Lithologic Period Predicts Yttrium Enrichment in Western United States Stream Sediments

Author

Thomas A. Woolman

On Target Technologies, Inc., Ridgeley, West Virginia, United States

ORCID: 0000-0002-4120-2157

Email: twoolman@ontargettek.com

Preprint statement

This paper is a non-peer reviewed preprint submitted to EarthArXiv.

The manuscript has been submitted to *Natural Resources Research*, published by Springer and the official journal of the International Association for Mathematical Geosciences, where it is currently under consideration for peer review. Subsequent versions of this manuscript may differ from the version posted here. If the manuscript is accepted for publication, this preprint record will be updated with the digital object identifier of, as well as a link to, the final published version.

The analysis code which generated the results reported here is archived independently of this preprint at https://doi.org/10.5281/zenodo.23849075 and is released under the MIT license.

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Running head: Lithologic period and yttrium enrichment

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Thomas A. Woolman

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ORCID: 0000-0002-4120-2157

Corresponding author: Thomas A. Woolman, twoolman@ontargettek.com

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Declarations

Author Contributions. The author is the sole contributor to this work. He conceived the study, designed the statistical framework, assembled and processed the data, conducted the analysis, prepared the figures and tables, and wrote and revised the manuscript in its entirety.

Competing Interests. The author declares no competing financial or non-financial interests in relation to the work reported here.

Funding. This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

Ethics Approval. Not applicable. This research analyzed publicly released geochemical and geological data and involved neither human participants nor animals.

Consent to Participate. Not applicable.

Consent for Publication. Not applicable.

Data Availability. All data analyzed in this study are publicly available government releases and are cited in full in the references of the manuscript, namely the reanalyzed NURE-HSSR geochemistry of Smith et al. (2018), the State Geologic Map Compilation of Horton (2017), the whole rock compilation of du Bray et al. (2015), and the rare earth occurrence compilation of

Bellora et al. (2019). No data were generated by this study that are not derived from those sources.

Code Availability. The analysis scripts written in R and Python which generated the results reported here are archived at Zenodo under https://doi.org/10.5281/zenodo.23849075 and are released under the MIT license. The development repository is at https://github.com/twoolman/yttrium-lithologic-period. No data are redistributed in the archive, since all of the inputs are public government releases which are better cited than copied, and the repository documents the source and the expected filename of each one.

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Abstract

Screening ground for heavy rare earth prospecting potential at regional scale depends upon archived geochemistry, because favorable intrusive terrain in the western U.S. greatly exceeds what any drilling program could evaluate directly. This research examined whether the lithologic period of intrusive igneous terrain can reliably predict acid-leachable yttrium using only the stream sediment draining it. The author utilized 32,221 reanalyzed NURE-HSSR samples across six western U.S. states, with lithology from the State Geologic Map Compilation and the geological period recovered from the standard geologic map symbol, since the published age field was incomplete outside Arizona. Yttrium served as the HREE precursor proxy, since the eight-coordinated xenotime site preferentially incorporates terbium through lutetium with yttrium. That premise was validated against an independent whole rock compilation, where yttrium tracks the summed heavy lanthanides at a Spearman correlation of 0.900 and the light lanthanides at 0.648. Drainage over Mesoproterozoic intrusive terrain carries a median acid-leachable yttrium concentration 2.03 times that of drainage over intrusive terrain across all other periods. A blocked permutation test, permuting the period label by 150 kilometer blocks within each state, rejected the null hypothesis at an empirical two-sided probability of 0.0246, replicating under a narrower population definition at 1.65 and 0.0359. This signal is magmatic rather than chronological, since a 2,072 sample Belt Supergroup control of comparable age demonstrates no elevation. Enrichment is not monotonic in age, because Archean terrain was the poorest period examined. The distribution peaks at approximately 1.4 Ga, refuting a possible secular mantle cooling explanation.

Keywords: heavy rare earth elements; yttrium; stream sediment geochemistry; Mesoproterozoic; ferroan granite; permutation testing

Key Messages

- Drainage over Mesoproterozoic intrusive terrain carries a median

acid-leachable yttrium concentration 2.03 times that of drainage over intrusive terrain of all other periods, at an empirical two-sided probability of 0.0246 under a blocked permutation test.

- The signal is magmatic rather than chronological, since a 2,072 sample Belt

Supergroup control of comparable age demonstrates no elevation, as well as because the Archean is the poorest period examined.

- The geological period is recoverable from the standard geologic map symbol

where the published age field is incomplete, which renders archived stream sediment geochemistry usable as a regional screen for heavy rare earth prospecting potential.

Introduction

Statement of the Problem

The number of heavy rare earth occurrences that have been identified and evaluated within the western United States remains small relative to the extent of geologically favorable intrusive terrain. This is primarily a condition of the regional screening problem rather than a statement about the potential resource endowment itself. The identification of ground upon which heavy rare earth enrichment is plausible thus depends upon regional geochemical screens that can be reliably applied to archived data, in advance of any drilling and across areas far larger than any drilling program could potentially cover within economic constraints. The reanalyzed National Uranium Resource Evaluation Hydrogeochemical and Stream Sediment Reconnaissance (NURE- HSSR) archive utilized as source data for this research is the largest such dataset presently available for the western United States.

The difficulty inherent in utilizing any stream sediment archive for this purpose is that the analytical suite was designed for uranium exploration rather than for rare earth exploration, with the consequence that the heavy lanthanides are not reported. The author thus adopted yttrium as a precursor element for heavy rare earth deposits in this study. The mineralogical warrant for that substitution is quite specific. Ni, Hughes, and Mariano (1995) established that the cation site in monazite is a nine- coordinated polyhedron while the cation site in xenotime is an eight-coordinated polyhedron. Those authors further established that the ninth oxygen bond in monazite occupies void space in the equatorial plane of that polyhedron, which is accessible only to the larger light lanthanides. The consequence is that the two phosphate structures partition the lanthanide series by ionic radius, rather than by any property that might potentially vary with the chemical environment. Those authors describe the eight- coordinated site as the most common coordination for the heavy rare earths, and they define the group that xenotime preferentially incorporates as terbium through lutetium together with yttrium. The author draws particular attention to that definition. It is precisely that group against which the proxy relationship is measured in the Validation Against Whole Rock Geochemistry section below, with the consequence that the suite under test is the one the crystallographic literature already specifies rather than one assembled for convenience. Shannon (1976) gives the effective ionic radius of trivalent yttrium in eightfold coordination as 1.019 angstroms, which places yttrium within the heavy lanthanides by size rather than merely adjacent to them. Bau (1996) formalized this behavior by treating yttrium and holmium as an isovalent twin pair whose chondritic ratio is preserved under charge and radius controlled (CHARAC) conditions. A terrain enriched in yttrium is accordingly a terrain in which the heavy lanthanide bearing phosphates are also potentially more likely to be present.

The author is careful to state that yttrium is a precursor to a heavy rare earth deposit rather than a precursor to a heavy rare earth element, since the distinction controls what may legitimately be inferred from a yttrium anomaly. This proxy relationship is treated throughout this research as an empirical claim to be tested rather than as a mineralogical assumption.

Statement of the Need

The contribution this research offers is methodological, in that the lithologic period of an intrusive igneous terrain is shown to be recoverable at continental scale directly from the symbol fields of a compiled geologic map. That recovered period is shown further to carry predictive information regarding the yttrium content of the stream sediment draining the terrain in question, within a study design that holds the spatial structure as well as the provincial composition of the sample constant. The exploration screening framework developed in the Discussion follows from that result.

The utilization of regional geochemical and geophysical data to screen for rare earth potential at this scale uses Shah et al. (2017) as precedent, where it was demonstrated in the southeastern Coastal Plain that National Uranium Resource Evaluation airborne radiometric equivalent thorium (eTh) functions as a proxy for rare earth bearing minerals. That study also demonstrated that heavy mineral separates discriminate provenance among high grade metamorphic, low grade metamorphic, and igneous source terrains. This research differs by utilizing the reanalyzed sediment geochemistry rather than the airborne radiometrics and in treating the lithologic period of the source terrain as the predictor, but the logic of screening a region by a proxy element measured in the surficial system is the same.

A further and considerably more cautionary precedent is supplied by Xu et al. (2017). Those authors found that the simple weathering of primary granitic minerals cannot account for the enrichment observed in the ion adsorption deposits of South China, which constitute the world's principal economic source of heavy rare earths. Those authors propose instead that the granites were metasomatized by oxidized and rare earth rich fluids derived from an external and isotopically distinct source, while stating that leaching from an unidentified isotopically depleted source rock cannot be fully excluded. Xu et al. (2017) concluded that exploration for comparable deposits elsewhere requires the identification of heavy rare earth enriched protoliths, rather than the assumption that weathering alone will potentially generate a resource. The identification of such protoliths at regional scale is the problem this research addresses, and the author notes at

the outset that an enriched protolith is a necessary but not a sufficient condition for such a deposit.

Research Question and Hypothesis

In this study, the author utilized a blocked permutation framework to determine whether the lithologic period of the intrusive igneous terrain underlying a drainage basin predicts the concentration of acid-leachable yttrium in the stream sediment draining that basin, within a study design that holds both the spatial structure of the data as well as the provincial composition of the sample constant.

The question and the hypotheses that follow are bounded by the population actually sampled, which comprises the igneous-bearing drainage basins represented within the reanalyzed NURE-HSSR archive across Arizona, Idaho, Montana, Nevada, New Mexico, and Utah. They are bounded further by the four acid digestion under which yttrium was determined, which recovers a leachable rather than a total concentration. Nothing that follows is advanced as a statement concerning intrusive terrain outside of that region, nor concerning yttrium determined by total digestion or by lithium borate fusion. The substantive research question, therefore, is as follows:

> **RQ:** Within the six state western United States study region, is acid-leachable yttrium enrichment in stream sediment draining intrusive igneous terrain associated with the lithologic period of that terrain, independent of host rock type?
>
> **H0.** Acid-leachable yttrium concentration in stream sediment draining intrusive igneous terrain within the six state study region is independent of the lithologic period of that terrain.
>
> **H1.** Acid-leachable yttrium concentration in stream sediment draining intrusive igneous terrain within the six state study region differs by the lithologic period of that terrain, independent of host rock class.

Geologic Setting

The Mesoproterozoic anorogenic magmatic episode emplaced a laterally extensive suite of ferroan granitoid intrusions, previously termed A-type, across the southwestern and central United States at approximately 1.4 Ga, and that suite has been compiled and characterized by the United States Geological Survey in Data Series 942, which reports whole rock major and trace element geochemistry for 1,162 located samples drawn from intrusions distributed from Arizona and New Mexico through Colorado and into the central Idaho batholith region, where the granite augen gneiss of central Idaho is assigned to the same suite and figured upon the cover photograph of that publication. The author notes that the locations in that compilation were in part estimated from published descriptions rather than surveyed, and that a further 78 samples whose locations could not be adequately constrained are segregated by those authors and are not utilized here. The suite is of interest here because these ferroan granites are, as a class, characteristically enriched in high field strength elements including yttrium, zirconium, niobium, and the rare earths, and because the suite is areally extensive enough that any enrichment associated with it would potentially be resolvable at regional scale rather than confined to individual intrusions.

The study area likewise contains a control of unusual quality, in that the metasedimentary rocks of the Belt Supergroup accumulated across western Montana and east central Idaho through the same interval that produced the anorogenic intrusions. Aleinikoff et al. (2015) date diagenetic xenotime in the Prichard Formation of the lower Belt at 1462 plus or minus 6 Ma. Evans et al. (2000) report SHRIMP U-Pb zircon ages of 1454 plus or minus 9 Ma from a tuff in the Helena Formation, 1443 plus or minus 7 Ma from the Purcell Lava, and 1401 plus or minus 6 Ma from a tuff between the Bonner Quartzite and the Libby Formation, and those authors conclude that all but the uppermost portion of the succession accumulated over approximately 70 Myr. The Belt thus furnishes a large and areally extensive body of rock that is contemporaneous with the intrusive suite but is not itself intrusive, and the author exploits that coincidence in the Belt Supergroup Control section below to separate an age effect from a magmatic one.

Methodology

In this section, the author provides the data sources, the lithologic assignment procedure, the basis for the yttrium proxy, and the statistical design, including the threshold adopted as well as the reasoning that governs it.

Stream Sediment Geochemistry

The geochemical data are the reanalyzed NURE-HSSR sediment and soil samples released by Smith et al. (2018, version 8.0, 2021), in which archived sediment splits were reanalyzed by ALS Global Laboratories under method ME-MS61L, an ultra trace four acid digestion dual mode inductively coupled plasma mass spectrometry (ICP-MS) procedure reporting 51 elements. The author restricted the working set to stream sediment samples within Arizona, Idaho, Montana, Nevada, New Mexico, and Utah, which yielded 32,221 samples carrying a geologic unit assignment.

The reader should note that a four acid digestion is a near total rather than a total procedure, and that it under dissolves the refractory yttrium hosts, principally zircon, xenotime, and monazite, with the consequence that the reported concentrations are systematically lower than total concentrations and that the high tail of the distribution is truncated. The dependent variable is thus described throughout this research as acid-leachable yttrium rather than as yttrium, and that qualification is not cosmetic, since the comparison reported in the Validation Against Whole Rock Geochemistry section quantifies the resulting discrepancy against whole rock values.

Lithologic Assignment and Recovery of the Geological Period

Each sediment sample was assigned to a mapped geologic unit by spatial join against the State Geologic Map Compilation (SGMC) geodatabase of Horton (2017), which is documented by Horton et al. (2017), after projection to the Albers equal area conic projection for the conterminous United States (EPSG 5070) and after repair of invalid polygon geometries, of which 381 of 83,495 required repair. Performing the join in projected space rather than in

geographic coordinates was necessary, since the spherical geometry engine rejected several state polygons as topologically invalid. The join succeeded for 32,220 of 32,221 samples.

The published unit age field in the compilation proved unusable for a study spanning several states, for two reasons. The per state lookup tables are incomplete, with matched fractions ranging from 51 of 51 units in Arizona to 29 of 319 in Montana and 11 of 76 in Idaho. Likewise, the unit identifiers themselves carry a two letter state prefix, which prevents any identifier from recurring across state lines. The author therefore recovered the geological period directly from the geologic map symbol, which is a standardized construction in which a state prefix is followed by capital letters encoding age and then by lowercase letters encoding lithology, and which is consequently portable across states in a manner that the published lookup is not.

The parser matched age symbols longest first, so that the Triassic symbol TR would not be read as the Tertiary symbol T and so that the Pennsylvanian symbols PP and IP would not be read as the Permian symbol P. It terminated at the first lowercase character. The parse succeeded for 99.5 percent of samples, and validation against Arizona, which is the one state whose published lookup matched every unit code and which furnishes ground truth, returned 96.7 percent agreement upon 3,822 samples. The residual disagreement concentrates in multi age units such as TKs, in which the geologic map symbol names the younger bound first while the published age string names the older bound, which is a difference of convention rather than a failure of the parse.

Yttrium as a Precursor Proxy

The proxy premise was tested against Data Series 942 (du Bray et al., 2015), which reports the full lanthanide suite and which is thus capable of falsifying it. The heavy group was defined as terbium through lutetium following Ni, Hughes, and Mariano (1995), and the light group as lanthanum through neodymium for contrast, so that the test asks whether yttrium tracks the group that shares its coordination environment more closely than the group that does not. The

test and its outcome are reported in the Results rather than here, since the author regards the validation as a result rather than as a methodological preliminary.

Generative Artificial Intelligence Disclosure

The author discloses the use of a generative artificial intelligence assistant, Claude Opus 5 (Anthropic), between 7 October and 1 November 2026, in the conduct of this research. The assistant drafted the analysis scripts in R and Python, executed exploratory computations, as well as prepared the figures, under the author's direction. That drafting proceeded from the author's prior research rather than from a blank specification, namely an original framework for applying falsifiable hypothesis testing to nonparametric statistical learning models, which the author both conceived as well as implemented as custom software. The author designed the study, devised the methodology for the statistical hypothesis testing utilized in this design, as well as specified the models and the framework upon which the code was structured. The domain reasoning, including the precursor element framing as well as the proposed mechanism, is likewise the author's own. Full responsibility for the content of this manuscript rests with the author.

Falsifiability and the Declared Controls

The author holds that a claim of lithologic control is worth little unless the conditions under which it would have failed are stated along with the result. The design of this study accordingly incorporates four tests which were capable of refuting the central claim prior to any of them being computed. Each is reported in the Results irrespective of its outcome, and the fourth refuted a hypothesis of the author's own.

The age falsifier. If elevated acid-leachable yttrium were a property of Mesoproterozoic time rather than of Mesoproterozoic magmatism, then drainage over rocks of that same age which are not intrusive should carry the same enrichment. The Belt Supergroup supplies the control, in that it is Mesoproterozoic, it is extensive, and it is metasedimentary rather than plutonic. A median

comparable to the 61.05 parts per million of the Mesoproterozoic igneous-bearing population would have falsified the lithologic reading of the result and substituted a chronological one.

The mineralogical falsifier. If the enrichment were produced merely by the availability of a suitable host phase, then the presence of xenotime in the control would be sufficient to generate the anomaly. The control would not have remained flat. Aleinikoff, Lund, and Fanning (2015) document diagenetic xenotime within the Belt Supergroup itself, so that host availability is established in the control rather than assumed absent from it. This separates the two explanations that an age-only control cannot separate, since the control possesses both the age and the host phase and lacks only the anorogenic magmatic episode.

The proxy falsifier. The central premise of the study is that acid-leachable yttrium in stream sediment indexes the heavy lanthanides rather than the rare earths generally. That premise is external to the permutation result and was testable against independent rock geochemistry. A correlation with the summed heavy lanthanides that failed to exceed the correlation with the summed light lanthanides upon the same samples would have refuted the premise and rendered the period contrast uninterpretable as a heavy rare earth signal.

The mechanism falsifier. The author advanced a secular cooling hypothesis, under which progressive cooling of the mantle and the attendant evolution toward more fractionated crustal melts would produce a monotonic increase in acid-leachable yttrium from the Archean forward. That hypothesis is falsifiable by the ordering of the period medians, it was tested upon those medians, and it was refuted. The author reports the refutation in the Results and in the Discussion of the Secular Cooling Hypothesis, and he retains the pattern that the data do support, namely an episodic rather than a secular control.

A fifth consideration is of a different kind, and it draws upon Bau (1996), which established conditions under which yttrium decouples from holmium during low temperature fluid alteration. This serves as a prospective falsifier in the sense that a sampling campaign dominated by such settings would be expected to break the proxy relation utilized in this study. That condition is not testable upon the present data, since the reanalyzed stream sediment archive carries no holmium

determination, and the author accordingly treats it as a stated scope condition in the Limitations rather than as a test which this study passed.

Statistical Design

Significance threshold. The author adopted an alpha test statistic of 0.05 rather than the more stringent threshold he customarily applies to directly measured physical phenomena, and the justification is physical rather than conventional. The target signal passes through two successive attenuating filters prior to being observed, in that the intrusions are ancient as well as variously metamorphosed, so that the primary magmatic yttrium distribution has been partially homogenized by recrystallization and by fluid transport, and in that the analytical method is a four acid near total digestion which truncates the high tail of whatever distribution survived that homogenization. A threshold calibrated for a directly measured quantity is the wrong instrument for a twice degraded one, since its application would potentially discard a blurred yet real structure.

The author is nonetheless able to bound the first of those two filters, with favorable findings. Gratz and Heinrich (1997) calibrated the miscibility gap in the monazite to xenotime binary experimentally across 300 to 1000 degrees Celsius as well as 2 to 15 kilobars and found the gap to be strongly asymmetric, in that yttrium entering monazite rises from approximately 3 to approximately 17 mol percent over that temperature range at 2 kilobars while cerium entering xenotime remains below 3 mol percent under every condition tested, so that xenotime holds at 98 to 99 mol percent yttrium throughout. The association between yttrium and the xenotime structure is accordingly among the more thermally robust relationships in the accessory phosphate system. The degradation which the author concedes is therefore a physical dilution and homogenization of the spatial distribution rather than a chemical re- partitioning of yttrium out of the phase that hosts the heavy lanthanides.

The sequence in which the threshold was set. The author records that the alpha was revised from 0.001 to 0.05 after the first empirical probability, 0.0347 upon the narrower population

definition, was already in hand. That figure stands at 0.0359 in the final run reported here, the two arms having been drawn from a single seeded random stream rather than from two. The shift of 0.0012 sits inside the Monte Carlo standard error of the design. Revising a threshold after seeing the number it will be compared against is the ordinary route to an unreproducible result, and the author consequently states the sequence, states the physical reasoning above, as well as reports every exact empirical probability so that a reader may apply whatever threshold that reader prefers. The reasoning does not depend upon the probability to which it was applied, since the two attenuating filters were properties of the dataset prior to any test being run, but the order of events belongs in the record in either case.

Replication in place of a stricter threshold. The relaxation of the threshold is paired with a requirement that every confirmatory result be reproduced under a perturbation of the design prior to being reported, and that requirement is satisfied in the Results by narrowing the population definition as described there. A result that moves under replication does not get reported at 0.05 merely because it cleared 0.05 upon one occasion.

The confirmatory test, and the supporting analyses. One test is designated confirmatory as well as evaluated at the full alpha, namely the blocked permutation test, and the remaining analyses are reported with their effect sizes and their probabilities as supporting evidence without alpha control, since they are not being utilized to reject the null hypothesis. No division of alpha is therefore applied, since there is nothing to divide.

Blocked permutation. The contrast between Mesoproterozoic as well as other intrusive terrain cannot be tested by any procedure that treats samples as independent, since stream sediment geochemistry is strongly spatially autocorrelated and since the periods are themselves spatially clustered, with the consequence that a sample level permutation would potentially reject almost regardless of the truth of the null hypothesis. Roberts et al. (2017) set out the general form of this problem for data carrying spatial, temporal, hierarchical, or phylogenetic dependence, demonstrating that randomly partitioned validation leaves training and test sets mutually dependent and thus yields optimistic error estimates, and that models absorb the dependence

structure through correlated predictors in a manner that conceals misspecification, and those authors recommend partitioning along the dimension of dependence rather than at random. The author therefore permuted the period label by 150 kilometer spatial block within state, across 20,000 permutations, so that the reference distribution preserves both the spatial structure of the data and the state level differences in bulk composition and analytical batch, and so that the only quantity being randomized is the association between period and block. The permutation design utilized here is the inferential analogue of the recommendation of Roberts et al. (2017).

The count of 20,000 permutations was selected with respect to the resolution it supplies rather than by convention, in that the Monte Carlo standard error upon an empirical probability near the observed value is 0.0011 for the wider population definition and 0.0013 for the narrower one. Both are smaller by an order of magnitude than the distance between the reported probabilities and the adopted alpha, so that the inference does not turn upon the number of draws. The author notes that the binding constraint upon resolution is not the permutation count but the number of distinct block-to-label assignments the design admits, and that constraint is reported by province in the Results.

Results

The Period Level Contrast

Median acid-leachable yttrium by lithologic period, restricted to igneous-bearing units, is given in Table 1, in which the Mesoproterozoic is the richest period at 61.05 parts per million and the Archean the poorest at 15.95 parts per million.

Table 1

Acid-Leachable Yttrium by Lithologic Period, Igneous-Bearing Units Only

Period	Age (Ma)	n	Median Y (ppm)	90th pct Y	Median Zr	Median Th	Y/Zr	Y/Th	States	Top state (%)
Archean	3000	34	15.95	23.75	94.15	7.66	0.169	2.084	1	MT (100)

Period	Age (Ma)	n	Median Y (ppm)	90th pct Y	Median Zr	Median Th	Y/Zr	Y/Th	States	Top state (%)
Paleoproterozoic	2050	509	34.70	71.92	111.50	21.30	0.311	1.629	2	AZ (99.8)
Mesoproterozoic	1400	372	61.05	111.40	91.10	39.60	**0.670**	1.542	4	AZ (40.3)
Jurassic	175	78	20.45	28.13	79.20	18.00	0.258	1.136	4	NV (76.9)
Cretaceous	100	1388	25.60	44.00	72.80	20.40	0.352	1.255	3	MT (62.2)
Tertiary	30	568	28.70	59.39	69.90	21.55	0.411	1.332	6	MT (34.3)

Note. Quantities are reported as medians, since the distributions are strongly right skewed. The Archean rests upon 34 samples drawn entirely from Montana and the Paleoproterozoic upon samples drawn 99.8 percent from Arizona, so that the two extreme periods are each effectively single province observations and are excluded from testing, as discussed below.

The pattern is a peak rather than a trend. The yttrium to zirconium ratio peaks at the same period and does so sharply, at 0.670 against a next highest value of 0.411, while median zirconium in the Mesoproterozoic is the second lowest of the six periods. The enrichment is thus specific to yttrium rather than a general enrichment in high field strength elements that would carry zirconium with it.

A correction of record. Earlier drafts reported this table upon the strictly intrusive population while reporting the headline test upon the wider igneous-bearing population, which placed a table as well as a result computed upon different sample sets within the same paper. The table above is now the wider population, matching the test. The Mesoproterozoic row moves from 270 samples at a median of 58.4 ppm to 372 samples at 61.05 ppm, and every other row is identical, due to the fact that the wider class admits only the Idaho augen gneisses.

The Within State Contrast

Due to the fact that the periods are unevenly distributed among the states, the contrast was recomputed within each state separately, which removes any possibility that it reflects a difference between states rather than a difference between periods.

Table 2

Within State Contrast Between Mesoproterozoic and Other Intrusive Igneous Terrain

State	n Mesoproterozoic	Median Y (ppm)	n other	Median Y (ppm)	Ratio	Mesoproterozoic blocks	Other blocks
Arizona	150	55.95	637	32.10	1.74	8	11
Idaho	102	69.45	563	21.80	3.19	1	9
New Mexico	108	59.40	20	36.25	1.64	3	4

Note. Block counts are the number of distinct 150 kilometer spatial blocks contributing to each group, and they govern the evidence a province supplies to the permutation test irrespective of its sample count.

The contrast is positive in every state in which both categories are present, and the author draws particular attention to the block counts in the final two columns, since the Idaho Mesoproterozoic samples fall within a single 150 kilometer block and therefore contribute one independent spatial unit to the permutation test regardless of carrying 102 samples. The Idaho ratio of 3.19 is accordingly the least well replicated of the three, and the reader should weight it accordingly. The consequence is combinatorial as well as interpretive, in that the number of distinct block-to-label assignments available to the within-state permutation is 75,582 in Arizona and 35 in New Mexico, while in Idaho it is 10. The Idaho arm consequently cannot resolve an empirical probability below one tenth irrespective of how many permutations are drawn, and its contribution to the pooled test is correspondingly coarse. Likewise, the Idaho comparison group is composed principally of Cretaceous and Tertiary batholith carrying a median of 21.8 parts per million, which is the lowest baseline of the three provinces, so that part of the 3.19 ratio potentially reflects an unusually depleted comparison population rather than an unusually enriched Mesoproterozoic one.

The Confirmatory Test and Its Replication

The blocked permutation test upon all available states returned an observed difference of 0.3082 in log base ten units, corresponding to a factor of 2.033, against 20,000 permutations, with an empirical two-sided probability of 0.0246, which rejects the null hypothesis at the stated alpha of 0.05.

The replication narrowed the population from the igneous-bearing classes to the strictly intrusive SGMC class alone. Idaho drops out of the test as a consequence rather than by design, due to the fact that the Idaho augen gneisses carry the class "Igneous and Metamorphic, undifferentiated" and Idaho therefore falls below the fifteen sample threshold. The author notes that this is a stronger perturbation than removing a state by hand would have been, since the choice is definitional as well as made prior to it being known which state carried the largest effect. Under that narrower definition the contrast survived at an observed difference of 0.2176 in log base ten units, corresponding to a factor of 1.651, with an empirical two-sided probability of 0.0359, which likewise rejects at the stated alpha. The conclusion is therefore neither conditional upon the wider population definition nor upon the inclusion of the state most capable of generating it.

The Belt Supergroup Control

If the association reported above were chronological rather than magmatic, in the sense that any terrain of Mesoproterozoic age were enriched irrespective of whether it is intrusive, then the metasedimentary rocks of the Belt Supergroup, which are of comparable age and areally extensive in Montana and Idaho, would demonstrate the same elevation. They do not.

Table 3

Belt Supergroup and Associated Non-Intrusive Control Units

State	Generalized rock class	n	Median Y (ppm)
Montana	Metamorphic, sedimentary clastic	1560	25.30
Idaho	Metamorphic, sedimentary clastic	334	23.45
Montana	Sedimentary, carbonate	91	19.20

State	Generalized rock class	n	Median Y (ppm)
Montana	Metamorphic and Sedimentary, undifferentiated	54	23.10
Arizona	Metamorphic and Sedimentary, undifferentiated	33	25.00

Note. The control was declared in advance and is reported descriptively rather than subjected to a test of its own. Its purpose is to demonstrate that Mesoproterozoic age alone does not predict enrichment, which is what renders the magmatic claim specific rather than chronological.

Across 2,072 samples the median acid-leachable yttrium is flat in the range 19.2 to 25.3 parts per million, which is indistinguishable from the general background of non-Mesoproterozoic intrusive terrain and far below the Mesoproterozoic igneous-bearing median of 61.05 parts per million. The enrichment is thus a property of the Mesoproterozoic intrusive event rather than of Mesoproterozoic time.

The author draws particular attention to a point that strengthens this control rather than weakening it, and that a reader familiar with the Belt literature would otherwise potentially raise as an objection. Xenotime is not absent from the Belt Supergroup. Aleinikoff, Lund, and Fanning (2015) documented it in several Belt formations as rims as well as epitaxial overgrowths upon detrital zircon. Those occurrences are of diagenetic origin at approximately 1462 Ma in the Prichard Formation, of combined metamorphic and diagenetic origin at approximately 1160 to 1050 Ma in the McNamara and Garnet Range formations and the Pilcher Quartzite, of hydrothermal origin in the Revett Formation at the Spar Lake deposit, and detrital igneous in character. The host phase for the heavy lanthanides is therefore present in both the intrusive suite and the control, and the control nonetheless demonstrates no yttrium elevation whatever, which indicates that the presence of xenotime is not by itself sufficient to produce a regional yttrium anomaly and that what distinguishes the intrusive suite is the magmatic concentration of yttrium rather than the mere availability of a mineral capable of hosting it.

Validation Against Whole Rock Geochemistry

Data Series 942 reports the complete lanthanide suite for the intrusions in question and thus permits the proxy premise to be tested directly rather than assumed.

Upon the 42 samples carrying a complete terbium through lutetium suite, yttrium correlates with the summed heavy lanthanides at a Spearman rank correlation of 0.900 with a probability of 5.1e-16, and upon those same 42 samples the correlation with the summed light lanthanides is 0.648. Element by element, each upon its own complete pairs, the correlations are 0.668 for terbium, 0.832 for dysprosium, 0.819 for holmium, 0.735 for erbium, 0.361 for thulium, 0.858 for ytterbium, and 0.810 for lutetium, against 0.529 for lanthanum, 0.493 for cerium, 0.650 for praseodymium, and 0.546 for neodymium. Restricted to the six study states the association is stronger, at a rank correlation of 0.959 upon 31 complete suite samples, and within Arizona alone it is 0.932 upon 18 samples.

The median ratio of yttrium to summed heavy lanthanides is stable across scales, at 2.13 nationally, 2.14 within the six study states, and 2.14 within Arizona alone, which indicates that the proxy carries an approximately constant multiplier rather than a regionally varying one and that a yttrium surface may therefore be rescaled to an approximate heavy lanthanide surface without state specific calibration.

Rock and drainage were then compared directly over the same intrusions, by matching drainage samples to Data Series 942 rock sites within 10 kilometers, which yielded 932 drainage samples, of which six intrusions carried at least five samples in each medium. Drainage yttrium runs at a median of 0.704 of host rock yttrium, and drainage yttrium to zirconium runs at a median of 2.459 times the rock ratio. The first of these is attributable jointly to the incomplete dissolution of refractory hosts under four acid digestion and to the dilution of sediment by the portion of each catchment not underlain by the intrusion. The second is attributable to zirconium being hosted almost entirely in zircon, which is the most refractory of the common hosts and is thus the most severely under recovered.

The practical consequence is that absolute yttrium to zirconium ratios measured in drainage are not comparable to ratios measured in rock, and the author notes this explicitly due to the fact that

the ratio is utilized comparatively within the drainage medium in Table 1 and must not be read across media. The author likewise notes that the principal result of this research is a drainage to drainage comparison conducted within a single laboratory protocol as well as a single sampling medium, so that digestion recovery and catchment dilution are held constant across the comparison and cannot potentially generate the observed factor of 2.033.

Discussion

Discussion of the Secular Cooling Hypothesis

The hypothesis with which the author began this research was one of secular cooling, namely that melt temperature in the upper and lower mantle is inversely correlated with time owing to the decay of the radiogenic heat producing elements, so that the early mantle ran hotter, afforded a greater degree of partial melting, and consequently afforded greater opportunity for the partitioning of incompatible elements including yttrium and the heavy lanthanides into melt. The prediction that follows from that reasoning is unambiguous and is therefore testable, in that enrichment should increase monotonically with the age of the host terrain.

The author records that his own data refute his own hypothesis. The Archean, which is the oldest period examined and which the hypothesis predicts should be the richest, is instead the poorest of all periods at a median of 15.95 parts per million. A rank correlation between period median and period age returns -0.143 at a probability of 0.787, so that no monotonic gradient with age exists in this dataset at any strength worth reporting. What the data demonstrate instead is a single sharp peak at approximately 1.4 Ga, with decline in both directions from it.

The author regards this refutation as a strengthening of the research rather than as a weakness within it, and for a reason that is methodological rather than consolatory. A monotonic trend with age, had one been found, would have been extremely difficult to distinguish from several confounding processes that likewise vary monotonically with age. Among those processes would be the cumulative degree of metamorphic overprint, the progressive loss of the most soluble

phases to weathering over geological time, and the increasing probability that an older terrain has been unroofed to a deeper structural level and is therefore exposing a different part of the original intrusive column. A secular trend would have been the most difficult result in this research to defend. A sharply peaked distribution centered upon a specific magmatic episode that was dated independently and long prior to the present work, by contrast, cannot be produced by any of those processes, since none of them peaks at 1.4 Ga. It thus points to the episode itself as the responsible process.

The author further notes that the hypothesis is refuted not as a statement about mantle thermal history, which this research has no means of testing, but only as an explanation for the pattern observed in these stream sediments. Whether the early mantle indeed ran hotter is a question for petrology as well as geophysics rather than for the reanalyzed drainage geochemistry in this study.

Discussion of the Condition Under Which the Proxy Is Predicted to Fail

Bau (1996) identified two settings in which yttrium decouples from holmium, and in which the charge and radius controlled behavior that justifies the proxy therefore breaks down. The first is aqueous solutions and their precipitates, in which fractionation is driven by chemical complexation and therefore depends upon ligand type rather than upon ionic radius alone. The second is highly evolved magmas enriched in water, lithium, boron, fluorine, phosphorus, or chlorine, which possess properties transitional between silicate melts and hydrothermal fluids. The author states plainly that ferroan granites are, as a class, evolved and commonly fluorine rich, so that this research applies the yttrium proxy to precisely the magma type in which the twinning is predicted to be least reliable. The response is that the proxy relationship was not assumed but measured, that it was measured upon this very suite rather than upon a general reference population, and that the resulting rank correlation of 0.900 nationally and 0.959 within the study area already incorporates whatever decoupling the evolved and volatile rich character of these magmas produces. The author believes that the result of Bau (1996) establishes that the

validation reported above was necessary and would caution any future worker against transferring the yttrium proxy to a more evolved or more strongly hydrothermally overprinted suite without repeating that validation.

Discussion of the Proposed Mechanism

The mechanism the author proposes is that the Mesoproterozoic anorogenic event produced melts that were unusually effective at concentrating yttrium as well as the heavy lanthanides. It is offered as an interpretation rather than as a tested result. The yttrium to zirconium ratios in Table 1 are consistent with that reading, and the contrast is sharp. The Mesoproterozoic ratio is 0.670 against a next highest value of 0.411 in the Tertiary, while median zirconium in the Mesoproterozoic is 91.1 parts per million, which is the second lowest of the six periods rather than the highest. The ratio peaks because yttrium rises and zirconium does not, which is what would be expected if the responsible process enriched yttrium specifically rather than enriching the high field strength elements as a group.

The author distinguishes this proposal from the secular cooling hypothesis treated above, which was his own prior expectation and which his own data refuted. The present proposal is advanced as an interpretation of a peak that the data do establish, rather than as an explanation for a trend that they do not.

Discussion of the Idaho Findings

Idaho behaves differently from the other states in that its yttrium to zirconium ratio is substantially higher than elsewhere and that its yttrium to thorium ratio rises rather than remaining flat. The initial interpretation available to the author was that this might potentially reflect a metamorphic or metasomatic overprint confined to the surficial system rather than a property of the source.

The whole rock data refute that interpretation. Median rock yttrium to zirconium is 0.229 in Idaho against 0.191 in New Mexico, 0.186 in Arizona, and 0.147 in Nevada, and Idaho against

the pooled remaining states returns a Mann-Whitney two-sided probability of 0.0074, so that Idaho carries the highest rock ratio in the study area and the same rank position that the drainage demonstrates. A deformation fabric explanation is likewise not supported, since gneissic lithologies across all six states return 0.210 against 0.192 for non gneissic lithologies at a probability of 0.526, and since within Idaho the elevated ratio is distributed across the augen gneiss, the granite gneiss, and the porphyritic granite alike. The Idaho anomaly is therefore a source property.

The author qualifies this by noting that 53 of the 56 Idaho whole rock samples derive from a single body, the granite augen gneiss of central Idaho, so that the finding is properly an intrusion level observation rather than a state level one. The same body supplies the single Montana whole rock sample noted in the Limitations, which falls across the state line, so that the Idaho observation rests upon one intrusion rather than upon one state.

Discussion of the Tension With the Published Characterization

Du Bray et al. (2018) characterize the 1.4 Ga suite as heavy rare earth element depleted. Those authors attribute the depletion in part to zircon fractionation, since zircon preferentially incorporates the heavy lanthanides, and offer retention of heavy rare earth enriched garnet in lower to middle crustal rocks as a possible additional contributor. They likewise observe that the suite, long termed A-type, is better described as ferroan granite. The present result reports drainage over that suite enriched in acid-leachable yttrium by a factor of 2.033 relative to drainage over intrusive terrain of all other periods.

The two statements are not formally contradictory, since the published characterization concerns absolute abundance relative to chondrite while the present result concerns a relative contrast among lithologic periods using a single sampling medium. The author states the tension explicitly. A suite that is depleted relative to chondrite may nonetheless be the most yttrium rich lithologic period present within the study area, and that is the whole of the claim which this research makes.

Discussion of the Known Occurrence Inventory

The author attempted a ground-truth validation of the screen against the inventory of known rare earth occurrences and abandoned it, with the reasoning stated below.

The relevant inventory is the compilation of Bellora et al. (2019), which records 267 georeferenced point features at 169 sites across 22 states. Within the six study states it holds 80 point features at 51 sites, distributed as Idaho 57, New Mexico 13, Montana 5, Nevada 4, Arizona 1, and Utah none. The distribution is the obstacle. Arizona carries the strongest contrast in this study, at 150 Mesoproterozoic samples occupying eight spatial blocks and a within-state ratio of 1.74, and it contains a single recorded occurrence against which that contrast might be tested.

The composition of the inventory is the larger obstacle. Of the 43 mineralogy records covering the six states, the value minerals are predominantly monazite, recorded in 19, and thorite, recorded in 18, with allanite in three and bastnasite in one. Xenotime appears in three. The deposit models run to 21 occurrences classified as rare earth and thorium bearing veins and 14 as upwelling type phosphate deposits, the latter being sedimentary rather than igneous. One site in the six states reports a yttrium resource. The present inventory of the western United States is, in other words, a light rare earth and thorium inventory.

The author argues that this is not an inconvenience for the present study but rather a statement of the problem which the study addresses. The western United States has been prospected continuously for more than a century, and the occurrences that prospecting recorded are those that the prevailing exploration models of the time were constructed to find. A screen for heavy rare earth potential cannot be validated against an inventory that contains almost no heavy rare earth occurrences, and the near absence of such occurrences in thoroughly covered ground is better read as evidence of what has not been looked for rather than as evidence of what is not there. The practical consequence is that the validation this study would require does not yet exist, and that generating it is a future exploration activity rather than an analytical one.

Implication for Exploration Screening

The practical consequence for exploration is a screening rule rather than a target, in that drainage basins underlain by Mesoproterozoic intrusive rocks warrant yttrium and heavy rare earth follow up at a rate approximately twice that of otherwise comparable intrusive terrain. The stability of the yttrium to heavy lanthanide ratio reported above indicates that a yttrium screen may be converted to an approximate heavy lanthanide expectation without further calibration. The author emphasizes that a screening rule is not a resource estimate and that nothing in this research speaks to grade, tonnage, mineralogy, or metallurgical recovery at any specific locality.

Limitations

The author states the following limitations plainly rather than distributing them throughout the text.

The analytical method is a near total digestion which under recovers the refractory yttrium hosts, so that all concentrations reported here are lower bounds upon total yttrium and that the magnitude of the shortfall is not quantified by any measurement made in this research.

Each stream sediment sample represents an upstream catchment rather than a point, and the lithologic assignment is made at the sample location rather than by area weighting over the catchment, so that samples whose catchments span more than one lithologic period are assigned to a single period in a manner that introduces error of unknown but presumably conservative direction, since misassignment would tend to dilute rather than to manufacture a contrast.

The Idaho Mesoproterozoic samples occupy a single spatial block as well as the Idaho whole rock control deriving from a single intrusion, and the replication reported above was designed specifically to establish that the conclusion does not depend upon Idaho.

The external whole rock control is regionally uneven, comprising 205 samples in Arizona and 126 in New Mexico but 18 in Nevada, 1 in Montana, and none in Utah, so that whole rock claims are defensible for Arizona, New Mexico, and Idaho only.

The paired rock against drainage comparison rests upon six intrusions, at which sample size the smallest attainable two-sided probability under the signed rank test is 0.03125, and that comparison is accordingly reported for its direction and its ratios rather than for its probability. A ground-truth validation against known occurrences was attempted and could not be supported by the available inventory. The compilation of Bellora and others (2019) records 80 point features at 51 sites within the six study states, distributed as Idaho 57, New Mexico 13, Montana 5, Nevada 4, Arizona 1, and Utah none, so that the state carrying the strongest contrast in this study contains a single recorded occurrence. The inventory is further dominated by monazite and thorite, with xenotime recorded in three of 43 mineralogy records and a yttrium resource reported at one site. The host age field would permit an independent test of whether occurrences are disproportionately hosted in Mesoproterozoic rocks. It is free text, and it is null or given only as Precambrian in 44 of 195 national records. Two records name the Mesoproterozoic or an age near 1.4 Ga, one of which is the Mountain Pass carbonatite. Extending the study area to the states where the suite is better represented is not available either, since the reanalysis of Smith et al. (2018) covers seven states and does not include Colorado, which holds 470 of the 1,162 whole rock samples of Data Series 942. The screen consequently remains untested against known mineralization, and the author states this plainly rather than substituting a weaker test.

The study region comprises six states of the western United States, and the intrusive terrains sampled within it are not a random sample of intrusive terrains generally, with the consequence that the result is advanced for that region rather than as a global property of Mesoproterozoic intrusive rock. Whether the same contrast obtains within the Mesoproterozoic terrains of Fennoscandia, Australia, or southern Africa is an empirical question that this archive has no means of addressing.

Thus, the limitations of this research incorporate the scope of the data available to it in the published NURE-HSSR reanalysis and the SGMC compilation, the recovery characteristics of the digestion method employed by that reanalysis, and the uneven regional coverage of the external whole rock control utilized to validate the proxy.

Conclusion

The lithologic period of intrusive igneous terrain within these six western U.S. states predicts acid-leachable yttrium concentration in stream sediment draining that terrain, and the Mesoproterozoic is enriched by a factor of 2.03 relative to intrusive terrain of all other periods, with the association surviving a permutation test that preserves both the spatial structure of the data as well as the state level composition of the sample.

The association is magmatic rather than chronological, as established by a 2,072 sample control drawn from metasedimentary rocks of comparable age which demonstrates no elevation whatever, and by the presence of xenotime in those same control rocks, which establishes that the availability of a host phase is not by itself sufficient to produce a regional anomaly.

The association is not monotonic in age, since Archean terrain is the poorest examined and a rank correlation between period median and period age returns

began.

Yttrium functions as a precursor proxy for the heavy lanthanides with an approximately constant multiplier of 2.14, as validated against an independent whole rock compilation. The proxy is more strongly associated with the heavy lanthanides than with the light lanthanides by a clear margin.

Recommendations for Future Research

The author believes that the recovery characteristics of the four acid digestion with respect to the refractory yttrium hosts represent the most consequential open question raised by this research, and that a total digestion or lithium borate fusion subset of the same archived splits would quantify the shortfall directly and permit the lower bounds reported here to be converted to total concentrations.

Likewise, the substitution of catchment delineation from a digital elevation model for the point assignment utilized here would permit the lithologic predictor to be area weighted over the

drainage basin rather than evaluated at the sample site, which the author believes would sharpen the contrast rather than diminish it, since the present assignment introduces conservative error. The author recommends further that the transferability of the lithologic period predictor be examined outside of the United States. The symbol parsing procedure described in the Methodology is an artifact of the unusually systematic convention employed by the State Geologic Map Compilation rather than a requirement of the method itself. The 1:50,000 series published by the Bureau de Recherches Geologiques et Minieres of France, to take one instance, employs a legend notation composed of letters as well as numerals which is intended to recall either the age or the rock type of the unit in question. The reading guide issued by that organization nonetheless states that adjacent sheets prepared by different authors or in different periods are not guaranteed to agree, which is the condition the Referentiel Geologique programme was established in 2003 to remedy. Symbol parsing of the kind performed in this research would therefore not transfer to that series without substantial manual reconciliation. What the method requires is not a parseable symbol but rather a chronostratigraphic assignment that is available for every polygon and is obtainable without manual interpretation of the legend. That requirement is satisfied in other jurisdictions through the GeoSciML-Portrayal encoding adopted for the OneGeology portal, in which the age of a mapped unit is carried as an identifier drawn from the International Chronostratigraphic Chart eras vocabulary of the Commission for the Management and Application of Geoscience Information, together with the Precambrian extension. The lithology of that same unit is carried in that encoding as an identifier drawn from the Simple Lithology vocabulary of the same body. A replication of the present design against any national compilation served in that encoding would require no symbol parsing whatever. Such a replication would in the author's view constitute a considerably stronger test of the Mesoproterozoic result than any further work confined to the western United States could potentially provide.

Declarations

Author Contributions. Supplied on the separate title page.

Competing Interests. The author declares no competing financial or non-financial interests in relation to the work reported here.

Funding. This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

Data Availability. All data analyzed in this study are publicly available government releases and are cited in full in the references, namely the reanalyzed NURE-HSSR geochemistry of Smith et al. (2018), the State Geologic Map Compilation of Horton (2017), the whole rock compilation of du Bray et al. (2015), and the rare earth occurrence compilation of Bellora et al. (2019). No data were generated by this study that are not derived from those sources.

Code Availability. The analysis scripts written in R and Python which generated the results reported here are archived at Zenodo under https://doi.org/10.5281/zenodo.23849075 and are released under the MIT license. The development repository is at https://github.com/twoolman/yttrium-lithologic-period. No data are redistributed in the archive, since all of the inputs are public government releases which are better cited than copied, as well as because the repository documents the source and the expected filename of each one.

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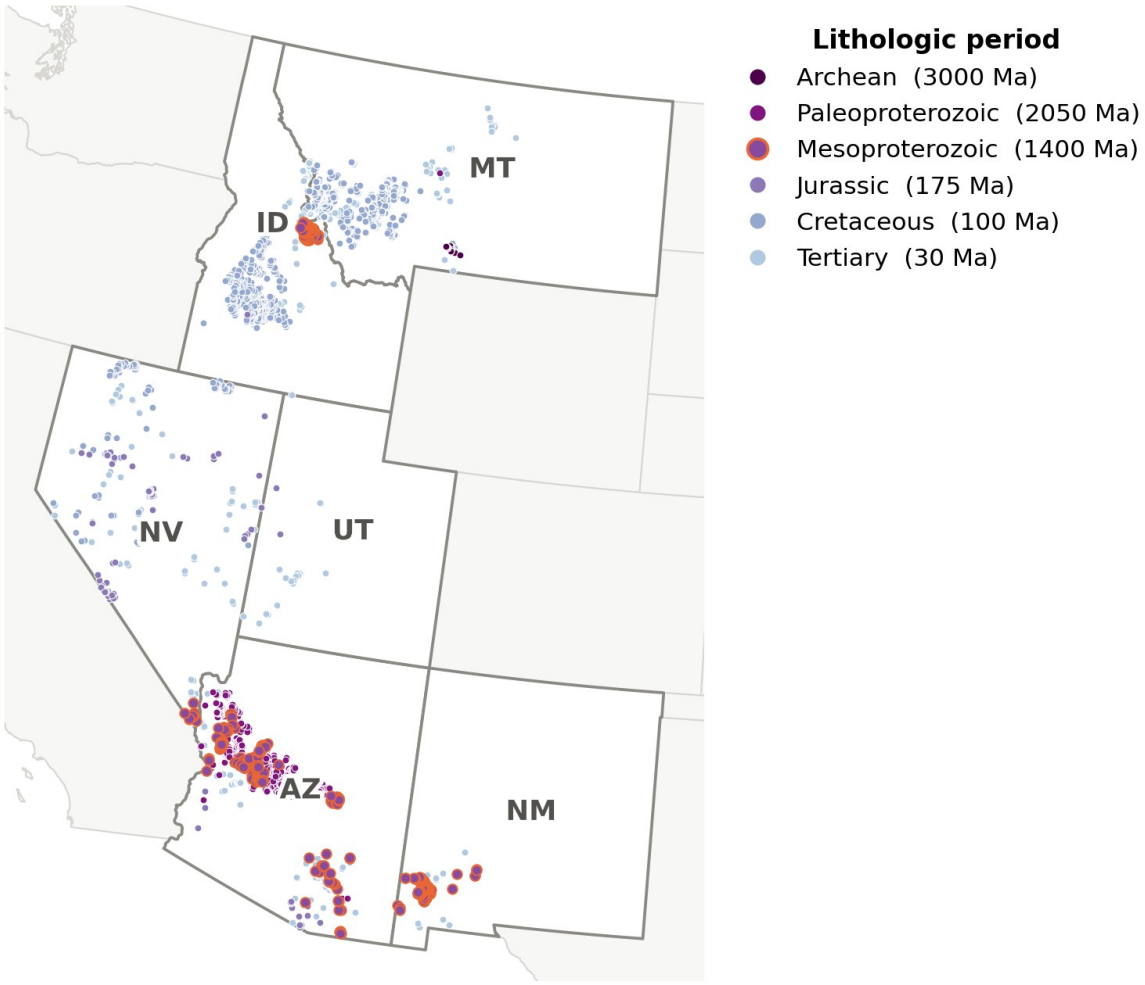
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Figures

All five figures are supplied at 600 dpi raster. Each is regenerated from the analysis rather than from a cached array, and the probabilities displayed upon Figure 3 are those of the source of record.

Fig. 1 Igneous-bearing stream sediment sample sites, colored by lithologic period of the mapped host unit. Albers equal area conic, EPSG 5070. Shading runs light to dark with increasing age of the host unit. Mesoproterozoic samples are drawn larger, ringed, and above the other classes, since they are the subject of the test

Figure 1. Igneous-bearing stream sediment sample sites, colored by lithologic period of the mapped host unit



Albers equal area conic, EPSG 5070. Shaded light to dark with increasing age of the host unit. Mesoproterozoic samples are drawn larger, ringed, and on top, since they are the subject of the test.

Fig. 2 Median and 90th percentile yttrium by lithologic period, igneous-bearing units only. The Archean is the poorest period of all, at a median of 15.95 ppm, which refutes a monotonic increase of yttrium with the age of the host terrain

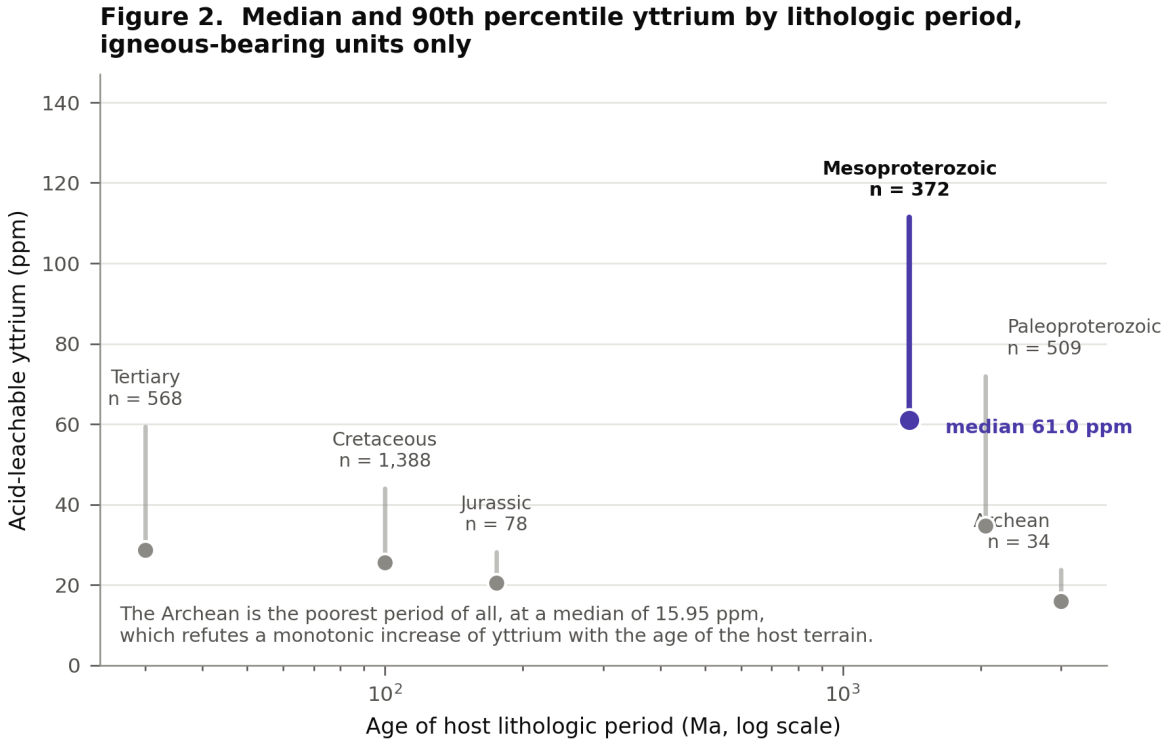


Fig. 3 Blocked permutation null distributions, 20,000 permutations each, with the observed statistic marked. Labels are permuted by 150 kilometer spatial block within state, preserving both the spatial structure and the provincial composition. The dashed line marks the opposite tail used for the two-sided probability. The probabilities shown are those of the source of record, eon_enrichment_v4.R at seed 20260707

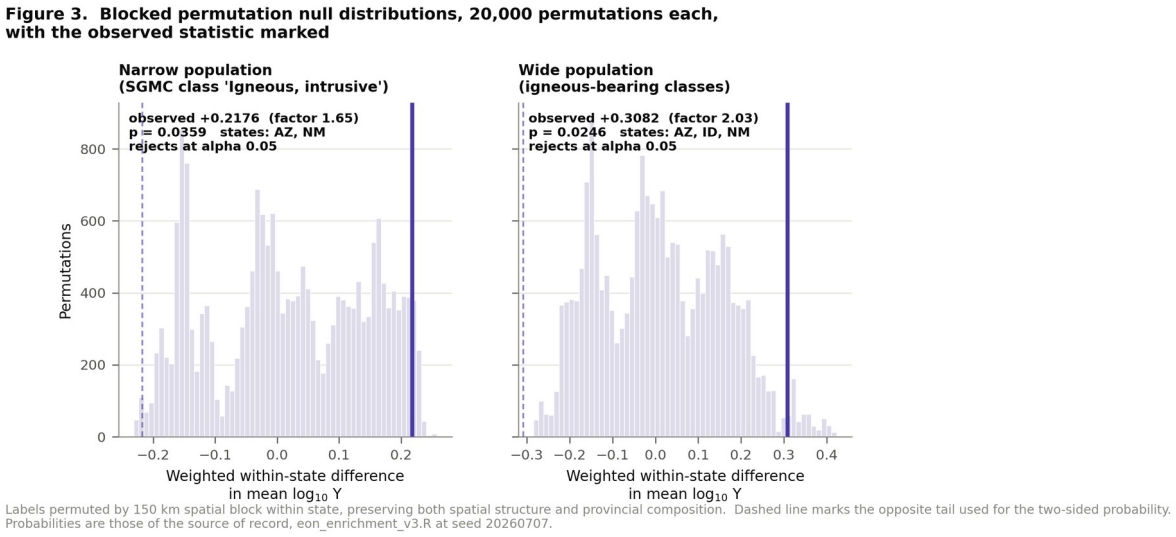


Fig. 4 The Belt Supergroup control, in which Mesoproterozoic age without Mesoproterozoic magmatism shows no yttrium elevation. The control totals 2,072 samples and is flat across all three non-igneous classes

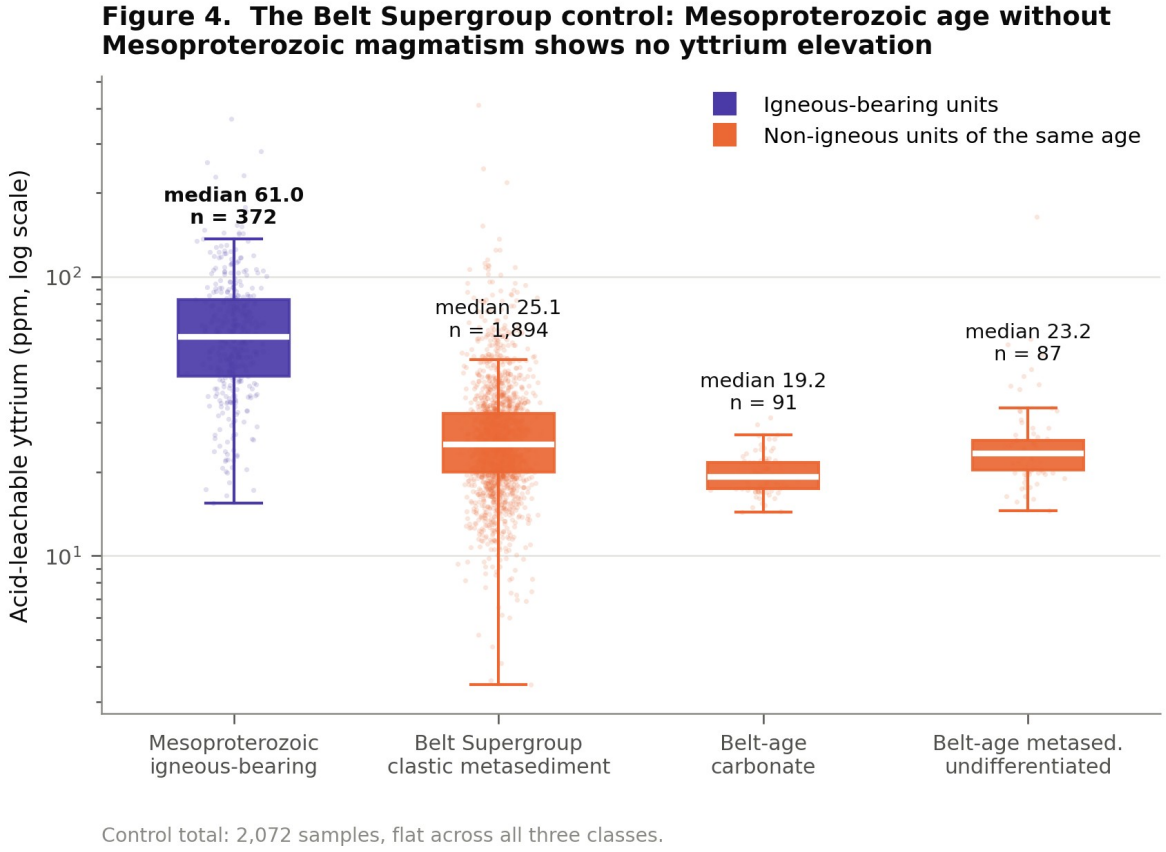
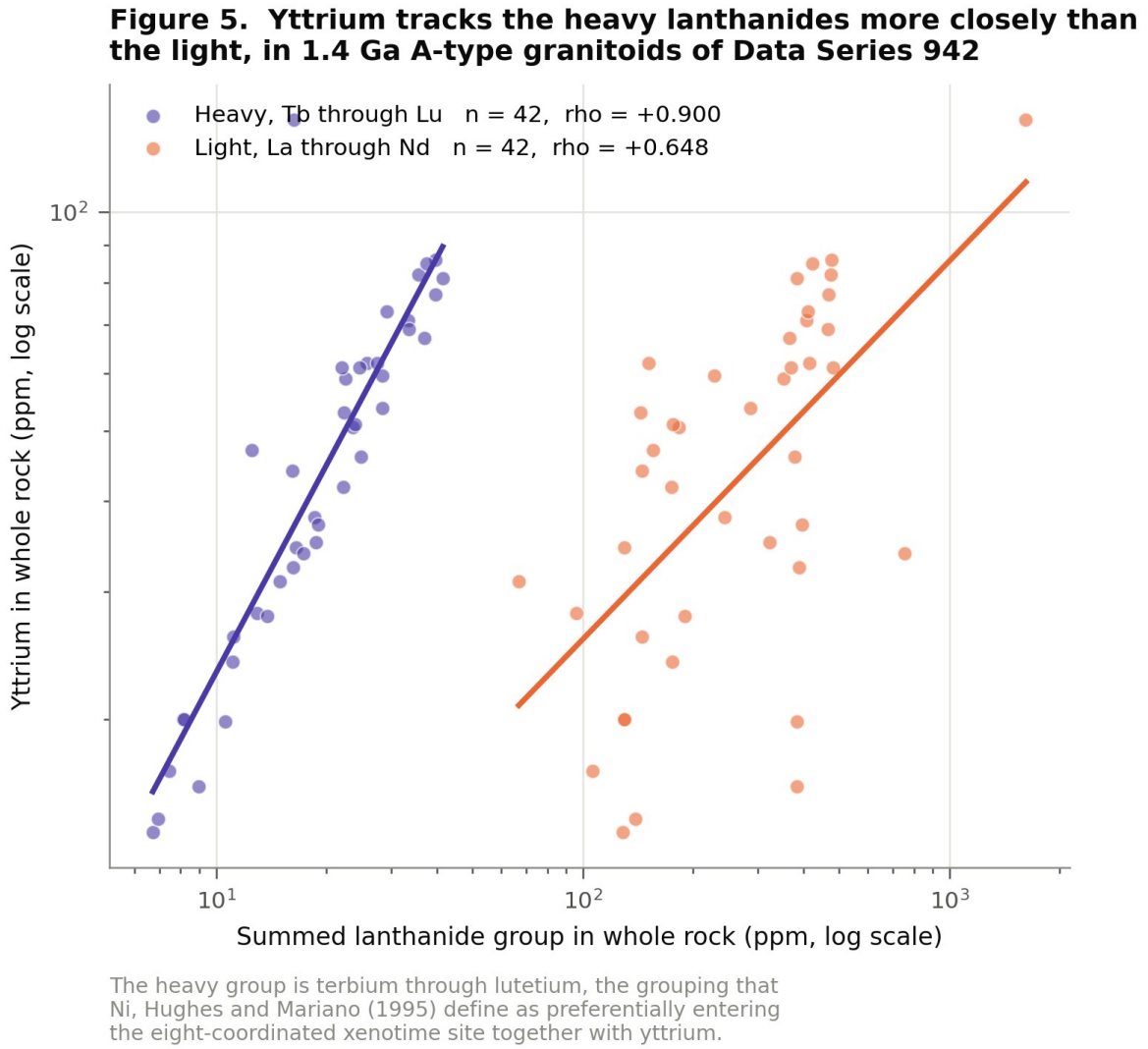


Fig. 5 Yttrium tracks the heavy lanthanides more closely than the light, in 1.4 Ga A-type granitoids of Data Series 942. The heavy group is terbium through lutetium, the grouping that Ni, Hughes, and Mariano (1995) define as preferentially entering the eight-coordinated xenotime site together with yttrium. Both groups are evaluated upon the same 42 samples carrying a complete heavy suite



Note. Magnitude as well as ordered classes utilize the project BuPu ramp truncated at the palest 0.30, which was adopted due to the fact that it remains monotonic in lightness under all three dichromacies and in grayscale print. The two figures requiring categorical rather than ordered color, namely Figures 4 and 5, utilize violet against orange, a pair validated rather than selected by eye, returning all-pairs colorblind separation of 29.5 in protanopia and 37.2 in tritanopia upon the OKLab hundred-point scale, normal vision separation of 37.6, and contrast above 3:1 against white.