

Volcanic-affinity compositional shifts obscure chemical weathering signals in black shales

Wei Tian

davidtian@pku.edu.cn

Peking University <https://orcid.org/0000-0003-4125-4704>

Zhichen Wu

Peking University <https://orcid.org/0009-0001-9053-8909>

Xinping Liang

Peking University <https://orcid.org/0000-0003-0994-9290>

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Volcanic-affinity compositional shifts obscure chemical weathering signals in black shales

Abstract: Major-element weathering proxies underpin deep-time palaeoenvironmental reconstructions, but compositional mixing can decouple index values from source-area alteration. We analyse 1,546 literature-curated black-shale samples using probabilistic Al–Ca–Na–K modelling, compositional diagnostics and grouped out-of-fold evaluation. Chemical index of alteration (CIA) values decline strongly along a model-derived volcanic-affinity exposure ranking (Spearman’s $\rho = -0.703$), while related indices shift coherently towards apparently weaker weathering. Much of this coherence reflects shared Al–Ca–Na–K geometry rather than independent confirmation of weathering change. Compositional exposure and signed departure from the reference-model CIA baseline are coupled but not interchangeable. High exposure does not necessarily imply baseline departure. Across the full cohort, 1,262 of 1,546 samples (81.6%) remain baseline-consistent under the present reference model. An emulator using routine geochemical data recovers the ranking in held-out reference studies ($R^2 = 0.968$). The joint exposure–departure framework guides independent scrutiny of records before coherent major-element signals are interpreted as palaeoweathering change.

Introduction

Silicate weathering links rock–water reactions to long-term atmospheric CO₂ consumption and carbon cycling¹. Major-element records in sedimentary archives therefore underpin reconstructions of source-area alteration, palaeoclimate, and Earth-system change, although translating weathering intensity into flux requires additional hydrological, lithological and spatial constraints². Black shales are particularly informative because they integrate organic-carbon burial, depositional conditions, redox evolution and broader environmental perturbations^{3–8}. Their value for palaeoweathering reconstruction depends, however, on whether bulk sediment composition preserves an alteration signal distinguishable from mixing and post-depositional modification.

The chemical index of alteration (CIA), plagioclase index of alteration (PIA), chemical index of weathering (CIW) and weathering index of Parker (WIP) translate major-

element composition into measures of apparent silicate alteration^{9–13}, commonly interpreted relative to average-shale and upper-crustal compositions^{14–16}. Their compositional limitations are well established. Potassium metasomatism, source lithology and the apportionment of Ca among silicate, carbonate and phosphate hosts can alter index values independently of source-area hydrolysis^{11,17,18}. Drainage-basin tests and reviews question a simple correspondence between index value and weathering intensity^{19,20}, while hydrodynamic sorting, sediment recycling, grain size and lithological variability introduce further ambiguity^{21,22}. Related approaches likewise treat archive composition and inferred alteration as distinct quantities²³. CIA, CIW and PIA also reuse overlapping Al–Ca–Na–K terms, so agreement among them is not independent confirmation of weathering change.

Numerical simulations have examined mineralogical, grain-size and source-lithology biases in weathering indices²⁴, while marine observations document pyroclastic influences²⁵ and ACNK reviews caution against idealised weathering paths and CIA corrections¹⁸. Comparing a continuous model-derived exposure ranking with signed CIA departure from an empirical reference relationship provides a way to assess these ambiguities for individual samples and identify contrasting cases for independent geological review.

Volcanic-affinity material provides a focused test bed for this problem in black shales. It may occur as visible ash beds or their altered equivalents, as glass, crystals or lithic fragments, or as reworked and cryptically dispersed volcanoclastic components^{26–28}. Relatively fresh feldspar- and mafic-silicate-bearing material can displace bulk Al–Ca–Na–K composition towards lower CIA-family values even where no discrete ash bed is recognised²⁵. A basin-scale example has already linked low weathering-index values to independent evidence for drying and increased felsic-volcanic lithic input²⁹. This compositional pathway is distinct from volcanic effects on nutrient supply, runoff, productivity, redox conditions, organic-matter preservation and dilution^{29–32}. These pathways may coexist, but they require different evidence. Throughout, volcanic affinity denotes a model-defined compositional relation rather than a provenance assignment.

Here we develop and evaluate a probabilistic framework that pairs volcanic-affinity compositional exposure with signed CIA departure from an empirical reference baseline

to screen black-shale weathering records. We apply the framework to 1,546 literature-curated black-shale samples. Probabilistic A–CN–K modelling yields posterior $E[f_{volc}]$, a model-derived ranking of volcanic-affinity compositional exposure. A complementary diagnostic, R_{CIA} , records signed, standardised departure from the residual-centred reference-like (M_0) CIA baseline; positive values lie above the baseline and negative values below it. At section scale, we assess mineral-carrier plausibility using Early Permian Lucaogou Formation black shales from the J10025 well on the southern margin of the Junggar Basin, northwestern China. Grouped out-of-fold modelling then tests whether routine geochemical variables can recover the exposure ranking when entire reference studies, formations or basins are withheld.

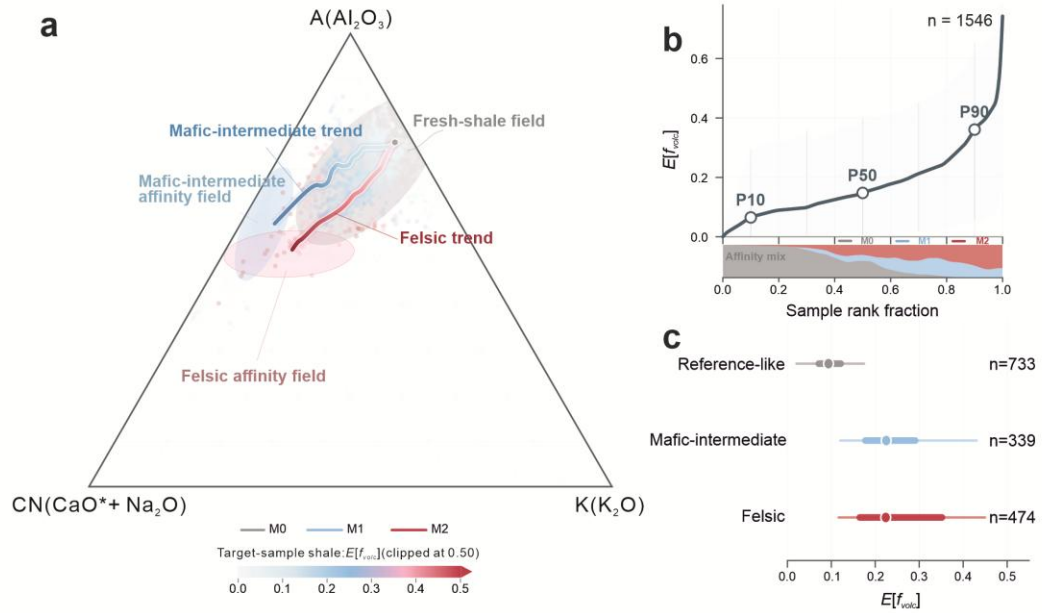
CIA, CIW and PIA decline strongly along the exposure ranking, whereas WIP shifts more weakly towards fresher-silicate compositions. Much of this coherence reflects shared A–CN–K geometry rather than independent confirmation of weaker weathering. Exposure rank and reference-model CIA departure are related but not interchangeable: a higher rank does not determine the sign or magnitude of departure from the residual-centred reference baseline. An emulator based on routine geochemical variables recovers the exposure ranking with high predictive performance in grouped within-cohort tests. The joint representation distinguishes high-exposure records that remain baseline-consistent from lower-exposure records with substantial CIA departure, providing different starting points for independent mineralogical, stratigraphic and provenance review.

Results

Volcanic-affinity compositions define an A–CN–K exposure gradient

The literature-curated cohort comprised 1,546 black-shale samples assigned to three model-defined compositional domains: M_0 /reference-like ($n=733$), M_1 /mafic–intermediate-affinity ($n=339$) and M_2 /felsic-affinity ($n=474$). In A–CN–K space, the samples formed a continuum from the fresh-shale/reference-like field towards the model-defined M_1 and M_2 affinity fields and trends (Fig. 1a). These domains describe compositional affinity within the model; they do not identify verified source populations.

90 Posterior $E[f_{volc}]$ ranks samples continuously by volcanic-affinity compositional
 91 exposure. M_0 /reference-like samples dominated the lower ranks, whereas M_1 and M_2
 92 became progressively more common towards the upper ranks (Fig. 1b). The affinity
 93 classes were not cleanly separated: M_1 and M_2 spanned broad, overlapping score ranges
 94 (Fig. 1c). Values above 0.50 were retained in all analyses and clipped only for display in
 95 Fig. 1a. Supplementary Fig. S1 distinguishes the literature-curated cohort from the
 96 broader compilation. Supplementary Fig. S2 documents the model-support geometry and
 97 sample-level posterior replay.



98
 99 **Fig. 1 | Model-defined A–CN–K compositional setting and exposure ranking.** a, Literature-curated
 100 black-shale samples ($n=1,546$) in closed molar A–CN–K space, where
 101 $A=Al_2O_3$, $CN=CaO^*+Na_2O$, $K=K_2O$, shown relative to the M_0 /reference-like, M_1 /mafic–intermediate-
 102 affinity and M_2 /felsic-affinity domains and trends. Point colour denotes posterior $E[f_{volc}]$; values
 103 above 0.50 are clipped for display. The affinity fields are model-defined compositional domains and
 104 do not establish provenance. b, Posterior values ordered by sample-rank fraction, with P_{10} , P_{50} and
 105 P_{90} and the corresponding affinity-class mixture. c, Posterior distributions for M_0 ($n=733$), M_1
 106 ($n=339$) and M_2 ($n=474$); dots and horizontal marks summarise the distributions.

Weathering proxies vary coherently along the exposure gradient

CIA, CIW and PIA decreased as posterior $E[f_{volc}]$ increased, whereas WIP increased weakly, consistent with greater retention of mobile cations in fresher silicate compositions (Fig. 2a). CIA gave Spearman's $\rho=-0.703$ and a Theil–Sen slope of -5.871 index units per 0.1 exposure. The corresponding responses were stronger for CIW ($\rho=-0.968$; slope = -9.221) and PIA ($\rho=-0.953$; slope = -10.891). WIP showed a weaker positive association ($\rho=+0.215$; slope = $+3.493$; $n=1,512$), compared with $n=1,546$ for CIA, CIW and PIA.

CIA distributions across five equal-count exposure windows shifted progressively towards lower values, and their median departures from the lowest-exposure reference window became increasingly negative (Fig. 2b). These windows describe variation along a compositional-exposure ranking rather than a temporal sequence, climatic trajectory or corrected weathering record. The four responses form a directionally coordinated apparent weaker-weathering signature, but they are structurally non-independent because CIA, CIW and PIA reuse overlapping Al–Ca–Na–K information. Their directions were generally retained across analytical subsets and CIA slope comparisons (Supplementary Fig. S3a,b). An explicit exception is the literature-coded strong-evidence subset ($n=81$): CIA and WIP associations are weak (Spearman's $\rho=-0.161$ and $+0.015$), whereas CIW and PIA remain strongly negative ($\rho=-0.922$ and -0.886). This evidence label is literature-curation metadata, not independently measured volcanic abundance for each sample.

The primary CIA calculation used the no-phosphate-subtraction CaO^* route. Applying phosphate correction before the Na cap retained the negative association ($\rho=-0.682$; bootstrap 95% CI, -0.720 to -0.645 ; Theil–Sen slope = -5.882 per 0.1 exposure). These composition-space tests were available only for the archived phosphate-corrected-first CIA route. In that implementation, the observed CIA–exposure alignment was not unusual relative to 5,000 random directions in centred-log-ratio space ($P=0.3907$). After rank residualisation against the two isometric-log-ratio coordinates, only a small positive association remained ($\rho=+0.156$; 95% CI, $+0.108$ to $+0.198$). These tests do not decompose the exact primary $\rho=-0.703$ association. Together with the sequential controls

in Supplementary Fig. S3c and Supplementary Table 3, these tests indicate that much of the CIA–exposure alignment reflects shared A–CN–K geometry. The geological origin of the small residual remains unresolved.

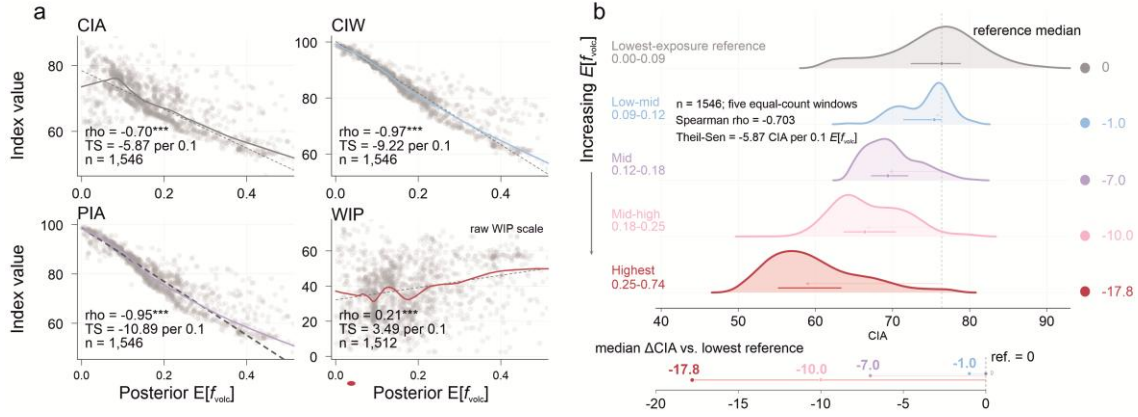


Fig. 2 | Coordinated weathering-index responses along the compositional-exposure ranking. a, CIA, CIW and PIA ($n=1,546$) and WIP ($n=1,512$) versus posterior $E[f_{volc}]$, with Spearman correlations and Theil–Sen slopes per 0.1 exposure. CIA, CIW and PIA show inverse responses, whereas WIP shows a weaker positive response towards fresher-silicate compositions. b, CIA distributions across five equal-count exposure windows. Dots and horizontal bars denote medians and interquartile ranges; the vertical reference marks the lowest-exposure-window median, and annotations show median Δ CIA from that window. The responses are structurally non-independent because the indices share major-element terms. Windows rank samples by exposure and imply no temporal or climatic trajectory or correction to CIA. Coloured curves show smooth trends; dashed lines show Theil–Sen fits. *** $P < 0.001$ (two-sided Spearman rank correlation).

Compositional exposure and reference-model CIA departure are non-equivalent

For each of the 1,546 samples, R_{CIA} records the signed, standardised departure of observed CIA from the residual-centred M_0 /reference-like baseline. Positive values place observed CIA above that baseline, whereas negative values place it below. The baseline-consistent, caution and strong-departure bands are defined solely by $|R_{CIA}|$: $|R_{CIA}| < 2$, $2 \leq |R_{CIA}| < 3$ and $|R_{CIA}| \geq 3$, respectively. Posterior exposure supplies compositional context but does not contribute to the band assignment (Fig. 3a).

The full cohort contained 1,262 baseline-consistent samples (81.6%), 174 caution cases (11.3%) and 110 strong-departure cases (7.1%). Positive and negative departures occurred across the exposure ranking, including among samples with elevated posterior

161 scores. Values extending beyond the displayed R_{CIA} range were retained and plotted as
162 boundary symbols. Higher compositional exposure therefore did not consistently
163 correspond to either a larger-magnitude departure or a more negative R_{CIA} .

164 The signed distributions also differed among the compositional-affinity classes (Fig. 3b).
165 Median R_{CIA} was 0.000 for M_0 , +1.868 for M_1 and -0.442 for M_2 ; the corresponding
166 interquartile ranges were -0.755 to 0.564, 0.881 to 2.705 and -1.001 to 0.156. Although
167 M_1 had the largest departure share, 55.5% of its samples remained baseline-consistent,
168 and its median departure was positive rather than negative. Figure 3b displays the R_{CIA} -
169 defined departure-state shares for each affinity class; posterior exposure is retained as
170 continuous compositional context and does not enter departure-band assignment.
171 Exposure and departure are compositionally coupled but not interchangeable. A baseline-
172 consistent classification means that the present reference model flagged no substantial
173 departure; it does not validate a climatic interpretation. Supplementary Fig. S4a,b
174 documents baseline construction and signed standardisation, Supplementary Fig. S4c
175 provides the affinity-stratified detail, and Supplementary Fig. S4d reports threshold and
176 baseline-fitting robustness.

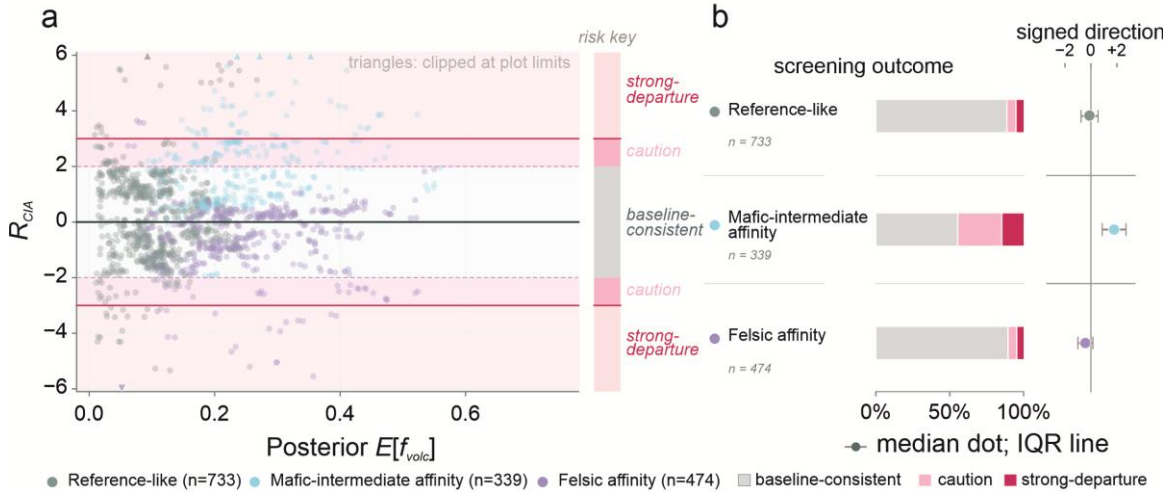


Fig. 3 | Compositional exposure and reference-model CIA departure are non-equivalent. a, Posterior $E[f_{volc}]$ versus R_{CIA} for the literature-curated cohort ($n=1,546$), coloured by affinity class. R_{CIA} is signed, standardised departure from the residual-centred M_0 /reference-like CIA baseline; signs indicate above- or below-baseline values. Bands denote baseline-consistent ($|R_{CIA}| < 2$), caution ($2 \leq |R_{CIA}| < 3$) and strong-departure ($|R_{CIA}| \geq 3$) states; triangles mark observations clipped only for display. b, State shares and signed R_{CIA} medians and interquartile ranges for M_0 , M_1 and M_2 . Departure states are defined by $|R_{CIA}|$ alone.

J10025 observations support plausible mineral carriers

The J10025 section contains local mineral assemblages compatible with feldspar- and mafic-silicate carriers of A–CN–K displacement. Depth profiles place the selected samples within their section-scale total organic carbon (TOC) and mineralogical context (Fig. 4a). Quantitative X-ray diffraction (XRD) compositions include substantial feldspar contributions (Fig. 4b). The feldspar–mafic mineral index, VMI_{XRD} , is the reported sum of plagioclase, K-feldspar, pyroxene and amphibole; it reached 47.4% in J10025-164, 44.0% in J10025-32, 34.6% in J10025-26 and 31.5% in J10025-23.

Targeted scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM–EDS) analyses identified feldspar-like, Ti–Fe/mafic and Ca-phosphate point-chemistry classes together with carbonate, Fe-sulfide, mixed and quartz/silica classes (Fig. 4c). The compatible-point counts record occurrences at the targeted analytical sites. Representative backscattered-electron images show analysed feldspar-like sites and associated Ti–Fe–Mn accessory material, carbonate, quartz/silica and Fe-sulfide microtextures in J10025-26, J10025-32, J10025-57 and J10025-36, respectively (Fig. 4d–

g; Supplementary Table 5). Ca-phosphate points additionally document a non-silicate Ca-bearing component relevant to CaO* handling. Because the EDS locations were targeted, these observations are non-modal and provide local, section-scale carrier plausibility rather than a quantitative calibration of the cohort-wide posterior ranking.

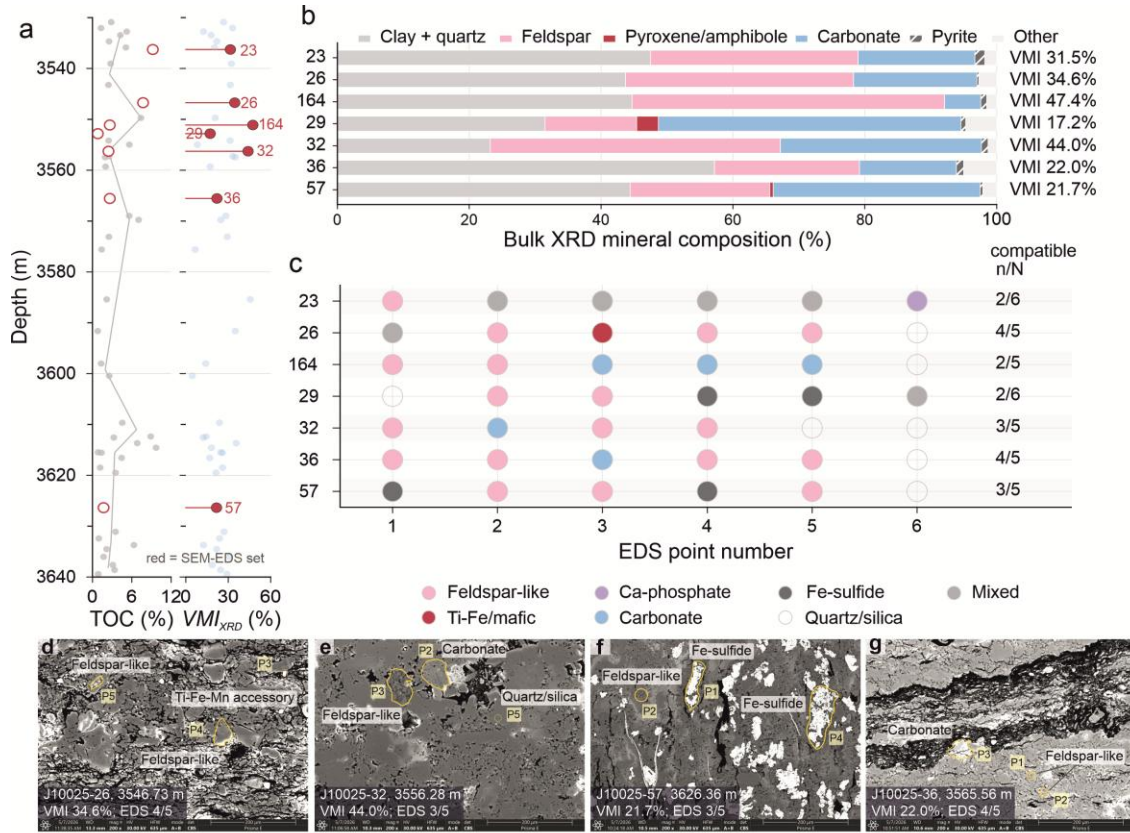


Fig. 4 | J10025 observations support section-scale mineral-carrier plausibility. a, TOC and VMI_{XRD} depth profiles; red symbols mark SEM-EDS samples. b, XRD phase-group compositions and VMI_{XRD} for seven samples. c, SEM-EDS point-chemistry classes and compatible-point counts (n/N). d–g, Backscattered-electron images and sites for J10025-26, -32, -57 and -36. VMI_{XRD} sums plagioclase, K-feldspar, pyroxene and amphibole. TOC, XRD and SEM-EDS denote total organic carbon, X-ray diffraction and scanning electron microscopy–energy-dispersive X-ray spectroscopy. Targeted non-modal counts document local occurrence, not abundance, provenance or posterior calibration.

Routine geochemical data recover the exposure ranking

An eight-feature ExtraTrees emulator recovered posterior $E[f_{volc}]$ under five-fold, within-cohort grouped out-of-fold (OOF) evaluation (Fig. 5a,b). With complete reference studies

held out, pooled performance was $R^2 = 0.968$, root-mean-square error (RMSE) = 0.020 and rank $\rho=0.990$; ($n=1,546$). Holding out complete formations or basins gave similar pooled R^2 values of 0.966 and 0.967, respectively. The three designs comprised 42 reference-study, 40 formation and 56 basin groups, with each group confined to a single fold.

The reference-study OOF predictions followed the model-derived ranking across most of its range (Fig. 5b). Median residuals became increasingly negative in the sparsely populated upper tail, indicating increasing underprediction of the highest posterior scores. The same pattern occurred under formation and basin grouping (Supplementary Fig. S6a). Model and feature-set comparisons provided context for this recoverability (Fig. 5c). The selected eight-feature set gave $R^2 = 0.968$, compared with 0.963 for A–CN–K plus CIA and 0.949 for the weathering-indices-only set. CIA-only Ridge and ExtraTrees models gave $R^2 = 0.460$ and 0.438, respectively. The contrast was therefore primarily between single-index and multivariate representations rather than among the highest-performing multivariate implementations.

For operational triage, an archived posterior score of 0.25 defined the reference high-score set, and the same value applied to OOF predictions defined screen-positive samples (Fig. 5d). This operating point gave precision = 0.936, recall/capture = 0.968, specificity = 0.983 and $F_1 = 0.952$ while flagging 21.1% of the cohort. Capture denotes recall of samples above the archived posterior-score operating point. The value 0.25 is an operational score threshold for this within-cohort screen, not a geological boundary or material-abundance threshold.

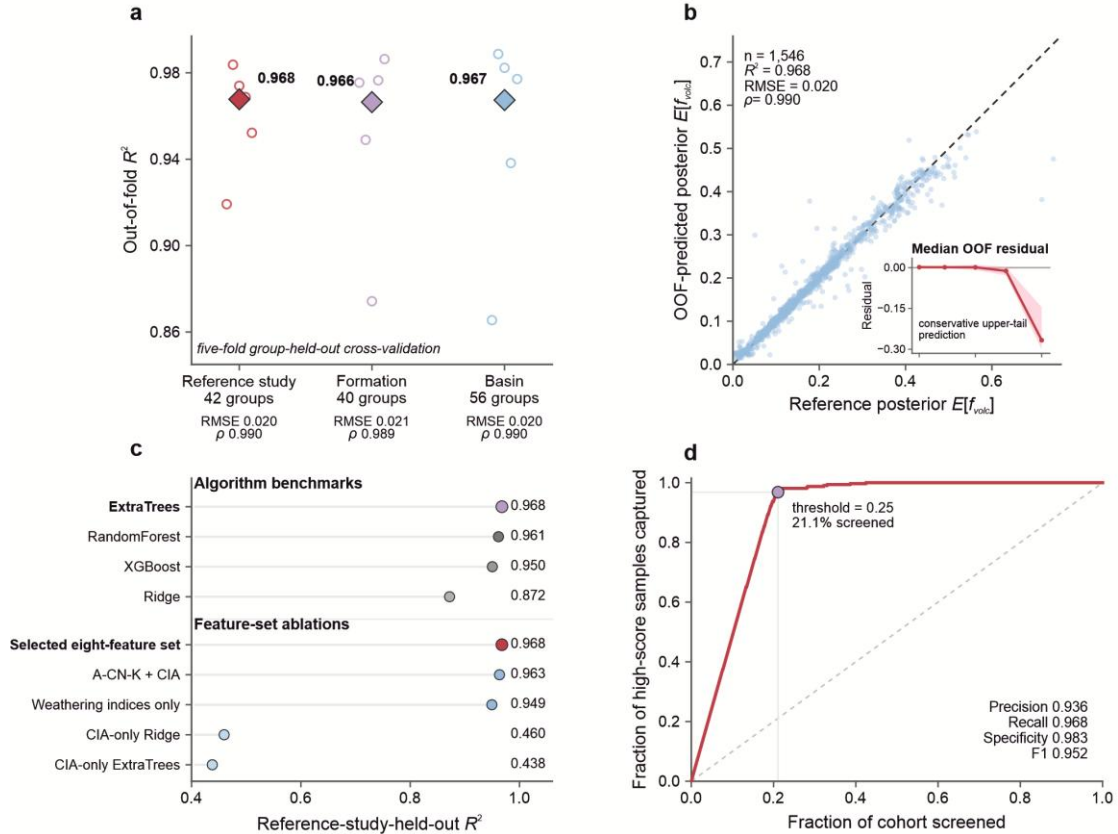


Fig. 5 | Grouped out-of-fold recovery and operational exposure triage. a, Pooled (diamonds) and fold-level (open circles) performance for five-fold ExtraTrees models grouped by reference study, formation or basin; all values are within-cohort grouped-OOF estimates. b, Archived posterior $E[f_{volc}]$ versus reference-study-grouped OOF prediction ($n=1,546$), with the 1:1 line and median residuals (prediction minus reference) across score ranges. c, Algorithm benchmarks and feature-set ablations on the same folds. d, Cumulative capture of archived high-score samples along the OOF-predicted ranking. Capture denotes recall above the archived posterior operating point of 0.25; displayed metrics also include the flagged cohort share, precision, specificity and F_1 . The 0.25 threshold is a fixed, study-specific operating point, not a geological boundary (Methods).

The emulator relies on stable, shared geochemical structure

Reference-study-grouped OOF Shapley additive explanations (SHAP) attributions were concentrated in CIW, PIA and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (Fig. 6a). When pooled by feature family, weathering indices accounted for 75.1% of mean absolute attribution, oxide-to-Al ratios for 16.0% and the A-CN-K coordinate for 8.9% (Fig. 6b). These proportions summarise fitted-model reliance within the selected correlated predictor set.

Feature ordering was stable across the five reference-study OOF folds. The median pairwise Spearman rank correlation was $\rho=0.952$, and the top-five overlap was 5/5 (Fig. 6c). Every pairwise fold correlation was positive; the heatmap colour scale encodes correlation magnitude over 0.85–1.00 rather than correlation sign. The ordering of the leading features was also retained under formation and basin grouping (Supplementary Fig. S6b), while Supplementary Fig. S6c compares the full-data-refit and reference-study OOF ranks and Supplementary Fig. S6d shows fold-level family contributions. Because the target ranking and its predictors share major-element compositional structure, the prominence of CIA-family variables is expected. SHAP describes model attribution within the correlated predictor set; it does not establish causality or independent volcanic evidence.

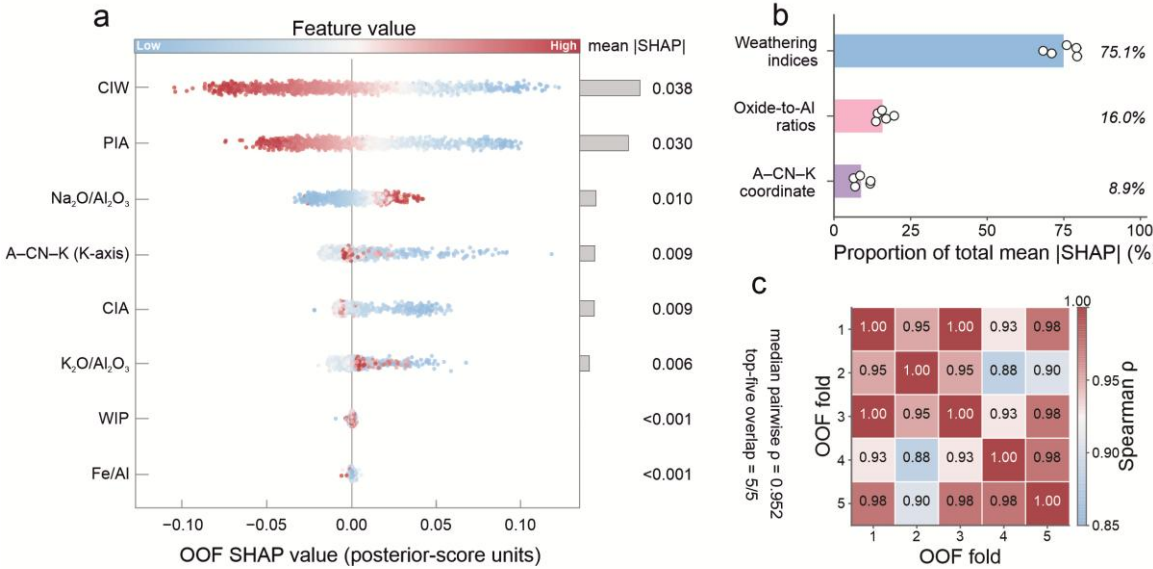


Fig. 6 | Grouped-OOF model attribution and fold stability. a, Reference-study-grouped OOF Shapley additive explanations (SHAP) distributions for eight emulator features, coloured by feature value; right-hand bars show pooled mean absolute attribution. b, Total mean absolute SHAP shares for weathering indices, oxide-to-Al ratios and the A–CN–K coordinate; open circles show fold-level estimates. c, Pairwise Spearman correlations of feature ranks across five OOF folds. All correlations are positive; the blue–red scale maps magnitude over 0.85–1.00, not sign. SHAP describes fitted-model attribution conditional on correlated predictors, not causal or independent volcanic evidence.

Discussion

From known compositional sensitivity to diagnosable interpretive vulnerability

Compositional sensitivity of CIA-family indices to parent material, K metasomatism, Ca-host assignment, sediment recycling, hydrodynamic sorting and grain size is well established^{11,17–23}. The heterogeneous black-shale cohort displays the same susceptibility. Along a continuous volcanic-affinity exposure ranking, CIA, CIW and PIA decline concordantly, while WIP shifts more weakly towards fresher-silicate compositions. Fu et al.²⁴ used numerical simulations to assess compositional biases, and Somelar et al.²⁵ documented pyroclastic effects in marine sediments. These simulations and observations, together with cautions against idealised ACNK weathering paths¹⁸, motivate our joint assessment of continuous exposure and empirical-reference departure across a targeted, cross-study cohort.

Compositional exposure and reference-model CIA departure must be distinguished. A sample can occupy a compositionally vulnerable part of the A–CN–K continuum while retaining CIA close to the residual-centred reference-like baseline; conversely, a pronounced CIA departure can occur at relatively low modelled exposure. This non-equivalence means that volcanic-affinity composition alone neither invalidates nor validates a weathering interpretation. The contrasting cases in Fig. 3 and Table 1 guide independent geological review. These model-defined categories do not establish whether a sample preserves a reliable weathering signal.

Why coordinated proxy behaviour does not resolve the ambiguity

The coordinated response follows the geochemical construction of the indices. CIA, CIW and PIA share Al, Ca and Na terms, with CIA and PIA additionally responding to K, whereas WIP increases with retention of mobile alkali and alkaline-earth cations in fresher silicates^{9,11–13,18}. Addition of Ca–Na-bearing feldspar or mafic silicates can therefore lower the three CIA-family indices while increasing WIP. The weaker WIP association is consistent with its different formulation and additional dependence on Mg, but its direction remains compatible with the same fresh-silicate displacement. In this cohort, cross-index agreement can therefore reflect a common compositional shift rather than independent replication of a climatic signal.

Composition-aware tests constrain how far this inference can be taken. Phosphate correction before the Na cap preserved the negative CIA–exposure relation, indicating that alternative handling of apatite-associated Ca does not reverse the observed direction. In the archived phosphate-corrected-first implementation, however, the CIA–exposure alignment was not unusual relative to 5,000 random directions in centred-log-ratio space ($P=0.3907$). After rank residualisation against the two isometric-log-ratio coordinates, only a small positive association remained ($\rho=+0.156$, 95% confidence interval $+0.108$ to $+0.198$). Much of the strong raw alignment is therefore embedded in the closed A–CN–K geometry shared by the proxy and the exposure model. The small residual could reflect incomplete removal of nonlinear compositional dependence, uncertainty in Ca-host allocation and phosphate correction, unmeasured mineralogical heterogeneity, or between-study analytical and preprocessing differences. Weak covariation between source-area weathering and source composition also cannot be excluded. Matched quantitative mineralogy and bulk chemistry, harmonised preprocessing and more flexible conditional models are needed to distinguish these possibilities. Until then, no unique geological cause can be assigned to the residual.

This ambiguity extends beyond volcanic-affinity displacement. K metasomatism, source lithology, Ca-host assignment, recycling, sorting and diagenesis can generate related changes in bulk major-element chemistry^{11,17–23}. Volcanic material can also enter a basin through primary fallout, reworking or cryptically dispersed detritus^{26–28}, so the absence of a visible ash bed does not eliminate the compositional pathway. The appropriate conclusion is therefore that a weathering-only interpretation becomes non-unique, rather than that the climatic component has been shown to be false.

Fidelity before intensity

Posterior $E[f_{volc}]$ and R_{CIA} answer complementary questions. The posterior ranks compositional susceptibility along the model-defined volcanic-affinity continuum. R_{CIA} records how far observed CIA lies above or below the residual-centred M_0 /reference-like baseline. Their functions differ, but both are derived from overlapping major-element structure and should not be treated as independent or orthogonal evidence.

Departure states are defined by $|R_{CIA}|$. Posterior exposure provides the complementary susceptibility ranking. A baseline-consistent sample has no large departure flagged under the current reference model; this does not validate a climatic signal. A strong negative departure identifies CIA below the residual-centred reference expectation but does not by itself specify volcanic input. A positive departure at elevated exposure remains compatible with alteration, clay enrichment or source-composition effects. The framework therefore identifies where independent evidence is most needed before a weathering interpretation is accepted.

The sequence matters for Earth-system inference. Compositional fidelity precedes estimation of source-area weathering intensity; weathering flux then requires hydrology, lithology, reactive area and other system properties, and carbon-cycle interpretation requires explicit connections between those fluxes and CO_2 consumption or burial². Ambiguity introduced at the archive-composition stage can propagate through each downstream step. The framework addresses that first transition by flagging model-defined compositional ambiguity for independent assessment before a major-element signal is converted into weathering intensity, flux or carbon-cycle consequences.

Table 1 | Reading compositional-exposure context with the R_{CIA} departure band for pre-interpretation triage.

Compositional-exposure context	Signed CIA-baseline departure	Diagnostic reading	Recommended use
Lower exposure context	Baseline-consistent	No large CIA departure is flagged under the present reference model; other controls remain unresolved.	Proceed only after routine checks of source lithology, sorting, K metasomatism, diagenesis and Ca-host assignment.
Lower exposure context	Strong negative departure	CIA lies below the baseline without elevated exposure context.	Evaluate Ca hosts, sorting, alteration, source lithology and analytical uncertainty.
Higher exposure context	Baseline-consistent	Compositional susceptibility is elevated but no large reference-model CIA departure is flagged.	Retain for contextual review and seek independent mineralogical, stratigraphic and provenance evidence.
Higher exposure context	Strong negative departure	Elevated compositional vulnerability coincides with CIA below the residual-centred reference-like baseline.	Do not interpret CIA in isolation; prioritise independent supporting evidence.
Higher exposure context	Strong positive departure	CIA lies above the baseline despite elevated compositional exposure.	Evaluate alteration, clay enrichment, source composition and other non-unique controls.

Operational screening, geological evidence and scope

When full probabilistic modelling is impractical, the emulator offers an operational screen. Similar grouped out-of-fold performance under reference-study, formation and basin partitions indicates that routine multivariate geochemistry can recover the exposure ranking across groups omitted from fitting. The archived value of 0.25 was applied unchanged to both posterior scores and out-of-fold predictions in this comparison, although its original selection rationale cannot be established from the available historical record. In this cohort, it flagged 21.1% of samples while capturing 96.8% of archived high-score cases, illustrating the trade-off between review burden and capture. It is a study-specific operating point, not a geological boundary or a universal optimum. Independent external cohorts are needed to test transfer and recalibrate the operating point beyond the curated data domain.

Weathering indices dominate SHAP attribution because the target and predictors share major-element structure. Stable fold rankings show that this model reliance is reproducible across group partitions, but they are not an external geological test. The emulator therefore translates an existing compositional ranking into a routine-data screen; provenance and causality must be assessed with independent geological evidence.

J10025 provides a section-scale test of the proposed mineral-carrier mechanism. Its XRD assemblages and targeted SEM–EDS classes show that feldspar- and mafic-silicate-compatible phases occur in an organic-rich shale succession. The targeted point counts are non-modal; they document carrier occurrence and do not calibrate the compilation-wide posterior ranking or R_{CIA} values. This local evidence is important because it links the proposed compositional displacement to observed mineral hosts. Broader validation will require paired quantitative mineralogy and bulk geochemistry across multiple basins and exposure ranks. The 1,546 samples likewise form a targeted analytical cohort rather than a prevalence sample. The M_0 – M_2 supports and M_0 baseline require domain checks before application to unusual lithologies, intense diagenesis or strongly altered ash.

Volcanism may also affect black-shale deposition through nutrient delivery, productivity, redox change, preservation and dilution^{29–38}. These depositional pathways lie outside the core compositional-fidelity framework; the supplementary OSI-conditioned TOC

analysis is retained only as contextual evidence and remains separate from the R_{CIA} fidelity screen.

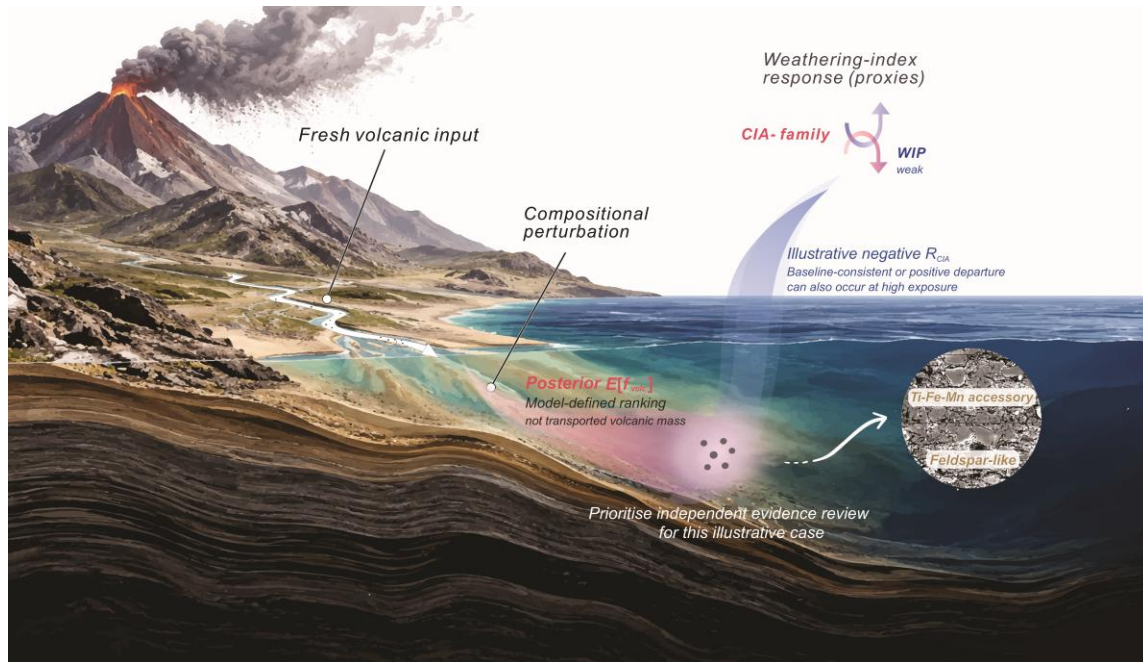


Fig. 7 | Conceptual synthesis of compositional overprinting and proxy-fidelity assessment. Feldspar- and mafic-silicate-bearing volcanic-affinity inputs can shift bulk A–CN–K composition, lower CIA-family indices and weakly increase WIP towards fresher-silicate compositions. Posterior $E[f_{volc}]$ ranks model-defined exposure; R_{CIA} records signed departure from the residual-centred M_0 /reference-like CIA baseline, whose sign and magnitude are not determined by exposure. Together, they identify records that require independent mineralogical, stratigraphic and provenance assessment. The negative-departure route is illustrative: baseline-consistent and positive departures can also occur at elevated exposure.

The geological interpretation can be tested against independent evidence. Interpreting a high exposure score as volcanic-affinity input predicts compatible mineralogical, stratigraphic or provenance evidence. Where those lines of evidence are absent, alternative sources of compositional displacement should be considered, although the model-defined compositional exposure remains. Strong R_{CIA} departure without elevated exposure likewise directs testing towards Ca hosts, sorting, alteration, source lithology and analytical uncertainty. Figure 7 summarises these parallel diagnostic routes: exposure identifies susceptibility, departure records the signed reference-model deviation, and

independent evidence adjudicates geological interpretation. Proxy fidelity should therefore be assessed before weathering intensity is inferred.

Conclusions

Across 1,546 literature-curated black-shale samples, volcanic-affinity compositions define a continuous A–CN–K exposure gradient. Along this gradient, CIA, CIW and PIA decrease strongly, whereas WIP changes more weakly in the direction expected for fresher silicate compositions. Composition-space diagnostics show that much of this coherence reflects shared A–CN–K geometry, so agreement among related indices is not independent confirmation of source-area alteration. Posterior $E[f_{volc}]$ and R_{CIA} distinguish compositional susceptibility from signed CIA departure from the residual-centred empirical reference baseline. High exposure does not determine the sign or magnitude of reference-model departure. Across the full cohort, 1,262 of 1,546 samples (81.6%) remain baseline-consistent under the reference model. Mineralogical observations from J10025 provide section-scale support for plausible feldspar and mafic-silicate carriers of A–CN–K displacement. An eight-feature emulator recovers the exposure ranking in grouped within-cohort tests that withhold entire reference studies, formations or basins ($R^2 = 0.966\text{--}0.968$), allowing the model-derived ranking to be estimated from routine geochemical data. The framework does not correct CIA or assign volcanic provenance; it identifies where independent mineralogical, stratigraphic and provenance evidence is most needed before coherent major-element signals are translated into palaeoweathering intensity, flux or Earth-system consequences.

Methods

Data architecture, cohort definition and analytical populations

The data architecture comprised two parallel layers. The broad compilation contained 56,915 database rows representing 56,659 unique sample identifiers, including 26,522 records with the major elements required for A–CN–K coordinates. It combined black-shale records, volcanic-ash and igneous references, standard shale endmembers and records from the Deep-Time Marine Sedimentary Element Database³⁹. Separately, a 1,546-sample black-shale cohort was assembled by manual, literature-guided selection of

published studies and stratigraphic intervals reporting or interpreting volcanic, volcaniclastic or volcanic-ash influence; reference-like samples from the same sources were retained for comparison. The cohort was not obtained by numerical filtering of the broad compilation or by posterior or best-model selection. It comprised 733 M_0 /reference-like, 339 M_1 /mafic–intermediate-affinity and 474 M_2 /felsic-affinity samples. These labels were assigned by the model component with the largest posterior probability; they are model classes rather than manual provenance labels. Study- and interval-level evidence does not establish volcanic provenance for every sample, and the cohort is a targeted analytical population rather than a global prevalence sample.

Oxide data were harmonised to wt% where source reporting permitted a traceable conversion. Each analysis retained samples with valid required inputs and, where applicable, the grouping metadata required by its design; denominators were therefore analysis-specific rather than products of a single exclusion cascade. WIP additionally required MgO. Detailed eligibility rules, fields, quality-control metadata and analysis membership are provided in Supplementary Note 1, Supplementary Table 1 and Supplementary Data 1–3.

Major-element conversion, CaO^* routes and weathering indices

Weathering indices were calculated from oxide-molar abundances. For each oxide,

$$m_i = \frac{w_i}{M_i},$$

where concentration is expressed in wt% (g per 100 g of sample) and molar mass in g mol^{-1} . The primary route capped silicate Ca without phosphate subtraction:

$$m_{\text{CaO}^*} = \min(m_{\text{CaO}}, m_{\text{Na}_2\text{O}}).$$

This CaO^* term was used in A–CN–K coordinates and in CIA, CIW, PIA and WIP:

$$\text{CIA} = 100 \frac{m_{\text{Al}_2\text{O}_3}}{m_{\text{Al}_2\text{O}_3} + m_{\text{CaO}^*} + m_{\text{Na}_2\text{O}} + m_{\text{K}_2\text{O}}},$$

following Nesbitt and Young⁹;

$$\text{CIW} = 100 \frac{m_{\text{Al}_2\text{O}_3}}{m_{\text{Al}_2\text{O}_3} + m_{\text{CaO}^*} + m_{\text{Na}_2\text{O}}},$$

following Harnois¹²;

$$PIA=100\frac{m_{Al_2O_3}-m_{K_2O}}{m_{Al_2O_3}+m_{CaO^*}+m_{Na_2O}-m_{K_2O}},$$

following Fedo et al.¹¹; and

$$WIP=100[\frac{2m_{Na_2O}}{0.35}+\frac{m_{MgO}}{0.90}+\frac{2m_{K_2O}}{0.25}+\frac{m_{CaO^*}}{0.70}],$$

using the Parker coefficients¹³. WIP therefore includes MgO and uses capped CaO*, rather than uncapped total CaO.

A separate phosphate-corrected-first sensitivity subtracted apatite-associated Ca before applying the Na cap:

$$m_{CaO,P}=\max[m_{CaO}-\frac{10}{3}m_{P_2O_5},0],$$

$$m_{CaO^*,P}=\min(m_{CaO,P},m_{Na_2O}).$$

This route was evaluated separately from the primary no-phosphate-subtraction calculation. Exact molar masses, missing-phosphate handling and the high-Ca, high-phosphate, uncapped-Ca and loss-on-ignition boundary tests are documented in Supplementary Note 1 and Supplementary Table 3.

Probabilistic A–CN–K compositional-exposure model

A–CN–K compositions were defined in molar space as

$$A=Al_2O_3, \quad CN=CaO^*+Na_2O, \quad K=K_2O$$

and closed to unit sum before transformation to two orthonormal isometric log-ratio coordinates^{40–42}. The exact basis was:

$$z_1=\sqrt{\frac{1}{2}}\ln\left(\frac{A}{CN}\right)$$

$$z_2=\sqrt{\frac{2}{3}}\ln\left(\frac{\sqrt{A\cdot CN}}{K}\right).$$

Posterior inference used frozen support arrays containing 2,219 M_0 /reference-like, 112,587 M_1 /mafic–intermediate-affinity and 49,788 M_2 /felsic-affinity records. The three components were specified from reference libraries before the cohort was scored, rather than learned by clustering the 1,546 samples. Reference-like shale compositions defined the zero-exposure endpoint; basalt, basaltic andesite and andesite supplied the mafic–

intermediate reference arm; and dacite and rhyolite supplied the felsic reference arm. Reference-library membership was then subjected to A–CN–K validity checks and robust compositional cleaning, with full rules and audit counts reported in Supplementary Note 2 and Supplementary Table 2. M_0 represented the reference-like zero-exposure component, whereas M_1 and M_2 represented the mafic–intermediate- and felsic-affinity components. Their shared endpoint anchored $f=0$ and did not define an additional source population.

For each sample, a KD-tree identified the 360 nearest simulated compositions in ilr space, and Gaussian weights downweighted more distant neighbours. The archived specification used 180,000 draws per model with random seed 20260427; bandwidth was defined by the median distance to the 360th neighbour across the historical 44,558 A–CN–K-valid scoring rows, with a floor of 0.05. M_0 contributed a point mass at $f=0$, whereas M_1 and M_2 used a Uniform(0,1) model-coordinate prior. Endmember modelling followed the compositional framework of Weltje⁴³; the prior, Gaussian-kernel likelihood and model-averaged local expectation were custom components. Realised bandwidths and the remaining implementation details are given in Supplementary Table 2. For each model and neighbour,

$$w_i = \exp\left[-\frac{1}{2}\left(\frac{d_i}{b_m}\right)^2\right]$$

$$L_m = \max\left[k^{-1} \sum_i w_i, 10^{-300}\right]$$

$$P_m = \frac{L_m}{\sum_j L_j}$$

$$E[f_{volc}] = P_1 \mu_1 + P_2 \mu_2$$

$$\hat{m} = \operatorname{argmax}_{m \in \{0,1,2\}} P_m.$$

Here, the local mean within each affinity component was Gaussian-weighted. No additional kernel-normalisation factor was applied, the three components had equal implicit weights of $\frac{1}{3}$, and the M_0 contribution to the posterior expectation was fixed at zero.

Posterior $E[f_{volc}]$ is the expectation of this model coordinate and is used only as a model-derived ranking of volcanic-affinity compositional exposure; it is not volcanic abundance, a direct mass fraction or a provenance assignment. Its empirical reference domains and model weights do not provide calibrated geological probabilities.

The supplied frozen support arrays and fixed inference specification reproduce the cohort posterior, but their upstream construction cannot be regenerated from the archived precursor material. The frozen arrays therefore define the bounded reproducibility starting point; cleaner, support-lineage, bandwidth, local-quantile and replay audits are reported in Supplementary Note 2, Supplementary Table 2 and Supplementary Data 2. Stored medians and interval limits are probability-weighted summaries of local M_1/M_2 quantiles; they are not full-mixture posterior quantiles and do not imply 95% posterior coverage.

Signed CIA departure from the M_0 /reference-like baseline

R_{CIA} quantifies signed, robustly standardised departure of observed CIA from a residual-centred M_0 /reference-like baseline. Principal component analysis was fitted only to the 733 M_0 samples after mean-centring their two ilr coordinates without variance standardisation. The first component explained 87.994231% of M_0 variance and defined the reference coordinate onto which all 1,546 samples were projected:

$$x = (z - \text{centre}) \cdot \text{loading}.$$

CIA was fitted against this coordinate by robust LOWESS with fraction 0.35 and three robustness iterations. Values outside the training range used constant nearest-endpoint extrapolation. The fitted LOWESS curve is an empirical relationship, not a universal ideal weathering path¹⁸. For each sample,

$$r_i = CIA_{obs,i} - \widehat{CIA}_{LOWESS}(x_i),$$

With MAD denoting the median absolute deviation of the M_0 residuals, the residual centre and robust scale are

$$c_0 = \text{median}(r_{M_0}), s_0 = 1.4826 \times \text{MAD}(r_{M_0}).$$

$$R_{CIA,i} = \frac{r_i - c_0}{s_0}.$$

Equivalently, the residual-centred reference baseline and signed departure are

$$\widehat{CIA}_{ref}(x) = \widehat{CIA}_{LOWESS}(x) + c_0 R_{CIA,i} = \frac{CIA_{obs,i} - \widehat{CIA}_{ref}(x_i)}{s_0}.$$

Positive R_{CIA} places observed CIA above this residual-centred reference baseline, whereas negative R_{CIA} places it below. Departure states were baseline-consistent for $|R_{CIA}| < 2$, caution for $2 \leq |R_{CIA}| < 3$ and strong-departure for $|R_{CIA}| \geq 3$. Posterior exposure does not enter band assignment, and R_{CIA} is not a corrected CIA value. PCA constants, endpoint handling and robustness audits are given in Supplementary Note 3, Supplementary Fig. S4, Supplementary Table 3 and Supplementary Data 3.

Statistical Analyses

Weathering-index behaviour along posterior $E[f_{volc}]$ was summarised using affinity-class distributions, five equal-count exposure windows, Spearman rank correlations and Theil–Sen slopes, expressed per 0.1 exposure where reported. Effect sizes, confidence intervals and analysis-specific denominators are reported with the corresponding results.

We bootstrapped the phosphate-corrected-first CIA–exposure association and compared its direction with 5,000 random directions in centred-log-ratio space. We then evaluated the residual rank association after controlling for both ilr coordinates. These tests assess the extent to which the alignment is embedded in shared A–CN–K geometry; they do not identify causal processes.

Complete sensitivity populations, sequential controls, bootstrap implementation and denominators are reported in Supplementary Note 3, Supplementary Fig. S3, Supplementary Table 3 and Supplementary Data 3.

J10025 mineralogical characterisation

The J10025 module evaluated mineral-carrier plausibility in Early Permian Lucaogou Formation black shales from the J10025 well on the southern margin of the Junggar Basin, northwestern China. It was analysed independently of the compilation-wide posterior and R_{CIA} calculations. Quantitative XRD phase estimates described the mineral assemblage, and TOC provided local stratigraphic context. Targeted backscattered-electron imaging and SEM–EDS were used to identify candidate carrier sites following established mineralogical and microanalytical procedures^{44–48}. The feldspar–mafic mineral index was $VMI_{XRD} = \text{plagioclase} + \text{K-feldspar} + \text{pyroxene} + \text{amphibole}$, using reported XRD phase abundances. Because EDS sites were targeted rather than spatially random, their counts are non-modal occurrence records. This local module does not establish cohort-wide abundance, provenance

or posterior calibration; sample records, chemistry classes and crosswalks are provided in Supplementary Table 5 and Supplementary Data 4–5.

OSI-conditioned TOC context

The OSI–TOC analysis was an independent supplementary contextual module. The archived 673-case OSI score was the sole downstream lineage for QC tiers, TOC regressions and adjusted- R^2 comparisons. The 652-case subset formed after 21 high-leverage exclusions was used only to audit PCA loading, orientation and construction stability; it did not define the downstream score, regression populations or Supplementary Fig. S5c–e. Within each archived complete-case tier, same-n models compared an OSI-only regression of $\log_{10}(\text{TOC}+1)$ with a model additionally containing posterior $E[f_{\text{volc}}]$; the difference in adjusted R^2 measured conditional fit beyond OSI. This module does not validate volcanic fertilisation, provenance, posterior-model validity or R_{CIA} fidelity. Proxy construction, QC tiers, dilution screens, influence diagnostics, spline specification and all thresholds are confined to Supplementary Note 4 and Supplementary Table 4.

Grouped OOF exposure emulator

The modelling target was posterior $E[f_{\text{volc}}]$. Predictors were supplied in the fixed order CIA, WIP, the A–CN–K K coordinate, CIW, PIA, $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and Fe/Al. Five-fold GroupKFold evaluation⁴⁹ was performed separately by reference study (42 groups), formation (40 groups) and basin (56 groups), with each group confined to one fold and all 1,546 samples represented in each design. The Fe/Al feature is the molar cation ratio; raw deployment requires explicitly harmonised total Fe as Fe_2O_3 -equivalent input on the common oxide mass basis (Supplementary Note 5).

Within every fold, median imputation was fitted only to the training groups before fitting the selected ExtraTrees model. Each sample received one prediction from a model that had not seen its group, and all reported performance metrics were calculated solely from these OOF predictions. Algorithm and feature-set benchmarks^{50–52} used the same reference-study folds. The full-data refit was reserved for deployment and secondary rank comparison. These designs measure within-cohort generalisation across omitted metadata-defined groups, not independent external validation.

We retained the archived value of 0.25 as a fixed high-score operating point and applied it unchanged to reference posterior scores and OOF predictions. The original selection rationale cannot be established from the available historical record; no claim is made that the value was prespecified or was never optimised against OOF results. The reported operating characteristics describe its fixed use in this comparison. It is not a geological boundary or an abundance threshold. External applications should retain the continuous score or establish a new operating point using an independent calibration set and report threshold sensitivity. Predictor conventions, model hyperparameters, operating-point metrics and deployment details are given in Supplementary Note 5 and Supplementary Data 5.

Held-out SHAP attribution and stability

After each fold-specific imputer and ExtraTrees model had been fitted, SHAP values^{53,54} were calculated only for samples held out from that fold. Pooled attribution was the mean absolute SHAP value across OOF records.

Features were also summarised as weathering indices, oxide-to-Al ratios and the A–CN–K K coordinate; fold-specific rank correlations and top-k overlaps were used to assess attribution stability. Full-data-refit SHAP was used only for secondary rank comparison. SHAP describes fitted-model dependence conditional on the correlated predictor set; it is neither causal evidence nor independent evidence for volcanic input. Perturbation settings, deployment objects, software details, the model hash and results of the 11 packaged tests are reported in Supplementary Note 5.

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