.33	226.91	121.59	1609.19	194.75		1474.2	459.86
7.33	171.33	155.85	1905.6	204.77		1131.4	173.02
15.74	265.71	120.39	1568.31	184.37		1560.26	615.63
10.91	202.38	110.56	1392	247.86		1370.49	567.43
5.39	84.94	127.73	1568.49	226.59		752.62	44.89
4.96	237.45	182.41	2152.53	196.03		1303.56	139.12
11.85	131.56	144.96	1723.95	243.52		964.56	99.34
68.61	504.8	220.54	2835.22	214.23		3916.92	2017.69
13.56	110.13	55.77	770.93	212.5		868.43	412.5
32.05	249.91	93.72	1397.49	203.19		1711.14	798.86
26.15	218.54	115.1	1457.6	209.4		1760.24	845.86
24.699725	111.81544	45.376551	568.30351	218.06867	322.63342	1682.0327	1537.6764
49.237164	345.29917	95.397115	1279.253	239.81444	626.69013	3480.7346	3235.069
99.467299	657.33763	208.73602	2684.5698	262.88882	689.35122	7234.2795	6762.1221
37.002926	179.2693	62.920211	738.62659	199.64414	380.3489	2829.051	2566.2065
50.021516	386.73712	81.090098	1511.8586	207.77737	478.36905	3750.6356	3543.5952
35.741303	197.06735	65.740088	812.03604	229.24973	391.25423	2837.7155	2591.2679
45.193814	216.95749	71.527393	860.83088	196.04777	369.29935	2899.1307	2646.4878
39.015593	168.69234	58.523215	733.00912	191.74773	363.2782	2742.2827	2481.6189
9.9954768	56.610794	16.391535	264.04939	183.82316	248.28873	598.61018	560.52196
11.256038	54.199926	18.151073	277.45166	174.93367	281.60574	921.32186	836.09334
23.438035	103.62679	32.312515	459.30881	167.62479	305.03161	1654.2013	1492.1169
31.25679	142.32568	42.517988	613.42576	195.85678	344.92745	2229.8712	2026.8947
36.273326	172.82704	56.390221	741.93904	171.92377	261.56458	2745.2064	2491.221
20.445314	99.636972	39.937175	515.14686	195.94828	243.63295	1367.4617	1253.7143
30.588338	167.80946	49.752333	765.44779	193.75135	282.21267	2626.0932	2356.9981
27.357175	133.67117	104.71902	1205.8437	178.36315	482.81876	1805.6064	1692.0329

43.936861	278.79013	114.2387	1530.1036	177.50239	372.26795	4659.8831	4183.8298
22.932504	125.69539	33.560126	568.58494	175.7159	309.6775	1894.1169	1703.3491
22.064419	114.06725	38.849775	529.65536	173.3361	229.67594	1660.2062	1511.6678
36.702321	154.59725	60.751178	838.82711	184.41092	252.49937	2617.2222	2381.1524
21.487164	98.458392	32.364782	469.87396	164.21472	200.47669	1467.4068	1327.6191
34.000247	186.43389	86.412519	871.37909	148.96337	362.25208	2084.4101	1465.9447
13.560286	140.74578	36.737249	513.13537	185.26699	1111.2066	3183.9318	2806.0866
14.002539	290.89567	64.234416	1174.3369	139.32294	222.76424	2080.1864	1204.7906
10.43353	141.747	25.746467	385.86175	237.91202	561.67778	2570.4582	2228.7945
12.75512	117.69113	20.569594	326.79489	224.98174	664.37204	3292.6907	3016.9514
37.726506	213.9843	80.996551	1099.9535	192.55338	302.67905	2128.2964	1346.0995
17.005871	144.27461	30.630683	436.90699	219.82117	430.88635	3622.3153	3250.2829
33.62075	268.19565	176.26308	2079.9369	159.11466	334.07471	1625.1343	361.51262
20.736213	319.68167	76.905878	1350.1247	153.2034	279.37959	2275.7533	1287.5794
33.006573	342.72196	128.41577	1708.869	170.94381	351.63649	2047.1469	813.60569
17.433893	199.92627	40.359733	616.19613	213.69463	1193.2689	2926.4849	2428.8604
8.505526	97.279429	19.925357	304.90754	171.23156	1117.4109	2041.0815	1803.7318
27.200171	477.06413	123.12884	1936.5655	196.11968	296.65437	3046.0183	1574.4709
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27.439558	205.83512	103.16169	1240.9212	172.29592	316.96152	1097.2265	284.56914
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18.624812	228.44073	58.23589	803.38299	229.44423	1028.2496	2510.9234	1884.3394
37.254196	140.61586	65.586481	635.55644	171.55956	546.41143	2402.5164	1953.6844
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78.346722	222.509	153.60585	1404.3026	213.89883	805.95804	3551.8682	2665.6226
23.234743	145.07591	73.612205	993.19729	161.64031	341.9557	774.81256	133.18637
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46.462723	170.61217	100.11455	899.80399	158.52368	299.96533	2051.2411	1419.0071
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26.794424	87.321545	46.172209	543.56189	159.42426	280.05164	1897.9509	1611.36
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565.97131	0.1215673	9.553958	0.2993532	0.0299353	49.1	200.7	0.182
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353.66837	0.0702841	5.7676888	0.4842218	0.0484222	28.91	230.3	0.384
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577.65812	0.1166268	9.5771383	0.4153173	0.0415317	46.76	213.3	0.185
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635.47504	0.1542622	5.0072078	0.2119872	0.0211987	18.07	330	0.136
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944.63	0.251294	0.4112235	0.2415744	0.0241574	0.22	747.8	0.025
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2027.2447	0.4711815	1.2145333	0.4755663	0.0475566	1.54	1296.5	0.021
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1120.1306	0.2631989	0.8724238	0.3990697	0.039907	1.73	503.7	0.03
611.30474	0.1423341	2.3492144	0.6007942	0.0600794	2.55	408.3	0.061
640.03159	0.1500862	2.2997675	0.7075281	0.0707528	2.4	444.3	0.049
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171.1052	0.0435155	1.3605794	0.6068539	0.0606854	1.58	101.8	0.151
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308.42432	0.0767733	2.6225408	0.707847	0.0707847	3.41	200.7	0.079
424.1617	0.1037587	2.38152	0.6859155	0.0685915	3.24	264.1	0.069
508.14281	0.1250082	2.43183	0.6525404	0.065254	3.06	350.2	0.05
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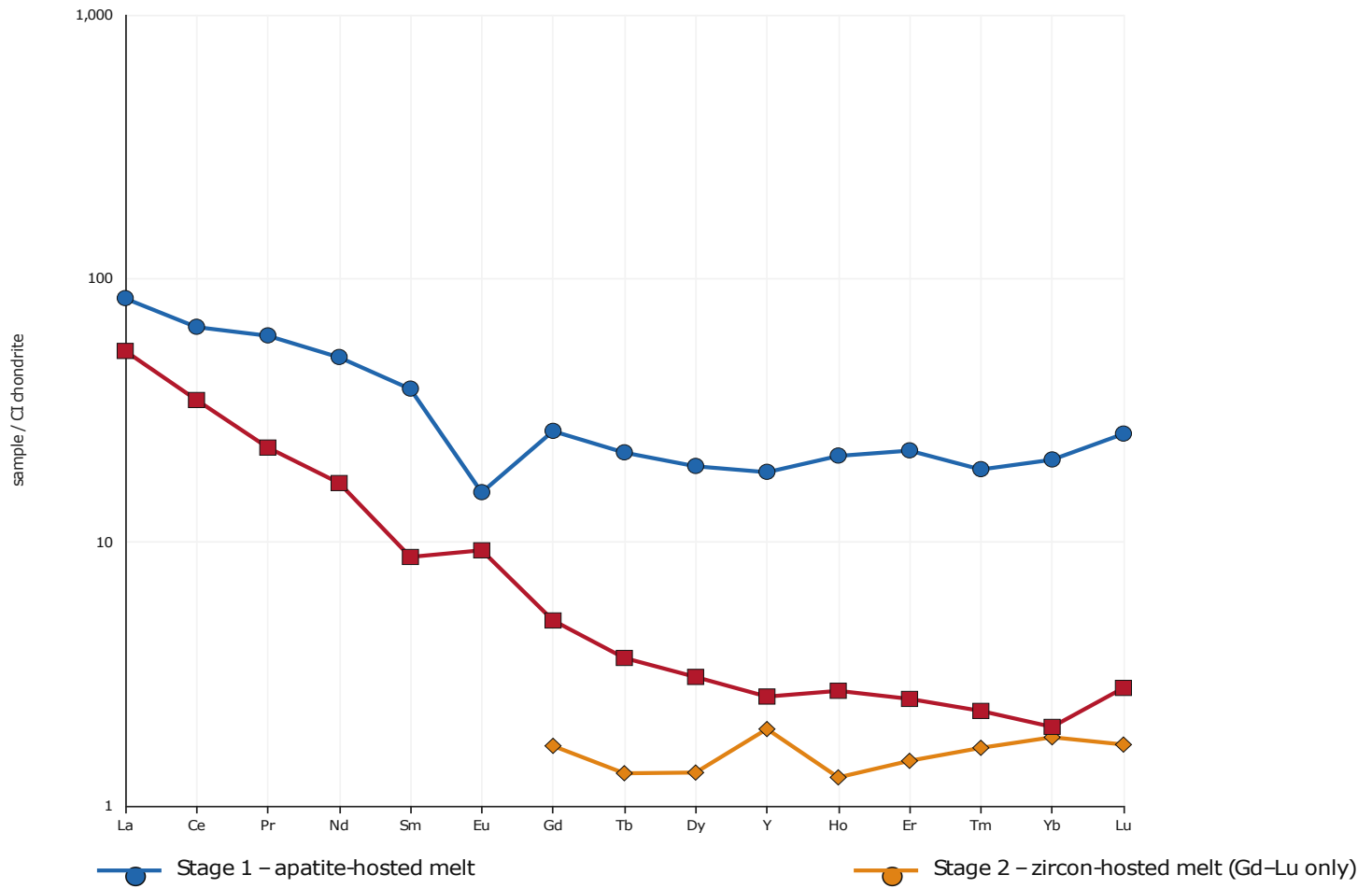
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487.60288	0.132643	2.4601985	0.7283181	0.0728318	2.64	377.3	0.048
282.86941	0.0752743	2.6277062	0.71758	0.071758	2.93	201	0.076
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875.39582	0.2049733	0.6252521	0.1724169	0.0172417	0.88	399	0.026
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275.7393	0.0602534	4.4412964	0.2844265	0.0284427	14.64	127.8	0.149
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1041.7373	0.2565779	0.9117017	0.1708808	0.0170881	0.44	1005.2	0.022
795.99396	0.1988432	2.6355346	0.2049293	0.0204929	3.18	449.9	0.027
1547.2607	0.3729356	2.3199575	0.1461312	0.0146131	2.16	1053.3	0.021
309.04945	0.0640309	4.3370099	0.3635722	0.0363572	29.51	68.1	0.171
689.44021	0.1961525	0.7367416	0.2869049	0.0286905	0.39	801.2	0.023
1192.308	0.2984226	0.1366184	0.6027156	0.0602716	0.09	894.2	0.029
353.56963	0.0833059	2.7795298	0.2708164	0.0270816	3.25	303.4	0.122
700.1105	0.1657277	0.25611	0.6748933	0.0674893	0.24	445	0.051
526.85814	0.1336198	0.2959021	0.4955661	0.0495566	0.26	448.9	0.063
1085.533	0.2652975	1.4463615	0.2378221	0.0237822	0.96	844.1	0.021
1138.2257	0.2707714	1.9485659	0.1838652	0.0183865	2.56	614.8	0.034
886.34049	0.2189146	1.8322668	0.1806894	0.0180689	2.46	529.1	0.038
479.43034	0.1209267	1.0200282	0.2864221	0.0286422	0.62	366.3	0.043
2670.7779	0.6393269	1.2470928	0.1895941	0.0189594	0.92	1986.9	0.009
734.5689	0.192264	1.4257461	0.1826596	0.018266	0.66	695.3	0.026
917.39458	0.2318008	0.68789	0.2505786	0.0250579	0.58	604.3	0.031
688.33645	0.1766949	4.6030461	0.4573584	0.0457358	4.48	588	0.032
718.49743	0.2094331	1.24017	1.403401	0.1403401	0.4	608	0.03
483.25711	0.1313356	1.5107602	1.1615831	0.1161583	0.7	385.4	0.062
795.16741	0.2198749	0.7810324	1.3656479	0.1365648	0.16	807.5	0.027
406.50017	0.1078689	1.570485	0.7649937	0.0764994	0.98	331.8	0.047
478.04434	0.1331939	3.7403053	1.2342134	0.1234213	1.14	575.5	0.043
695.80532	0.1426906	2.5031969	0.1767672	0.0176767	8.91	243.1	0.059
278.4447	0.0693456	1.093218	0.5847993	0.0584799	1.6	213.2	0.088
954.31769	0.2296703	2.4072407	0.3230133	0.0323013	3.02	617.5	0.032
317.05923	0.0860621	4.6204829	0.8799539	0.0879954	4.22	286.8	0.064
386.19282	0.097888	4.8794416	0.8583877	0.0858388	4.19	314.3	0.073
518.52836	0.119883	2.6169378	0.3059093	0.0305909	8.81	161.3	0.099
907.39992	0.1903568	3.843731	0.2592827	0.0259283	11.41	376.5	0.084
712.07613	0.16108	4.5080457	0.1169575	0.0116958	16.48	328.4	0.103
1310.0349	0.3573447	1.5722707	0.3224106	0.0322411	1.43	1151.5	0.014
443.26481	0.1063131	5.7009243	0.3659329	0.0365933	10.86	245.9	0.058
176.52058	0.0466452	4.4880144	0.8686212	0.0868621	4.94	130.6	0.126
2370.9836	0.5725475	0.9206407	0.2716467	0.0271647	0.94	1656.7	0.021
1466.0572	0.3040625	2.1808892	0.1584224	0.0158422	8.74	473.9	0.07
316.06011	0.0991954	2.2853083	0.4004701	0.040047	1.02	312.2	0.013
1667.5067	0.4203771	1.8318602	0.5087632	0.0508763	0.76	1590.9	0.018
1316.9904	0.2927086	2.5040024	0.1710717	0.0171072	11.89	314.4	0.039

1089.7984	0.2727779	4.2633167	0.260006	0.0260006	4.4	810.8	0.031
2273.6717	0.6186229	1.0341299	0.3007788	0.0300779	0.61	1807.9	0.017
1299.6964	0.3716502	0.2942392	0.2566762	0.0256676	0.07	1295.1	0.012
1780.4081	0.4846307	0.2257441	0.1670625	0.0167062	0.08	1439.9	0.014

MT24-06

3.01 Ga · Ti-in-zircon 710 °C



Supplementary 1

Sample	Type	Y	La	Ce	Pr	Nd
MT24-15	Whole rock	25.76	128.19	254.64	24.15	76.21
MT24-32	Whole rock	10.08	137.67	241.33	24.99	88.97
MT24-06	Whole rock	4.08	12.59	21.21	2.12	7.66
MT24-29	Whole rock	12.66	15.44	34.16	4.46	18.39
MT24-18	Whole rock	3.81	9.91	17.23	1.77	5.69
YK24-33	Whole rock	19.68	20.87	42.34	4.87	18.61
YK24-38	Whole rock	11.24	15.97	29.29	3.27	12.02
YK24-61	Whole rock	16.67	129.59	208.13	19.29	61.53
YK24-06	Whole rock	6.15	50.49	87.66	8.47	28.03
GL25-23	Whole rock	40.47	44.72	102.96	13.41	57.22
AG0909	Whole rock	4.50	50.70	89.60	8.23	25.90
AG09016	Whole rock	11.20	39.60	65.60	6.68	22.30
AG0909	Apatite melt	62.44	5.34	12.30	1.69	8.67
AG09016	Apatite melt	68.26	2.85	6.79	1.08	5.98
GL25-23	Apatite melt	32.29	11.32	28.62	3.89	17.98
MT24-06	Apatite melt	28.93	19.90	40.08	5.63	22.95
MT24-15	Apatite melt	68.69	3.05	8.69	1.46	9.35
MT24-18	Apatite melt	74.42	25.92	57.31	6.88	28.25
MT24-29	Apatite melt	35.64	3.64	12.97	2.31	14.51
MT24-32	Apatite melt	76.36	14.01	36.50	5.06	22.87
YK24-06	Apatite melt	48.98	38.48	74.93	8.69	32.31
YK24-33	Apatite melt	29.97	4.70	11.45	1.58	7.34
YK24-38	Apatite melt	38.80	26.15	59.60	7.23	31.59
MT24-06	Zircon melt	3.07	-	-	-	-
MT24-32	Zircon melt	21.80	-	-	-	-

Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm
11.22	1.38	7.42	1.01	5.17	0.97	2.92	0.32
13.75	1.84	8.80	0.78	2.85	0.40	0.96	0.12
1.30	0.52	1.00	0.13	0.76	0.15	0.41	0.06
4.20	0.86	3.38	0.44	2.62	0.48	1.15	0.16
1.10	0.44	0.89	0.11	0.70	0.15	0.39	0.05
3.99	1.06	4.13	0.58	3.77	0.77	2.16	0.31
2.43	0.62	2.10	0.35	1.94	0.38	1.21	0.18
7.44	1.43	5.06	0.60	3.05	0.56	1.74	0.23
3.91	1.11	2.39	0.25	1.28	0.20	0.60	0.08
11.32	2.35	10.16	1.30	8.05	1.49	4.19	0.53
3.48	0.94	2.15	0.25	1.13	0.18	0.44	0.06
3.88	0.79	3.01	0.42	2.15	0.38	0.98	0.13
3.43	0.96	7.13	1.29	10.41	2.44	8.07	1.17
3.40	0.37	7.09	1.38	10.44	2.58	7.95	1.20
3.95	1.00	4.87	0.66	4.47	1.12	3.43	0.55
5.64	0.87	5.24	0.79	4.77	1.16	3.56	0.47
5.60	0.86	8.25	1.53	11.40	2.45	7.81	1.21
8.18	0.55	10.72	2.03	13.56	2.87	9.20	1.38
4.77	0.77	5.55	0.85	5.44	1.23	4.44	0.63
7.88	0.71	11.11	1.88	13.73	3.27	9.96	1.47
6.23	1.04	6.41	0.95	6.72	1.65	5.99	0.95
2.20	0.74	3.25	0.55	4.04	1.00	3.82	0.56
7.70	0.79	9.23	1.18	7.17	1.52	4.03	0.56
-	-	0.34	0.05	0.33	0.07	0.24	0.04
-	-	2.84	0.43	3.25	0.70	2.10	0.28

Yb	Lu
1.99	0.27
0.81	0.13
0.32	0.07
1.10	0.15
0.37	0.07
2.12	0.31
1.13	0.17
1.49	0.20
0.45	0.09
3.44	0.49
0.34	0.05
0.76	0.12
8.32	1.41
8.46	1.29
4.22	0.96
3.30	0.63
8.31	1.31
9.84	1.65
4.69	0.83
10.09	1.49
7.72	1.30
4.29	0.86
3.65	0.55
0.29	0.04
1.54	0.22

```
# -*- coding: utf-8 -*-  
"""
```

```
=====
```

```
apatite_melt_SiO2_pipeline.py
```

```
=====
```

Apatite-based inverse melt model with:

- REE + Y inverted through the lattice-strain partitioning model
- Sr handled separately (divalent -> NOT on the REE parabola)
- Whole-rock SiO₂ estimated from apatite Sr (Bruand et al. 2016, Geology)
- Monte-Carlo exploration of T and fO₂ (no zircon input required)

RUNNING IN SPYDER

- ```

```
1. Put this file and your apatite CSV in the same folder.
  2. Set INPUT\_CSV in PART 1 to your file name.
  3. Read the CALIBRATION block in PART 1 and set your anchor points.
  4. Press F5 (Run file). No command-line arguments needed.
  5. Results go to OUTPUT\_DIR; figures also appear in the Plots pane.

SCRIPT MAP (each PART has a banner comment in the code below)

```

```

PART 1 USER SETTINGS ..... every knob you may want to change  
PART 2 PHYSICAL CONSTANTS ..... ionic radii, chondrite values, redox  
PART 3 FILE INPUT / PARSING ..... CSV reading, below-detection handling  
PART 4 PARTITION COEFFICIENTS ... Jirku et al. 2025 lattice-strain D model  
PART 5 MONTE-CARLO INVERSION .... samples (T, fO<sub>2</sub>), inverts every grain  
PART 6 Sr -> SiO<sub>2</sub> PROXY ..... Bruand et al. 2016 two-step protocol  
PART 7 STATISTICS ..... percentile envelopes, Eu/Eu\*, Ce/Y  
PART 8 PLOTS ..... spiders, histograms, T-fO<sub>2</sub> heatmap  
PART 9 MAIN DRIVER ..... ties PART 3-8 together, writes outputs

REFERENCES

```

```

Blundy & Wood (1994) Nature 372, 452-454 ..... lattice-strain formalism  
Bruand et al. (2016) Geology 44, 11-14 ..... apatite Sr -> WR Sr -> SiO<sub>2</sub>  
Jirku et al. (2025) Mineral. Petrol. .... apatite REE D model  
McDonough & Sun (1995) Chem. Geol. 120, 223-253 .. CI chondrite values  
Schreiber et al. (1987) ..... Eu<sup>2+</sup>/Eu<sup>3+</sup> redox equilibrium  
Shannon (1976) Acta Cryst. A32, 751-767 ..... effective ionic radii

```
=====
```

```
"""
```

```
import os
import math
```

```
import numpy as np
import pandas as pd
import matplotlib.pyplot as plt
```

```
=====
PART 1 - USER SETTINGS
```

```

Everything you are likely to change lives in this block. Nothing below PART 1
needs editing for a routine run on a new sample.
=====

---- Input / output -----
INPUT_CSV = "Apatite-H405-LA.csv" # apatite analyses, ';' or ',' delimited
OUTPUT_DIR = "apatite_melt_SiO2_out"
ID_COLUMN = "Zircon #" # column identifying each grain

---- Monte-Carlo sampling space -----
T and fO2 are NOT independently constrained for apatite (no Ti-in-apatite
thermometer here), so they are sampled uniformly across a geologically wide
window and the result is reported as a RANGE of compatible melts.
T_MIN_C = 700.0 # lower bound of sampled temperature, degC
T_MAX_C = 1200.0 # upper bound of sampled temperature, degC
LOG_FO2_MIN = -25.0 # lower bound of sampled log10 fO2, bar
LOG_FO2_MAX = -5.0 # upper bound of sampled log10 fO2, bar
N_DRAWS = 15000 # number of (T, fO2) draws
RANDOM_SEED = 42 # fixed seed -> reproducible results

---- Uncertainties (log10 units unless stated) -----
SIGMA_ANALYTICAL_LOG10 = 0.05 # ~12 % relative, typical LA-ICP-MS
SIGMA_D0_LOG10 = 0.15 # experimental calibration of D0
DETECTION_LIMIT_FACTOR = 0.5 # '<0.5' becomes 0.5 * 0.5

=====
CALIBRATION OF THE Sr -> SiO2 PROXY (Bruand et al. 2016)

The GSA Data Repository PDF (item 2016023) is a SCANNED IMAGE: it has no text
layer, so the Table DR3 coefficients cannot be read out programmatically.
Rather than hard-code invented slopes, this script derives the regressions
from calibration points that YOU supply. Two ways to do that:
#
CALIBRATION_MODE = "anchor_points"
You give two or more (x, y) points per regression line, read directly
off the published figures. The script fits the line by least squares
and prints the resulting slope and intercept. This is the recommended
route if you only have the figures: reading two points off an axis is
far more reliable than eyeballing a slope.
#
CALIBRATION_MODE = "coefficients"
You already have the Table DR3 numbers (from the printed article, the
GSA HTML version, or by asking the authors). Enter slope and intercept
directly below.
#
Either way the script reports exactly which numbers it used, so the
provenance of every SiO2 value stays traceable.
=====

CALIBRATION_MODE = "anchor_points" # "anchor_points" or "coefficients"

STEP 1 CALIBRATION - apatite Sr -> whole-rock Sr (Bruand et al. Fig. 1A)

```

```

Anchor points: (Sr in apatite ppm, Sr in whole rock ppm)
Read two well-separated points off the Fig. 1A regression line.
The defaults below are PLACEHOLDERS read approximately off the figure.
STEP1_ANCHORS = [
 (200.0, 400.0), # <-- replace with a real point from Fig. 1A
 (600.0, 1300.0), # <-- replace with a real point from Fig. 1A
]
STEP1_SIGMA_PPM = 150.0 # 1-sigma scatter about the Fig. 1A line

Used only when CALIBRATION_MODE == "coefficients"
STEP1_SLOPE = 2.25
STEP1_INTERCEPT = -50.0

STEP 2 CALIBRATION - whole-rock Sr -> whole-rock SiO2 (Bruand Fig. 1C)

Two branches, selected by the 650 ppm cutoff. The cutoff is the Sr_wr value
of the most mafic end-member of the post-Archean trend (Bruand et al., text).
SR_WR_BRANCH_CUTOFF_PPM = 650.0

Branch A - sanukitoid / high Ba-Sr compilation (Fowler & Rollinson 2012)
Applied when Sr_wr > cutoff. Anchors: (Sr_wr ppm, SiO2_wr wt%)
STEP2_SANUKITOID_ANCHORS = [
 (650.0, 63.0), # <-- replace with a real point from Fig. 1C
 (1500.0, 52.0), # <-- replace with a real point from Fig. 1C
]
STEP2_SANUKITOID_SIGMA = 2.5 # 1-sigma on SiO2, wt%

Branch B - post-Archean granitoid trend
Applied when Sr_wr <= cutoff. Anchors: (Sr_wr ppm, SiO2_wr wt%)
STEP2_POSTARCHEAN_ANCHORS = [
 (100.0, 72.0), # <-- replace with a real point from Fig. 1C
 (650.0, 58.0), # <-- replace with a real point from Fig. 1C
]
STEP2_POSTARCHEAN_SIGMA = 3.0 # 1-sigma on SiO2, wt%

Used only when CALIBRATION_MODE == "coefficients"
STEP2_SANUKITOID_SLOPE = -0.0129
STEP2_SANUKITOID_INTERCEPT = 71.4
STEP2_POSTARCHEAN_SLOPE = -0.0255
STEP2_POSTARCHEAN_INTERCEPT = 74.5

Physically allowed SiO2 window; draws outside are discarded as unrealistic.
SIO2_VALID_MIN = 40.0
SIO2_VALID_MAX = 80.0

---- PART 8 settings: T-fO2 heatmap resolution -----
HEATMAP_N_T_BINS = 25
HEATMAP_N_FO2_BINS = 20

```

```

=====
PART 2 - PHYSICAL CONSTANTS

```

# =====

R\_GAS = 8.314462618 # J / mol / K  
AVOGADRO = 6.02214076e23 # 1 / mol

# --- Trivalent cations inverted through the lattice-strain parabola -----  
# Y3+ is included on purpose: in IX-fold coordination its radius (1.075 Å)  
# falls between Ho (1.072) and Dy (1.083), so Y sits ON the REE3+ parabola and  
# obeys the same D0, r0, E. This is why Y behaves as a "pseudo-HREE".  
TRIVALENT = ["La", "Ce", "Pr", "Nd", "Sm", "Eu", "Gd", "Tb",  
"Dy", "Y", "Ho", "Er", "Tm", "Yb", "Lu"]

# Elements used for the Onuma-parabola consistency test (PART 8 heatmap).  
# Eu is excluded because it is redox-sensitive and would bias the fit.  
TRIVALENT\_NO\_EU = [e for e in TRIVALENT if e != "Eu"]

# Shannon (1976) effective ionic radii, IX-fold coordination, Angstrom.  
# IX-fold is the coordination of the apatite Ca2 site.  
R\_IX\_TRIVALENT = {  
"La": 1.216, "Ce": 1.196, "Pr": 1.179, "Nd": 1.163, "Sm": 1.132,  
"Eu": 1.120, "Gd": 1.107, "Tb": 1.095, "Dy": 1.083, "Y": 1.075,  
"Ho": 1.072, "Er": 1.062, "Tm": 1.052, "Yb": 1.042, "Lu": 1.032,  
}

# --- Divalent cations -----  
# Sr2+ in IX-fold coordination is 1.31 Å. It is DIVALENT, so it belongs to a  
# separate divalent parabola with its own D0, r0 and E. Placing it on the  
# trivalent REE parabola would give a D wrong by orders of magnitude.  
# Because the Bruand et al. (2016) proxy in PART 6 is a direct empirical  
# mineral -> whole-rock correlation, no Sr partition coefficient is needed  
# anywhere in this script.  
R\_IX\_DIVALENT = {"Sr": 1.31, "Eu2": 1.30, "Ca": 1.18}

# --- CI chondrite, McDonough & Sun (1995), ppm -----  
CHONDRITE\_MS95 = {  
"La": 0.237, "Ce": 0.613, "Pr": 0.0928, "Nd": 0.457, "Sm": 0.148,  
"Eu": 0.0563, "Gd": 0.199, "Tb": 0.0361, "Dy": 0.246, "Y": 1.57,  
"Ho": 0.0546, "Er": 0.160, "Tm": 0.0247, "Yb": 0.161, "Lu": 0.0246,  
"Sr": 7.25,  
}

# --- Eu2+ / Eu3+ redox (Schreiber et al. 1987 formulation) -----  
#  $\log_{10}(\text{Eu}^{3+}/\text{Eu}^{2+}) = \text{SCH\_C} + \text{SCH\_S} * \log_{10}(f\text{O}_2) + \text{SCH\_K} / T(\text{K})$   
SCH\_C = -4.0  
SCH\_S = 0.25  
SCH\_K = 11840.0

# Partition coefficient of divalent Eu into apatite. Eu2+ substitutes for Ca2+  
# and is therefore COMPATIBLE, unlike in zircon where it is strongly excluded.  
D\_EU2\_APATITE = 2.0

# =====

# PART 3 - FILE INPUT / PARSING

```
=====
```

```
def parse_ppm(value, dl_factor=DETECTION_LIMIT_FACTOR):
```

```
 """
```

```
 Convert one table cell into a float concentration in ppm.
```

- plain number -> float
- below-detection string -> '<0.5' becomes  $0.5 * dl\_factor$
- blank / unparseable -> NaN

```
 """
```

```
 if pd.isna(value):
```

```
 return np.nan
```

```
 text = str(value).strip()
```

```
 if text == "":
```

```
 return np.nan
```

```
 if text.startswith("<"):
```

```
 try:
```

```
 return float(text[1:]) * dl_factor
```

```
 except ValueError:
```

```
 return np.nan
```

```
 try:
```

```
 return float(text)
```

```
 except ValueError:
```

```
 return np.nan
```

```
def load_apatite_csv(filepath, id_col=ID_COLUMN):
```

```
 """
```

```
 Load the apatite analyses.
```

The delimiter is detected by counting ';' versus ',' in the header line, so both European and Anglo-Saxon CSV exports work unchanged. Fully empty rows (common at the end of exported spreadsheets) are dropped.

```
 """
```

```
 with open(filepath, "r", encoding="utf-8", errors="replace") as fh:
```

```
 header_line = fh.readline()
```

```
 sep = ";" if header_line.count(";") > header_line.count(",") else ","
```

```
 df = pd.read_csv(filepath, sep=sep, engine="python")
```

```
 df.columns = [c.strip().strip('"') for c in df.columns]
```

```
 df = df.dropna(how="all").copy()
```

```
 if id_col not in df.columns:
```

```
 df[id_col] = ["grain-%d" % (i + 1) for i in range(len(df))]
```

```
 return df
```

```
def extract_grain_compositions(df, id_col=ID_COLUMN):
```

```
 """
```

```
 Turn the raw DataFrame into a clean list of dictionaries, one per grain.
```

Each dictionary holds the trivalent cations (REE + Y) plus Sr, all in ppm.

Grains with no usable trivalent data are discarded.

```

"""
grains = []
for _, row in df.iterrows():
 grain = {"id": row.get(id_col, "")}

 for element in TRIVALENT:
 grain[element] = parse_ppm(row.get(element, np.nan))

 # Sr is stored but never divided by a partition coefficient; it feeds
 # the empirical proxy in PART 6 instead.
 grain["Sr"] = parse_ppm(row.get("Sr", np.nan))

 has_data = any(
 np.isfinite(grain[e]) and grain[e] > 0 for e in TRIVALENT
)
 if has_data:
 grains.append(grain)

return grains

=====
PART 4 - PARTITION COEFFICIENTS (Jirku et al. 2025)

Forward model: given T and fO2, return D(apatite/melt) for each trivalent
cation. The inversion in PART 5 divides the measured apatite concentration by
this D to recover the melt.
=====

def apatite_lattice_parameters(T_K):
 """
 Temperature-dependent lattice-strain parameters for apatite.

 Returns

 D0 : strain-free partition coefficient (dimensionless)
 r0 : ideal site radius, Angstrom
 E : effective Young's modulus of the site, GPa
 """
 D0 = math.exp(12461.0 / T_K - 6.63)
 r0 = 51.91e-6 * T_K + 107.40e-2
 E = 0.285 * T_K - 62.7
 return D0, r0, E

def lattice_strain_D(D0, r0_A, E_GPa, r_cation_A, T_K):
 """
 Blundy & Wood (1994) lattice-strain equation.

$$D_i = D0 * \exp(-4\pi * E * Na / (R * T) * [(r0/2) * (ri - r0)^2 + (ri - r0)^3 / 3])$$

 The strain term penalises cations whose radius departs from the ideal site
 radius r0, producing the characteristic Onuma parabola.
 """

```

```

r0 = r0_A * 1e-10 # Angstrom -> metre
ri = r_cation_A * 1e-10
E = E_GPa * 1e9 # GPa -> Pa

strain_energy = 4.0 * math.pi * E * AVOGADRO * (
 (r0 / 2.0) * (ri - r0) ** 2 + (1.0 / 3.0) * (ri - r0) ** 3
)
return D0 * math.exp(-strain_energy / (R_GAS * T_K))

def eu3_fraction(T_K, log_fO2):
 """
 Fraction of total Eu present as Eu3+ (Schreiber et al. 1987 form).

 At high fO2 this tends to 1 (all Eu3+, no redox Eu anomaly); at low fO2 it
 tends to 0 (all Eu2+, compatible in apatite, giving a positive Eu anomaly
 in the mineral).
 """
 ratio = 10.0 ** (SCH_C + SCH_S * log_fO2 + SCH_K / T_K)
 return ratio / (1.0 + ratio)

def D_apatite(element, T_K, log_fO2, log10_D0_shift=0.0):
 """
 Apatite/melt partition coefficient for one trivalent cation.

 Parameters

 element : one of TRIVALENT (REE or Y)
 T_K : temperature in Kelvin
 log_fO2 : log10 oxygen fugacity in bar (only affects Eu)
 log10_D0_shift : Monte-Carlo perturbation of D0, in log10 units

 Notes

 Ji & Dygert (2024) showed experimentally that fO2 affects only D_Eu; the
 other REE show no systematic fO2 dependence. That is exactly the structure
 implemented here.
 """
 D0, r0, E = apatite_lattice_parameters(T_K)
 D0 = D0 * (10.0 ** log10_D0_shift)

 if element == "Eu":
 # Mixed valence: weighted average of the trivalent (parabola) and
 # divalent (compatible) end-members.
 x3 = eu3_fraction(T_K, log_fO2)
 D_eu3 = lattice_strain_D(D0, r0, E, R_IX_TRIVALENT["Eu"], T_K)
 return x3 * D_eu3 + (1.0 - x3) * D_EU2_APATITE

 return lattice_strain_D(D0, r0, E, R_IX_TRIVALENT[element], T_K)

=====
PART 6a - CALIBRATION FITTING

```

```

Defined before PART 5 because the Monte-Carlo loop calls the proxy.
Converts anchor points into slope/intercept, or passes through the
coefficients you supplied, depending on CALIBRATION_MODE.
=====

def fit_line_from_anchors(anchors, label):
 """
 Least-squares straight-line fit through anchor points.

 Parameters

 anchors : list of (x, y) tuples, at least two
 label : name used in error messages and in the printed report

 Returns

 (slope, intercept)
 """
 if anchors is None or len(anchors) < 2:
 raise ValueError(
 "Calibration '%s' needs at least two anchor points; got %s"
 % (label, 0 if anchors is None else len(anchors))
)

 x = np.array([float(p[0]) for p in anchors])
 y = np.array([float(p[1]) for p in anchors])

 if np.allclose(x, x[0]):
 raise ValueError(
 "Calibration '%s': all anchor x-values are identical, "
 "so no slope can be fitted." % label
)

 slope, intercept = np.polyfit(x, y, 1)
 return float(slope), float(intercept)

def build_calibration():
 """
 Assemble the three regressions used by the Sr -> SiO2 proxy.

 Returns a dictionary holding slope, intercept and sigma for:
 'step1' apatite Sr -> whole-rock Sr
 'step2_sanukitoid' whole-rock Sr -> SiO2, Sr_wr > cutoff
 'step2_postarchean' whole-rock Sr -> SiO2, Sr_wr <= cutoff
 plus the mode used, so it can be written to the output files.
 """
 calibration = {"mode": CALIBRATION_MODE}

 if CALIBRATION_MODE == "anchor_points":
 s1, i1 = fit_line_from_anchors(STEP1_ANCHORS, "Step 1 (Sr_ap -> Sr_wr)")
 s2a, i2a = fit_line_from_anchors(
 STEP2_SANUKITOID_ANCHORS, "Step 2 sanukitoid branch"
)

```

```

)
s2b, i2b = fit_line_from_anchors(
 STEP2_POSTARCHEAN_ANCHORS, "Step 2 post-Archean branch"
)

elif CALIBRATION_MODE == "coefficients":
 s1, i1 = STEP1_SLOPE, STEP1_INTERCEPT
 s2a, i2a = STEP2_SANUKITOID_SLOPE, STEP2_SANUKITOID_INTERCEPT
 s2b, i2b = STEP2_POSTARCHEAN_SLOPE, STEP2_POSTARCHEAN_INTERCEPT

else:
 raise ValueError(
 "CALIBRATION_MODE must be 'anchor_points' or 'coefficients', "
 "not %r" % CALIBRATION_MODE
)

calibration["step1"] = {
 "slope": s1, "intercept": i1, "sigma": STEP1_SIGMA_PPM,
}
calibration["step2_sanukitoid"] = {
 "slope": s2a, "intercept": i2a, "sigma": STEP2_SANUKITOID_SIGMA,
}
calibration["step2_postarchean"] = {
 "slope": s2b, "intercept": i2b, "sigma": STEP2_POSTARCHEAN_SIGMA,
}
return calibration

def report_calibration(calibration):
 """Print the regressions actually in use, for traceability."""
 print(" Calibration mode: %s" % calibration["mode"])
 print(" Step 1 Sr_wr = %.4f * Sr_ap + %.2f (1s = %.0f ppm)"
 % (calibration["step1"]["slope"],
 calibration["step1"]["intercept"],
 calibration["step1"]["sigma"]))
 print(" Step 2a SiO2 = %.5f * Sr_wr + %.2f (sanukitoid, 1s = %.1f wt%%)"
 % (calibration["step2_sanukitoid"]["slope"],
 calibration["step2_sanukitoid"]["intercept"],
 calibration["step2_sanukitoid"]["sigma"]))
 print(" Step 2b SiO2 = %.5f * Sr_wr + %.2f (post-Archean, 1s = %.1f wt%%)"
 % (calibration["step2_postarchean"]["slope"],
 calibration["step2_postarchean"]["intercept"],
 calibration["step2_postarchean"]["sigma"]))

def calibration_dataframe(calibration):
 """Flatten the calibration into a DataFrame for writing to CSV."""
 rows = []
 for key in ("step1", "step2_sanukitoid", "step2_postarchean"):
 rows.append({
 "regression": key,
 "slope": calibration[key]["slope"],
 "intercept": calibration[key]["intercept"],
 "sigma_1s": calibration[key]["sigma"],

```

```

 "calibration_mode": calibration["mode"],
 })
 return pd.DataFrame(rows)

```

```

=====
PART 6b - Sr -> SiO2 PROXY (Bruand et al. 2016, Geology 44, 11-14)

Two-step empirical protocol. Neither step uses a partition coefficient: both
are direct correlations calibrated on natural granitoid suites.
#
Step 1 (their Fig. 1A)
Sr in apatite correlates with Sr in the whole rock. Because apatite is
robust to alteration, this recovers the PRIMARY magmatic Sr_wr even
where the whole rock itself has been disturbed.
#
Step 2 (their Fig. 1C)
Sr_wr correlates negatively with whole-rock SiO2. Two branches:
- Sr_wr > 650 ppm -> sanukitoid compilation (Fowler & Rollinson 2012)
- Sr_wr <= 650 ppm -> post-Archean granitoid trend
The 650 ppm cutoff is the Sr_wr of the most mafic end-member of the
post-Archean trend.
#
The resulting SiO2 tells you which melt composition your partition
coefficients should correspond to, closing the loop on the inversion.
=====

```

```

def estimate_whole_rock_Sr(Sr_apatite_ppm, calibration, rng=None):
 """

```

```

 Step 1: apatite Sr -> whole-rock Sr (Bruand et al. 2016, Fig. 1A).

```

```

 If rng is supplied, the regression scatter is sampled so the uncertainty
 propagates into the final SiO2 distribution.
 """

```

```

 cal = calibration["step1"]
 Sr_wr = cal["slope"] * Sr_apatite_ppm + cal["intercept"]
 if rng is not None:
 Sr_wr += rng.normal(0.0, cal["sigma"])
 return max(Sr_wr, 0.0)

```

```

def estimate_whole_rock_SiO2(Sr_wr_ppm, calibration, rng=None):
 """

```

```

 Step 2: whole-rock Sr -> whole-rock SiO2 (Bruand et al. 2016, Fig. 1C).

```

```

 The branch is chosen by the 650 ppm cutoff. Returns NaN if the result falls
 outside the physically sensible SiO2 window.
 """

```

```

 if not np.isfinite(Sr_wr_ppm) or Sr_wr_ppm <= 0:
 return np.nan

```

```

 if Sr_wr_ppm > SR_WR_BRANCH_CUTOFF_PPM:
 cal = calibration["step2_sanukitoid"]
 else:

```

```

 cal = calibration["step2_postarchean"]

 SiO2 = cal["slope"] * Sr_wr_ppm + cal["intercept"]
 if rng is not None:
 SiO2 += rng.normal(0.0, cal["sigma"])

 if SiO2 < SIO2_VALID_MIN or SiO2 > SIO2_VALID_MAX:
 return np.nan
 return SiO2

def which_branch(Sr_wr_ppm):
 """Human-readable label for the branch used in Step 2."""
 if not np.isfinite(Sr_wr_ppm):
 return "undetermined"
 if Sr_wr_ppm > SR_WR_BRANCH_CUTOFF_PPM:
 return "sanukitoid / high Ba-Sr"
 return "post-Archean granitoid"

def summarise_SiO2(melts):
 """
 Collect the SiO2 estimates and report their distribution.

 Also reports Sr_wr so you can check which branch dominates.
 """
 # Both arrays MUST be built from the same filtered subset so that index i
 # refers to the same Monte-Carlo draw in each. Filtering them separately
 # de-synchronises them (a draw can have a valid Sr_wr but a NaN SiO2_wr
 # when the regression pushes SiO2 outside the physical window), which then
 # breaks any code that indexes both with a shared index array.
 paired = [
 m for m in melts
 if "Sr_wr" in m and np.isfinite(m["Sr_wr"])
 and "SiO2_wr" in m and np.isfinite(m["SiO2_wr"])
]
 SiO2_values = np.array([m["SiO2_wr"] for m in paired])
 Sr_wr_values = np.array([m["Sr_wr"] for m in paired])

 if SiO2_values.size == 0 or Sr_wr_values.size == 0:
 return None

 n_sanukitoid = int(np.sum(Sr_wr_values > SR_WR_BRANCH_CUTOFF_PPM))

 stats = {
 "n": int(SiO2_values.size),
 "SiO2_p2.5_wt%": float(np.percentile(SiO2_values, 2.5)),
 "SiO2_p16_wt%": float(np.percentile(SiO2_values, 16)),
 "SiO2_p50_wt%": float(np.percentile(SiO2_values, 50)),
 "SiO2_p84_wt%": float(np.percentile(SiO2_values, 84)),
 "SiO2_p97.5_wt%": float(np.percentile(SiO2_values, 97.5)),
 "Sr_wr_p16_ppm": float(np.percentile(Sr_wr_values, 16)),
 "Sr_wr_p50_ppm": float(np.percentile(Sr_wr_values, 50)),
 "Sr_wr_p84_ppm": float(np.percentile(Sr_wr_values, 84)),
 }

```

```

 "fraction_sanukitoid_branch": float(n_sanukitoid / Sr_wr_values.size),
 "branch_at_median": which_branch(float(np.median(Sr_wr_values))),
}
return stats, SiO2_values, Sr_wr_values

=====
PART 5 - MONTE-CARLO INVERSION

For each of N_DRAWS samples of (T, fO2):
1. perturb D0 by its calibration uncertainty
2. perturb every measured concentration by its analytical uncertainty
3. invert every grain: C_melt = C_apatite / D
4. propagate Sr through the PART 6 proxy to get Sr_wr and SiO2_wr
The pooled result is the range of melts compatible with the apatite data.
=====

def run_monte_carlo(grains, calibration, n_draws=N_DRAWS, seed=RANDOM_SEED,
 verbose=True):
 """
 Main Monte-Carlo loop.

 Returns

 melts : list of dict
 One entry per (draw x grain), holding the inverted melt concentrations
 plus the sampled T_C, log_fO2, Sr_wr and SiO2_wr.
 """
 rng = np.random.default_rng(seed)
 melts = []

 for i in range(n_draws):
 # --- sample the intensive variables -----
 T_C = rng.uniform(T_MIN_C, T_MAX_C)
 T_K = T_C + 273.15
 log_fO2 = rng.uniform(LOG_FO2_MIN, LOG_FO2_MAX)

 # --- one D0 perturbation per draw, shared by all elements -----
 # It is systematic (a calibration offset), not per-element noise.
 d0_shift = rng.normal(0.0, SIGMA_D0_LOG10)

 # --- precompute D for this draw so it is not recomputed per grain ----
 D_set = {}
 for element in TRIVALENT:
 D_set[element] = D_apatite(element, T_K, log_fO2, d0_shift)

 for grain in grains:
 record = {
 "grain_id": grain["id"],
 "T_C": T_C,
 "log_fO2": log_fO2,
 }
 usable = False

```

```

--- invert the trivalent cations (REE + Y) -----
for element in TRIVALENT:
 C_apatite = grain[element]
 if not np.isfinite(C_apatite) or C_apatite <= 0:
 continue

 # analytical noise, applied in log space
 C_perturbed = C_apatite * (
 10.0 ** rng.normal(0.0, SIGMA_ANALYTICAL_LOG10)
)

 D = D_set[element]
 if D > 0 and np.isfinite(D):
 record[element] = C_perturbed / D
 usable = True

--- PART 6 proxy: Sr does NOT go through a D -----
Sr_apatite = grain.get("Sr", np.nan)
if np.isfinite(Sr_apatite) and Sr_apatite > 0:
 Sr_perturbed = Sr_apatite * (
 10.0 ** rng.normal(0.0, SIGMA_ANALYTICAL_LOG10)
)
 Sr_wr = estimate_whole_rock_Sr(Sr_perturbed, calibration, rng)
 SiO2_wr = estimate_whole_rock_SiO2(Sr_wr, calibration, rng)
 record["Sr_apatite"] = Sr_perturbed
 record["Sr_wr"] = Sr_wr
 record["SiO2_wr"] = SiO2_wr

if usable:
 melts.append(record)

if verbose and (i + 1) % max(1, n_draws // 5) == 0:
 print(" ... %d / %d draws" % (i + 1, n_draws))

return melts

```

```

=====
PART 7 - STATISTICS

Percentile envelopes are computed in log10 space because concentrations span
orders of magnitude and their errors are multiplicative, not additive.
=====

```

```

def summarise_melt_envelope(melts):
 """

```

Per-element percentile envelope of the compatible melt compositions.

In addition to robust percentiles (p2.5, p16, p50, p84, p97.5), this also stores the absolute minimum and maximum melt reached in the Monte-Carlo and the corresponding T and log fO<sub>2</sub> of those extreme draws.

This lets you report not only the compatible melt range, but also the intensive conditions that produced the two end-members.

```

"""
rows = []
for element in TRIVALENT:
 subset = [m for m in melts
 if element in m and np.isfinite(m[element]) and m[element] > 0]
 values = np.array([m[element] for m in subset])

 if values.size < 10:
 rows.append({"element": element, "n": int(values.size)})
 continue

 logs = np.log10(values)
 i_min = int(np.argmin(values))
 i_max = int(np.argmax(values))
 melt_min = subset[i_min]
 melt_max = subset[i_max]

 rows.append({
 "element": element,
 "n": int(values.size),
 "r_ionic_IX_A": R_IX_TRIVALENT[element],
 "C_min_ppm": float(values[i_min]),
 "T_at_C_min_degC": float(melt_min["T_C"]),
 "log_fO2_at_C_min": float(melt_min["log_fO2"]),
 "C_p2.5_ppm": float(10 ** np.percentile(logs, 2.5)),
 "C_p16_ppm": float(10 ** np.percentile(logs, 16)),
 "C_p50_ppm": float(10 ** np.percentile(logs, 50)),
 "C_p84_ppm": float(10 ** np.percentile(logs, 84)),
 "C_p97.5_ppm": float(10 ** np.percentile(logs, 97.5)),
 "C_max_ppm": float(values[i_max]),
 "T_at_C_max_degC": float(melt_max["T_C"]),
 "log_fO2_at_C_max": float(melt_max["log_fO2"]),
 })

return pd.DataFrame(rows)

```

```

def summarise_ratios(melts):
 """
 Petrogenetically useful ratios of the reconstructed melt.

 Eu/Eu* : plagioclase involvement and/or redox state
 Ce/Y : LREE-HREE fractionation, the ratio Bruand et al. (2016) use to
 discriminate felsic from mafic magmas
 """
 eu_anomaly = []
 ce_over_y = []

 for m in melts:
 if all(k in m and m[k] > 0 for k in ("Sm", "Eu", "Gd")):
 eu_anomaly.append(m["Eu"] / math.sqrt(m["Sm"] * m["Gd"]))
 if all(k in m and m[k] > 0 for k in ("Ce", "Y")):
 ce_over_y.append(m["Ce"] / m["Y"])

```

```
def pack(values, label):
 arr = np.array(values)
 if arr.size == 0:
 return {"ratio": label, "n": 0}
 return {
 "ratio": label,
 "n": int(arr.size),
 "p2.5": float(np.percentile(arr, 2.5)),
 "p16": float(np.percentile(arr, 16)),
 "p50": float(np.percentile(arr, 50)),
 "p84": float(np.percentile(arr, 84)),
 "p97.5": float(np.percentile(arr, 97.5)),
 }

return pd.DataFrame([pack(eu_anomaly, "Eu/Eu*"), pack(ce_over_y, "Ce/Y")])
```

```
def onuma_misfit(melt_record):
 """
```

Goodness of fit of one inverted melt to a smooth Onuma parabola.

A physically self-consistent (T, fO<sub>2</sub>) pair produces D values that vary smoothly with ionic radius, so ln(C<sub>melt</sub>) against radius should define a clean parabola. A poor fit means the assumed conditions are not compatible with the observed apatite chemistry. Eu is excluded because its redox behaviour legitimately displaces it from the parabola.

Returns the RMS residual in ln units; lower is better.

```
"""
elements = [
 e for e in TRIVALENT_NO_EU
 if e in melt_record and np.isfinite(melt_record[e]) and melt_record[e] > 0
]
if len(elements) < 5:
 return np.nan
```

```
x = np.array([R_IX_TRIVALENT[e] for e in elements])
y = np.log(np.array([melt_record[e] for e in elements]))
```

```
try:
 coeffs = np.polyfit(x, y, 2)
except (np.linalg.LinAlgError, ValueError):
 return np.nan
```

```
residuals = y - np.polyval(coeffs, x)
return float(np.sqrt(np.mean(residuals ** 2)))
```

```
=====
```

```
PART 8 - PLOTS
```

```

```

```
Six figures:
```

```
1. raw ppm spider with the uncertainty envelope
```

```
2. chondrite-normalised spider (McDonough & Sun 1995), Y between Dy and Ho
```

```
3. whole-rock SiO2 histogram from the Bruand proxy
4. Sr_wr vs SiO2_wr showing which regression branch was used
5. T vs log fO2 heatmap of Onuma-parabola consistency
6. best-fit partition-coefficient parabola (Onuma diagram) + melt fit
=====
```

```
def plot_spider_raw(envelope_df, grains, outdir):
 """Figure 1 - inverted melt in raw ppm, with p16-p84 and p2.5-p97.5 bands."""
 valid = envelope_df.dropna(subset=["C_p50_ppm"])
 if valid.empty:
 return

 elements = list(valid["element"])
 x = np.arange(len(elements))

 fig, ax = plt.subplots(figsize=(12, 7))

 ax.fill_between(x, valid["C_p2.5_ppm"], valid["C_p97.5_ppm"],
 color="#d73027", alpha=0.13, label="melt p2.5-p97.5")
 ax.fill_between(x, valid["C_p16_ppm"], valid["C_p84_ppm"],
 color="#d73027", alpha=0.28, label="melt p16-p84")
 ax.plot(x, valid["C_p50_ppm"], "o-", color="#d73027", lw=2.5, ms=7,
 mfc="white", label="melt p50 (best estimate)")

 apatite_median = []
 for element in elements:
 vals = [g[element] for g in grains
 if np.isfinite(g.get(element, np.nan)) and g.get(element, 0) > 0]
 apatite_median.append(np.median(vals) if vals else np.nan)
 ax.plot(x, apatite_median, "s--", color="#4575b4", lw=2, ms=7,
 mfc="white", label="apatite observed (median)")

 ax.set_xticks(x)
 ax.set_xticklabels(elements)
 ax.set_yscale("log")
 ax.set_ylabel("Concentration (ppm)")
 ax.set_title("Apatite-derived melt, REE + Y\n"
 "Monte-Carlo over T = %.0f-%.0f degC and log fO2 = %.0f to %.0f"
 "% (T_MIN_C, T_MAX_C, LOG_FO2_MIN, LOG_FO2_MAX))")
 ax.grid(True, which="both", alpha=0.3)
 ax.legend(loc="best")
 fig.tight_layout()
 fig.savefig(os.path.join(outdir, "01_melt_spider_raw_ppm.png"), dpi=200)
 plt.show()
```

```
def plot_spider_chondrite(envelope_df, grains, outdir):
 """Figure 2 - the same data normalised to CI chondrite (McDonough & Sun 1995)."""
 valid = envelope_df.dropna(subset=["C_p50_ppm"])
 valid = valid[valid["element"].isin(CHONDRITE_MS95.keys())]
 if valid.empty:
 return

 elements = list(valid["element"])
```

```

x = np.arange(len(elements))
chond = np.array([CHONDRITE_MS95[e] for e in elements])

fig, ax = plt.subplots(figsize=(12, 7))

ax.fill_between(x, valid["C_p2.5_ppm"] / chond, valid["C_p97.5_ppm"] / chond,
 color="#d73027", alpha=0.13, label="melt p2.5-p97.5")
ax.fill_between(x, valid["C_p16_ppm"] / chond, valid["C_p84_ppm"] / chond,
 color="#d73027", alpha=0.28, label="melt p16-p84")
ax.plot(x, valid["C_p50_ppm"] / chond, "o-", color="#d73027", lw=2.5, ms=7,
 mfc="white", label="melt p50")

apatite_norm = []
for element in elements:
 vals = [g[element] for g in grains
 if np.isfinite(g.get(element, np.nan)) and g.get(element, 0) > 0]
 apatite_norm.append(
 np.median(vals) / CHONDRITE_MS95[element] if vals else np.nan
)
ax.plot(x, apatite_norm, "s--", color="#4575b4", lw=2, ms=7,
 mfc="white", label="apatite observed (median)")

mark Y, which sits between Dy and Ho by ionic radius
if "Y" in elements:
 ax.axvline(elements.index("Y"), color="#888", ls=":", lw=1, alpha=0.7)

ax.set_xticks(x)
ax.set_xticklabels(elements)
ax.set_yscale("log")
ax.set_ylabel("Sample / CI chondrite")
ax.set_title("Chondrite-normalised REE + Y (McDonough & Sun 1995)\n"
 "Y plotted at its ionic radius, between Dy and Ho")
ax.grid(True, which="both", alpha=0.3)
ax.legend(loc="best")
fig.tight_layout()
fig.savefig(os.path.join(outdir, "02_melt_spider_chondrite.png"), dpi=200)
plt.show()

```

```

def plot_SiO2_histogram(SiO2_values, stats, outdir):
 """Figure 3 - distribution of whole-rock SiO2 from the Bruand proxy."""
 if SiO2_values.size == 0:
 return

 fig, ax = plt.subplots(figsize=(10, 5.5))
 ax.hist(SiO2_values, bins=40, color="#1b7837", edgecolor="white")
 ax.axvline(stats["SiO2_p50_wt%"], color="red", ls="--", lw=2,
 label="p50 = %.1f wt%%" % stats["SiO2_p50_wt%"])
 ax.axvspan(stats["SiO2_p16_wt%"], stats["SiO2_p84_wt%"],
 color="red", alpha=0.12,
 label="p16-p84 = %.1f-%.1f wt%%"
 % (stats["SiO2_p16_wt%"], stats["SiO2_p84_wt%"]))
 ax.set_xlabel("Whole-rock SiO2 (wt%)")
 ax.set_ylabel("Count")

```

```

ax.set_title("Whole-rock SiO2 from apatite Sr\n"
 "Bruand et al. (2016) two-step proxy, branch: %s"
 % stats["branch_at_median"])
ax.legend(loc="best")
fig.tight_layout()
fig.savefig(os.path.join(outdir, "03_SiO2_histogram.png"), dpi=200)
plt.show()

```

```

def plot_Sr_vs_SiO2(Sr_wr_values, SiO2_values, calibration, outdir):
 """

```

Figure 4 - the Step 2 regression, showing both branches and the 650 ppm cutoff, with the sampled points overlaid.

```

 """

```

```

 if Sr_wr_values.size == 0:
 return

```

```

 fig, ax = plt.subplots(figsize=(10, 6.5))

```

```

 n_show = min(3000, Sr_wr_values.size)
 idx = np.random.default_rng(0).choice(Sr_wr_values.size, n_show, replace=False)
 ax.scatter(Sr_wr_values[idx], SiO2_values[idx], s=6, alpha=0.15,
 color="#1b7837", label="Monte-Carlo draws")

```

```

 cal_a = calibration["step2_sanukitoid"]
 cal_b = calibration["step2_postarchean"]

```

```

 sr_low = np.linspace(0, SR_WR_BRANCH_CUTOFF_PPM, 50)
 sr_high = np.linspace(SR_WR_BRANCH_CUTOFF_PPM,
 max(1600.0, float(np.nanmax(Sr_wr_values))), 50)

```

```

 ax.plot(sr_low, cal_b["slope"] * sr_low + cal_b["intercept"],
 "-", color="#4575b4", lw=2.5, label="post-Archean branch")
 ax.plot(sr_high, cal_a["slope"] * sr_high + cal_a["intercept"],
 "-", color="#d73027", lw=2.5, label="sanukitoid branch")
 ax.axvline(SR_WR_BRANCH_CUTOFF_PPM, color="black", ls="--", lw=1.5,
 label="cutoff = %.0f ppm" % SR_WR_BRANCH_CUTOFF_PPM)

```

```

 ax.set_xlabel("Whole-rock Sr (ppm), from apatite Sr")
 ax.set_ylabel("Whole-rock SiO2 (wt%)")
 ax.set_title("Step 2 of the Bruand et al. (2016) proxy\n"
 "branch selection by the 650 ppm Sr cutoff")
 ax.grid(True, alpha=0.3)
 ax.legend(loc="best")
 fig.tight_layout()
 fig.savefig(os.path.join(outdir, "04_Sr_vs_SiO2_branches.png"), dpi=200)
 plt.show()

```

```

def plot_T_fO2_heatmap(melts, outdir):
 """

```

Figure 5 - which (T, fO2) conditions actually produce a self-consistent melt.

Each draw is binned on a T vs log fO2 grid and its Onuma misfit averaged.

Dark blue cells are the conditions best supported by the apatite chemistry.

"""

```
T_edges = np.linspace(T_MIN_C, T_MAX_C, HEATMAP_N_T_BINS + 1)
F_edges = np.linspace(LOG_FO2_MIN, LOG_FO2_MAX, HEATMAP_N_FO2_BINS + 1)
```

```
total = np.zeros((HEATMAP_N_T_BINS, HEATMAP_N_FO2_BINS))
count = np.zeros((HEATMAP_N_T_BINS, HEATMAP_N_FO2_BINS), dtype=int)
```

```
for m in melts:
 misfit = onuma_misfit(m)
 if not np.isfinite(misfit):
 continue
 ti = np.searchsorted(T_edges, m["T_C"], side="right") - 1
 fi = np.searchsorted(F_edges, m["log_fO2"], side="right") - 1
 if 0 <= ti < HEATMAP_N_T_BINS and 0 <= fi < HEATMAP_N_FO2_BINS:
 total[ti, fi] += misfit
 count[ti, fi] += 1
```

```
with np.errstate(invalid="ignore", divide="ignore"):
 mean_misfit = np.where(count > 0, total / np.maximum(count, 1), np.nan)
```

```
if np.all(np.isnan(mean_misfit)):
 return None
```

```
fig, ax = plt.subplots(figsize=(11, 7))
im = ax.imshow(mean_misfit, origin="lower", aspect="auto",
 cmap="RdYlBu_r",
 extent=[LOG_FO2_MIN, LOG_FO2_MAX, T_MIN_C, T_MAX_C])
```

```
flat = np.nanargmin(mean_misfit)
bi, bj = np.unravel_index(flat, mean_misfit.shape)
best_T = 0.5 * (T_edges[bi] + T_edges[bi + 1])
best_F = 0.5 * (F_edges[bj] + F_edges[bj + 1])
ax.plot(best_F, best_T, "*", ms=22, mfc="white", mec="black", mew=2,
 label="best: %.0f degC, log fO2 = %.1f" % (best_T, best_F))
```

```
buffer curves for reference
T_line = np.linspace(T_MIN_C, T_MAX_C, 100)
T_line_K = T_line + 273.15
ax.plot(-25030.0 / T_line_K + 12.46, T_line, "k--", lw=2, label="FMQ")
ax.plot(-24440.0 / T_line_K + 11.86, T_line, "k:", lw=2, label="NNO")
```

```
ax.set_xlim(LOG_FO2_MIN, LOG_FO2_MAX)
ax.set_ylim(T_MIN_C, T_MAX_C)
ax.set_xlabel("log10 fO2 (bar)")
ax.set_ylabel("T (degC)")
ax.set_title("Which T-fO2 conditions give a self-consistent melt?\n"
 "colour = mean Onuma-parabola misfit (blue = best)")
fig.colorbar(im, ax=ax, label="mean RMS residual (ln units)")
ax.legend(loc="upper right")
fig.tight_layout()
fig.savefig(os.path.join(outdir, "05_T_fO2_heatmap.png"), dpi=200)
plt.show()
```

```
return {"best_T_C": float(best_T), "best_log_fO2": float(best_F)}
```

```
def plot_D_parabola_best_fit(melts, best, outdir):
 """
```

Figure 6 - best-fit partition-coefficient parabola (Onuma diagram).

PANEL A - the forward D model at the best-supported (T, fO<sub>2</sub>) from Fig. 5.

The continuous curve is D(r) for trivalent cations from the lattice-strain equation; markers are the individual REE and Y placed at their IX-fold radii. Eu appears TWICE on purpose:

- as pure Eu<sup>3+</sup>, which sits ON the parabola
- as its effective mixed-valence D, which sits ABOVE the parabola because Eu<sup>2+</sup> substitutes for Ca<sup>2+</sup> and is compatible in apatite

The vertical dashed line is the ideal site radius r<sub>0</sub>. The gap between the two Eu symbols IS the redox signal at these conditions.

PANEL B - the corresponding inverted melt. Since D varies smoothly with radius, ln(C<sub>melt</sub>) must also define a parabola. The fitted quadratic and its RMS residual are exactly the quantity minimised in the Fig. 5 heatmap, so this panel shows what "best fit" means in practice. Eu is plotted but excluded from the fit, for the reason given above.

Also writes best\_fit\_D\_parabola.csv with the D values behind Panel A.

```
"""
if best is None:
 return None
```

```
T_C = best["best_T_C"]
T_K = T_C + 273.15
log_fO2 = best["best_log_fO2"]
```

```
---- model parameters at the best-fit conditions -----
D0, r0, E = apatite_lattice_parameters(T_K)
```

```
continuous parabola for the trivalent (Eu3+-like) cations
radii_all = np.array([R_IX_TRIVALENT[e] for e in TRIVALENT])
r_span = np.linspace(radii_all.min() - 0.025, radii_all.max() + 0.025, 400)
D_curve = np.array([lattice_strain_D(D0, r0, E, r, T_K) for r in r_span])
```

```
per-element D: effective (Eu mixed valence) and pure-trivalent
D_effective = {e: D_apatite(e, T_K, log_fO2) for e in TRIVALENT}
D_eu3_pure = lattice_strain_D(D0, r0, E, R_IX_TRIVALENT["Eu"], T_K)
x3 = eu3_fraction(T_K, log_fO2)
```

```
---- pick the melt draw that best represents these conditions -----
T_tol = (T_MAX_C - T_MIN_C) / HEATMAP_N_T_BINS
F_tol = (LOG_FO2_MAX - LOG_FO2_MIN) / HEATMAP_N_FO2_BINS
candidates = [m for m in melts
 if abs(m["T_C"] - T_C) <= T_tol
 and abs(m["log_fO2"] - log_fO2) <= F_tol]
if not candidates:
 candidates = melts
```

```

scored = [(onuma_misfit(m), m) for m in candidates]
scored = [(s, m) for s, m in scored if np.isfinite(s)]
scored.sort(key=lambda pair: pair[0])
rms_best, best_melt = scored[0] if scored else (np.nan, None)

---- figure -----
fig, (axA, axB) = plt.subplots(1, 2, figsize=(15.5, 6.8))

===== PANEL A: the D parabola =====
axA.plot(r_span, D_curve, "-", color="#333333", lw=2.2,
 label="lattice-strain parabola, REE3+")

for element in TRIVALENT_NO_EU:
 r = R_IX_TRIVALENT[element]
 d = D_effective[element]
 colour = "#1b7837" if element == "Y" else "#4575b4"
 axA.plot(r, d, "o", ms=9, color=colour, mfc="white", mew=1.8, zorder=5)
 axA.annotate(element, (r, d), xytext=(0, 9), textcoords="offset points",
 ha="center", fontsize=8.5, color=colour)

Eu, twice
r_eu = R_IX_TRIVALENT["Eu"]
axA.plot(r_eu, D_eu3_pure, "o", ms=9, color="#4575b4", mfc="white",
 mew=1.8, zorder=5)
axA.annotate("Eu3+", (r_eu, D_eu3_pure), xytext=(-4, 9),
 textcoords="offset points", ha="right", fontsize=8.5,
 color="#4575b4")
axA.plot(r_eu, D_effective["Eu"], "D", ms=12, color="#d73027",
 mec="black", mew=1.2, zorder=6,
 label="Eu effective (mixed valence)")
axA.annotate("Eu eff.", (r_eu, D_effective["Eu"]), xytext=(6, -4),
 textcoords="offset points", ha="left", fontsize=8.5,
 color="#d73027")
axA.annotate("", xy=(r_eu, D_effective["Eu"]), xytext=(r_eu, D_eu3_pure),
 arrowprops=dict(arrowstyle="<->", color="#d73027", lw=1.4))

axA.axvline(r0, color="#1b7837", ls="--", lw=1.6,
 label="r0 = %.3f Å" % r0)

axA.set_yscale("log")
axA.set_xlabel("Ionic radius, IX-fold coordination (Å)")
axA.set_ylabel("D (apatite / melt)")
axA.set_title("A. Best-fit D parabola\n"
 "T = %.0f degC, log fO2 = %.1f" % (T_C, log_fO2))
axA.grid(True, which="both", alpha=0.3)
axA.legend(loc="lower left", fontsize=9)

axA.text(0.98, 0.97,
 "D0 = %.3g\nr0 = %.3f Å\nE = %.1f GPa\nEu3+/Eu_total = %.3f"
 "% (D0, r0, E, x3),
 transform=axA.transAxes, ha="right", va="top", fontsize=9,
 bbox=dict(boxstyle="round,pad=0.45", fc="#f5f5f5", ec="#999999"))

===== PANEL B: the melt parabola actually fitted =====

```

```

if best_melt is not None:
 fit_elements = [
 e for e in TRIVALENT_NO_EU
 if e in best_melt and np.isfinite(best_melt[e]) and best_melt[e] > 0
]
 x_fit = np.array([R_IX_TRIVALENT[e] for e in fit_elements])
 y_fit = np.log(np.array([best_melt[e] for e in fit_elements]))
 coeffs = np.polyfit(x_fit, y_fit, 2)

 x_curve = np.linspace(x_fit.min() - 0.02, x_fit.max() + 0.02, 300)
 axB.plot(x_curve, np.exp(np.polyval(coeffs, x_curve)), "-",
 color="#333333", lw=2.2, label="fitted quadratic")

 for element in fit_elements:
 r = R_IX_TRIVALENT[element]
 c = best_melt[element]
 colour = "#1b7837" if element == "Y" else "#4575b4"
 axB.plot(r, c, "o", ms=9, color=colour, mfc="white", mew=1.8,
 zorder=5)
 axB.annotate(element, (r, c), xytext=(0, 9),
 textcoords="offset points", ha="center",
 fontsize=8.5, color=colour)

 if "Eu" in best_melt and best_melt["Eu"] > 0:
 axB.plot(r_eu, best_melt["Eu"], "D", ms=12, color="#d73027",
 mec="black", mew=1.2, zorder=6,
 label="Eu (excluded from fit)")
 eu_expected = math.exp(np.polyval(coeffs, r_eu))
 axB.annotate("", xy=(r_eu, best_melt["Eu"]),
 xytext=(r_eu, eu_expected),
 arrowprops=dict(arrowstyle="<->", color="#d73027",
 lw=1.4))
 axB.annotate("Eu anomaly\nn= %.2f" % (best_melt["Eu"] / eu_expected),
 (r_eu, best_melt["Eu"]), xytext=(8, 0),
 textcoords="offset points", ha="left", fontsize=8.5,
 color="#d73027")

 axB.set_yscale("log")
 axB.set_xlabel("Ionic radius, IX-fold coordination (A)")
 axB.set_ylabel("Melt concentration (ppm)")
 axB.set_title("B. Inverted melt on the same parabola\n"
 "RMS residual = %.4f (ln units), n = %d"
 % (rms_best, len(fit_elements)))
 axB.grid(True, which="both", alpha=0.3)
 axB.legend(loc="best", fontsize=9)
else:
 axB.text(0.5, 0.5, "No melt draw with enough elements to fit",
 transform=axB.transAxes, ha="center", va="center")
 axB.set_axis_off()

fig.tight_layout()
fig.savefig(os.path.join(outdir, "06_D_parabola_best_fit.png"), dpi=200)
plt.show()

```

```

---- CSV behind Panel A -----
rows = []
for element in TRIVALENT:
 rows.append({
 "element": element,
 "r_ionic_IX_A": R_IX_TRIVALENT[element],
 "D_effective": D_effective[element],
 "D_trivalent_only": (D_eu3_pure if element == "Eu"
 else D_effective[element]),
 "melt_ppm_at_best_fit": (best_melt.get(element, np.nan)
 if best_melt else np.nan),
 "T_C": T_C,
 "log_fO2": log_fO2,
 "D0": D0,
 "r0_A": r0,
 "E_GPa": E,
 "Eu3_fraction": x3,
 })
pd.DataFrame(rows).to_csv(
 os.path.join(outdir, "best_fit_D_parabola.csv"), index=False
)

return {"D0": float(D0), "r0_A": float(r0), "E_GPa": float(E),
 "Eu3_fraction": float(x3),
 "rms_residual_ln": float(rms_best) if np.isfinite(rms_best) else None}

=====
PART 9 - MAIN DRIVER

Calls PART 3 -> PART 8 in order and writes every result to OUTPUT_DIR.
=====

def main():
 print("=" * 78)
 print("APATITE INVERSE MELT MODEL + Sr-BASED SiO2 PROXY")
 print("=" * 78)

 os.makedirs(OUTPUT_DIR, exist_ok=True)

 # ---- PART 6a: build and report the calibration -----
 print("\n[PART 6a] Sr -> SiO2 calibration")
 calibration = build_calibration()
 report_calibration(calibration)
 calibration_dataframe(calibration).to_csv(
 os.path.join(OUTPUT_DIR, "calibration_used.csv"), index=False
)

 # ---- PART 3: load -----
 print("\n[PART 3] Loading %s" % INPUT_CSV)
 df = load_apatite_csv(INPUT_CSV)
 grains = extract_grain_compositions(df)
 print(" %d rows read, %d usable grains" % (len(df), len(grains)))

```

```

sr_present = [g["Sr"] for g in grains if np.isfinite(g.get("Sr", np.nan))]
print(" Sr measured on %d / %d grains" % (len(sr_present), len(grains)))
if sr_present:
 print(" apatite Sr range: %.0f - %.0f ppm"
 % (min(sr_present), max(sr_present)))

y_present = [g["Y"] for g in grains if np.isfinite(g.get("Y", np.nan))]
print(" Y measured on %d / %d grains" % (len(y_present), len(grains)))

---- PART 5: Monte-Carlo -----
print("\n[PART 5] Monte-Carlo: %d draws x %d grains = %d inversions"
 % (N_DRAWS, len(grains), N_DRAWS * len(grains)))
melts = run_monte_carlo(grains, calibration)
print(" %d melt records generated" % len(melts))

---- PART 7: statistics -----
print("\n[PART 7] Percentile envelopes")
envelope_df = summarise_melt_envelope(melts)
envelope_df.to_csv(
 os.path.join(OUTPUT_DIR, "melt_percentile_envelope.csv"), index=False
)

ratios_df = summarise_ratios(melts)
ratios_df.to_csv(os.path.join(OUTPUT_DIR, "melt_ratios.csv"), index=False)

print("\n Compatible melt (ppm), median and 1-sigma band:")
for _, row in envelope_df.iterrows():
 if pd.notna(row.get("C_p50_ppm")):
 print(" %-3s %9.2f [%9.2f - %9.2f]"
 % (row["element"], row["C_p50_ppm"],
 row["C_p16_ppm"], row["C_p84_ppm"]))

print("\n Melt ratios:")
for _, row in ratios_df.iterrows():
 if row.get("n", 0) > 0:
 print(" %-8s p50 = %7.3f [%7.3f - %7.3f]"
 % (row["ratio"], row["p50"], row["p16"], row["p84"]))

---- PART 6b: SiO2 proxy -----
print("\n[PART 6b] Whole-rock SiO2 from apatite Sr")
sio2_result = summarise_SiO2(melts)

if sio2_result is None:
 print(" No Sr data available - SiO2 proxy skipped.")
 sio2_stats = None
 SiO2_values = np.array([])
 Sr_wr_values = np.array([])
else:
 sio2_stats, SiO2_values, Sr_wr_values = sio2_result
 pd.DataFrame([sio2_stats]).to_csv(
 os.path.join(OUTPUT_DIR, "whole_rock_SiO2_estimate.csv"), index=False
)
 print(" Step 1 Sr_wr p50 = %.0f ppm [%.0f - %.0f]"
 % (sio2_stats["Sr_wr_p50_ppm"],

```

```

 sio2_stats["Sr_wr_p16_ppm"],
 sio2_stats["Sr_wr_p84_ppm"]))
print(" Step 2 branch at the median: %s"
 % sio2_stats["branch_at_median"])
print(" %.0f%% of draws fall on the sanukitoid branch"
 % (100.0 * sio2_stats["fraction_sanukitoid_branch"]))
print(" RESULT SiO2_wr p50 = %.1f wt%% [%0.1f - %0.1f] (1-sigma)"
 % (sio2_stats["SiO2_p50_wt%"],
 sio2_stats["SiO2_p16_wt%"],
 sio2_stats["SiO2_p84_wt%"]))
if CALIBRATION_MODE == "anchor_points":
 print("\n Reminder: these SiO2 values are only as good as the")
 print(" anchor points set in PART 1. Check them against the")
 print(" published Fig. 1A / 1C before interpreting.")

---- raw draws for traceability -----
sample_n = min(5000, len(melts))
if sample_n > 0:
 sample_idx = np.random.default_rng(0).choice(
 len(melts), sample_n, replace=False
)
 pd.DataFrame([melts[i] for i in sample_idx]).to_csv(
 os.path.join(OUTPUT_DIR, "monte_carlo_draws_sample.csv"), index=False
)

---- PART 8: figures -----
print("\n[PART 8] Plotting")
plot_spider_raw(envelope_df, grains, OUTPUT_DIR)
plot_spider_chondrite(envelope_df, grains, OUTPUT_DIR)
if sio2_stats is not None:
 plot_SiO2_histogram(SiO2_values, sio2_stats, OUTPUT_DIR)
 plot_Sr_vs_SiO2(Sr_wr_values, SiO2_values, calibration, OUTPUT_DIR)
best = plot_T_fO2_heatmap(melts, OUTPUT_DIR)
if best:
 print(" Best-supported conditions: T = %.0f degC, log fO2 = %.1f"
 % (best["best_T_C"], best["best_log_fO2"]))

parabola = plot_D_parabola_best_fit(melts, best, OUTPUT_DIR)
if parabola:
 print(" D parabola at those conditions:")
 print(" D0 = %.3g, r0 = %.3f A, E = %.1f GPa"
 % (parabola["D0"], parabola["r0_A"], parabola["E_GPa"]))
 print(" Eu3+/Eu_total = %.3f" % parabola["Eu3_fraction"])
 if parabola["rms_residual_ln"] is not None:
 print(" melt fit RMS residual = %.4f (ln units)"
 % parabola["rms_residual_ln"])

print("\n" + "=" * 78)
print("Done. All results in: %s" % os.path.abspath(OUTPUT_DIR))
print("=" * 78)

return envelope_df, ratios_df, sio2_stats, calibration

```

```
In Spyder, pressing F5 runs this block. The returned objects stay in the
Variable Explorer so you can inspect them interactively.
if __name__ == "__main__":
 melt_envelope, melt_ratios, sio2_summary, calibration_used = main()
```