Secular oxidation of Archean upper mantle caused by increasing crustal recycling

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1 **Secular oxidation of Archean upper mantle caused by**
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The redox evolution of Archean mantle impacted Earth differentiation, mantle melting and the nature of chemical equilibrium between mantle, ocean and atmosphere of the early Earth. However, how and why it varies with time remain controversial. Archean mantle-derived volcanic rocks, especially basalts are ideal lithologies for reconstructing the mantle redox state. Here we show that the ~3.8-2.5 Ga basalts from fourteen cratons are subdivided geochemically into two groups, B-1, showing incompatible element depleted and modern mid-ocean ridge basalt-like features ($(\text{Nb/La})_{\text{PM}} \geq 0.75$) and B-2 ($(\text{Nb/La})_{\text{PM}} < 0.75$), characterized by modern island arc basalt-like features. Our updated V-Ti redox proxy indicates the Archean upper mantle was more reducing than today, and that there was a significant redox heterogeneity between ambient and modified mantle presumably related to crustal recycling, perhaps via plate subduction, as shown by B-1 and B-2 magmas, respectively. The oxygen fugacity of modified mantle exhibits a ~1.5-2.0 log units increase over ~3.8-2.5 Ga, whereas the ambient mantle becomes more and more heterogeneous with respect to redox, apart from a significant increase at ~2.7 Ga. These findings are coincident with the increase in the proportions of crustal recycling-related lithologies with associated enrichment of associated incompatible elements (e.g., Th/Nb), indicating that increasing recycling played a crucial role on the secular oxidation of Archean upper mantle.

The redox state of Archean upper mantle buffered atmospheric composition and influenced the early ocean-atmosphere system through the geochemical behaviour of volatile elements (e.g., S, C and N)¹⁻³. Previous investigations have mainly focused on the behaviour of redox-sensitive elements (e.g., V) in komatiites, showing a significant increase in mantle oxygen fugacity (fO_2 ; relative to the fayalite-magnetite-quartz buffer (ΔFMQ)) between ~3.5 Ga and 1.9 Ga^{3,4}. This change, however, might not reflect the nature of the upper mantle as komatiite magmas are generally thought to have originated from either the core-mantle or the upper-lower mantle boundaries⁵. Compared to komatiites, the widespread appearance of Archean basalts offer alternative insights into resolving these issues^{1,6,7}. Most studies indicated that the mantle fO_2 has been oxidized to present-day levels since ~3.9 Ga⁶, but others inferred a dominantly reducing upper mantle on the basis of the significantly lower V/Sc ratios in Archean mid-ocean ridge basalt (MORB)-like samples relative to their modern counterparts^{1,7}. The reason of these contrasting interpretations is attributed to the choices of different mantle melting reactions and partition coefficients (Kds) in converting V/Sc ratios to mantle fO_2 ^{1,6,7}. Our recent study found that the Kds of V, Sc and Ti are influenced not only by melting temperature, pressure and fO_2 , but also by the mantle mineral compositions⁸. Thus, suitable Kds and melting reactions are critical for accurate fO_2 estimation. Although the MORB-like basalts were increasingly used in mantle fO_2 calculation, limited investigations on another group of Archean basalts with similar characteristics to modern island arc basalt (IAB) impeded a comprehensive understanding of the

geodynamic interactions across the asthenosphere, lithosphere and atmosphere of the early Earth⁸⁻¹⁰.

We have assembled a global whole-rock geochemical database of Archean (~3.8-2.5 Ga) mantle-derived volcanic rocks (N = 2997; Details of data collection, filtration and statistics are listed in Methods) from fourteen cratons (Fig. 1; Supplementary Fig. 1). The basalts exhibit compositional diversity, which is divided into Basalt-1 (B-1) and Basalt-2 (B-2) groups with modern MORB- and IAB-like chemical features, respectively^{11,12}. We applied an updated V-Ti redox proxy, which may be more sensitive to V-Sc systematics because of the more incompatible character of Ti during mantle melting⁸, to this database and found: (1) The mean Ti/V ratios of Archean basalts are significantly lower than those of modern counterparts; (2) When converting to fO_2 , the Archean upper mantle was more reducing than it is today; and (3) As indicated by B-1 and B-2 magmas, respectively, there is a marked difference in redox state between ambient and modified mantle that was presumably related to crustal recycling, via plate subduction; (4) The modified mantle beneath the most cratons has become progressively oxidized over ~3.8-2.5 Ga. These changes are closely associated with the increase in the proportions of B-2, high-Mg andesite (HMA) and andesite samples, and the degree of enrichment in incompatible elements that on the modern Earth are related to the recycling of crustal materials via subduction zones. This indicates that the secular oxidation of Archean mantle was related to the increased crust recycling into the mantle.

Figure 1 Spatial and temporal distribution of global mantle-derived volcanic rocks. Top, Map of exposed Archean cratons. According to statistics, at least fourteen cratons have Archean mantle-derived volcanic rock records. **Bottom,** Simplified age distribution of mantle-derived magmatism for each selected craton.

Archean mantle-derived volcanic rocks

The ~3.8-2.5 Ga mantle-derived volcanic rocks in the whole-rock geochemical database were classified as komatiites ($N = 551$, $\text{MgO} \geq 18$ wt.%), basalts ($N = 2133$, $\text{MgO} < 18$ wt.%) and HMAs ($N = 313$, $\text{SiO}_2 = 54\text{-}65$ wt.%, $\text{MgO} \geq 5$ wt.% and $\text{Mg\#} \geq 45$, calculated as an atomic ratio of $100 \times \text{Mg}/(\text{Mg} + \text{Fe}_{\text{total}})$)¹³⁻¹⁷ (Supplementary Table 1).

A statistical analysis of modern basalts from established tectonic settings suggests that $(\text{Nb/La})_{\text{PM}} < 0.75$ (PM, primitive mantle normalized¹⁸) is a powerful criteria identifying primitive melts that were generated in subduction-related settings (Supplementary Fig. 2), whereas the non-subduction basaltic melts have $(\text{Nb/La})_{\text{PM}} \geq 0.75$. On this basis, Archean basalts are subdivided into B-1 and B-2 groups with $(\text{Nb/La})_{\text{PM}} \geq$ and < 0.75 , respectively. The B-1 samples ($N = 740$) predominantly belong to the tholeiitic rock series according to their low La/Yb ratios of 0.50-3.73 ($\text{La/Yb} \leq 2.6$ for tholeiitic and $\text{La/Yb} \geq 5.3$ for calc-alkaline rock series¹⁹) and have left-declined to nearly flat rare earth element (REE) patterns, similar to modern MORBs (Supplementary Fig. 3). Whereas the B-2 samples ($N = 1393$) are intermediate between tholeiitic and calc-alkaline rock series with a wide range in La/Yb ratios (up to 72), clearly distinct to B-1 samples, and show flat to right-declined patterns, similar to basalts in modern arcs and back-arc basins (Supplementary Fig. 3). The HMAs are mainly attributed to calc-alkaline rock series based on their high La/Yb ratios (up to 36), and have the lowest average $(\text{Nb/La})_{\text{PM}}$ ratio of 0.35¹⁵ (Supplementary Fig. 3). Detailed descriptions of each rock type are listed in Methods.

Redox state of Archean upper mantle

The principle of the V-Ti redox proxy is that V is a multivalent element (2+, 3+, 4+ and 5+), and its Kds vary with $f\text{O}_2$, melting P-T conditions and mineral compositions, in contrast with the Kds of Ti which are independent of $f\text{O}_2$ ^{1,6,8}. Based on a thorough

consideration of peridotite melting reactions and water contents, this method has successfully estimated the fO_2 of both modern ambient and arc (or modified) mantle⁸, providing a viable solution to the mantle fO_2 debate in the early Earth.

Before determining fO_2 , it is necessary to calculate melting conditions for the parental magmas of the basalts. We use the Fractionated-PT software, and only samples with MgO > 9 wt.% were used to avert possible effects from the late overprint of fractional crystallization and crust contamination²⁰ (Supplementary Table 2; Supplementary Fig. 4). Due to the lack of water content assessment for Archean samples, we tentatively used the modern values of MORBs (~0.2 wt.%) and IABs (~2-4 wt.%) to represent those of Archean B-1 and B-2 samples, respectively^{16,21,22}.

The results indicate that B-1 samples were derived at high temperatures ($T = \sim 1320-1658$ °C) and pressures ($P = \sim 0.8-4.7$ GPa), corresponding to the potential temperature (T_P) of ~ 1600 °C (Supplementary Fig. 4a), clearly distinct to that of komatiites ($T_P = \sim 1750-1950$ °C)⁵. In contrast, B-2 samples exhibit significantly lower level conditions with $T = \sim 1218-1583$ °C and $P = \sim 0.6-3.7$ GPa at 2 wt.% H_2O and $T = \sim 1199-1519$ °C and $P = \sim 0.7-3.4$ GPa at 4 wt.% H_2O ^{20,22}. The melting P-T conditions generally straddle the phase transition zone ($P = \sim 2.2$ GPa) between spinel- and garnet-facies^{20,23}. We therefore employ near fractional melting to perform both spinel (a) and garnet lherzolite (b) melting models for B-1 samples, and spinel lherzolite (c) melting for B-2 samples under hydrous conditions²⁴⁻²⁶ (Supplementary Table 3). Detailed parameter selections and calculation processes are listed in Methods.

The mean Ti/V ratios of B-1 and B-2 samples are 18.9 ± 0.4 (1 σ) and 18.6 ± 0.3 , respectively, significantly lower than those of the modern MORBs (29 ± 0.4) and IABs (25 ± 0.4) (Supplementary Table 1; Supplementary Fig. 5)⁸. When converting V-Ti systematics to mantle fO_2 , the results of ambient mantle indicated by B-1 magmas basically remain constant with $\Delta FMQ -1.18 \pm 0.12$ (1 σ) prior to ~ 3.2 Ga, consistent with those obtained by V-Sc redox proxy ($\Delta FMQ -1.19 \pm 0.33$)^{1,7}, but they become increasingly heterogeneous between ~ 3.2 Ga to 2.7 Ga (Fig. 2a; Supplementary Table 2). Subsequently, the ambient mantle has generally experienced a significant oxidation, as shown by a ~ 0.5 log unit increase from in ΔFMQ beneath the Dharwar Craton from -1.24 ± 0.09 to -0.66 ± 0.06 after ~ 2.8 Ga (Fig. 2a). There is also a significant fO_2 difference between B-1 and B-2 samples, indicating the redox heterogeneity between ambient and modified mantle (Fig. 2). The mantle sources of B-2 samples have experienced a secular oxidization process over ~ 3.8 -2.5 Ga^{3,4,27} (Fig. 2b,c). For example, the fO_2 values of modified mantle beneath the Dharwar Craton exhibit a ~ 1.5 log unit increase from $\Delta FMQ -1.75 \pm 0.31$ to $\Delta FMQ -0.40 \pm 0.14$ at 2 wt.% H₂O and $\Delta FMQ -1.25 \pm 0.33$ to $\Delta FMQ +0.02 \pm 0.16$ at 4 wt.% H₂O between ~ 3.4 Ga to 2.6 Ga, and those beneath the North Atlantic Craton have a ~ 1.0 log unit increase from $\Delta FMQ -1.86 \pm 0.15$ to $\Delta FMQ -0.90 \pm 0.11$ at 2 wt.% H₂O and $\Delta FMQ -1.37 \pm 0.15$ to $\Delta FMQ -0.67 \pm 0.06$ at 4 wt.% H₂O between ~ 3.8 Ga to 3.0 Ga (Fig. 2b,c; Supplementary Table 2). Although some Archean samples (e.g., from the Slave Province and the Yilgarn Craton) may have achieved a redox state similar to modern mid-oceanic ridges and magmatic arcs, most of the estimations are lower than

modern MORBs (FMQ -0.03 ± 0.38) and IABs (FMQ $+0.42 \pm 0.63$ at 2 wt.% H₂O and FMQ $+0.82 \pm 0.62$ at 4 wt.% H₂O)⁸ (Fig. 2a), indicating that the Archean upper mantle was intrinsically more reducing than it is today. Statistically, the whole-rock Ti/V ratios have a negative logarithmic correlation with the calculated mantle fO_2 values^{8,20}, indicative of the validity of the calculation methodology (Supplementary Fig. 5). Notably, the slopes of Archean and modern primitive basalts are significantly different (Supplementary Fig. 5), reflecting the difference in mantle melting conditions, which would directly influence the Kds of Ti and V⁸.

Figure 2 Redox state of Archean basalts calibrated by the updated V-Ti redox

proxy. a, The fO_2 estimations for B-1 samples. The fO_2 values of Archean MORB-like samples estimated by previous V-Sc redox proxy, komatiites by the V partitioning and modern MORBs and IABs by V-Ti redox proxy were used for comparisons^{3,7,8}. **b,** The fO_2 estimations for B-2 samples at 2.0 wt.%. **c,** The fO_2 estimations for B-2 samples at 4.0 wt.%. Error bars show the 1-standard errors of the means.

Increase in crustal recycling into the mantle

Based on the statistics, the Archean volcanic rocks have a significant three-stage temporal and spatial distribution: (1) Prior to ~3.2 Ga, the rock record is mainly characterized by tholeiitic chemical features (Supplementary Fig. 3b,c), represented by several ancient cratons (the Kaapvaal Craton, North Atlantic Craton, Dharwar Craton and Pilbara Craton)^{12,27,28} (Fig. 1), and the komatiites account for half of the global volcanic rock database (48 %), whereas the B-2, HMA and possible calc-alkaline andesite samples, are mainly concentrated in the North Atlantic Craton, which also accounts for a quarter (25 %) of synchronous sample size of the database (Fig. 3a), indicating that the non-subduction geodynamic regime play a dominant role during ~3.8-3.2 Ga^{17,27-29}; (2) During ~3.2-2.7 Ga, calc-alkaline magmatism is more widespread on a global scale^{30,31} (Supplementary Fig. 3d,e), and the proportions of B-2, HMA and andesite samples increase to 37 %, whereas komatiites decreased to 32 % (Fig. 3b), consistent with the global development of plate subduction or other similar mechanisms^{30,32,33}; and (3) Most of cratons experienced a long period of magmatic quiescence after ~2.7 Ga, with only the North China, Zimbabwe and Dharwar cratons displaying significant ~2.7-2.5 Ga magmatism^{34,35} (Fig. 1). Komatiite components are essentially absent from these younger cratons and were replaced by the dominant calc-alkaline compositions (82 %) (Fig. 3c).

Geochemical modelling indicates that the compositional diversity of Archean basalts was most likely related to the introduction of oceanic crust- and sediment-derived melts with high fO_2 , which are features related to the recycling of

crustal materials into the mantle on the modern Earth^{12,17,36} (Fig. 3d-f; Supplementary Fig. 6). The proportion of recycling increased significantly after ~3.2 Ga (Fig. 3d-f; see Methods for details). Similarly, the elevated Th/Nb ratios of B-2 samples from each craton can also indicate a significant increase in recycling of crustal materials into the mantle, perhaps via plate subduction during ~3.8-2.5 Ga, associated with a downward tendency of B-1 samples³⁷ (Supplementary Fig. 7). Along with plate subduction becoming the dominant regime, earlier small-scale mantle convection might be replaced by a modern large-scale convection^{30,38-40}, which would further accelerate mantle homogenization, resulting in the ambient mantle oxidation after ~2.7 Ga^{3,7,37} (Fig. 2a). Therefore, the increase in recycling of crustal materials into the mantle via plate subduction could be the most powerful mechanism leading to secular oxidation of Archean mantle.

Figure 3 2D-Pie chart of lithological proportions (a-c) and La/Yb versus Nb/Yb diagram of crustal recycling (d-e) for ~3.8-3.2 Ga, ~3.2-2.7 Ga and ~2.7-2.5 Ga volcanic samples, respectively. The values of N (norm)- and E (enriched)-MORB and oceanic island basalt (OIB) are from Sun and McDonough¹⁸. The shaded area was outlined by modern samples collected from mid-oceanic ridges, oceanic islands and

oceanic plateaus, of which parental magmas were not metasomatized by slab-derived fluids or melts and carbonatitic melts (data from the GEOROC database). The chemical tendencies were calculated using a series of binary mixing modelling between DM and possible metasomatic agents (oceanic crust- and sediment-derived melts), respectively ([see Methods for details](#)).

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Author contributions

L. Gao, S.W. Liu and P.A. Cawood conceived and designed the project. L. Gao and S.W. Liu wrote the manuscript. J.T. Wang helped to calculate the oxygen fugacity. G.Z. Sun, Y.L. Hu and F.Y. Hu built the geochemical database and performed data processing. All the authors contributed to the interpretation of the results and the revision of this manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available in the online version of the paper.

Methods

Data collection and filtration. In this study, the whole-rock geochemical database of ~3.8-2.5 Ga volcanic rocks is a combination of the GEOROC database (<http://georoc.mpch-mainz.gwdg.de/georoc/>) and a subset of the North China Craton volcanic database assembled by our research group. The principles for data filtration are as follows: (1) For accurate estimation of mantle redox state, the samples must be directly produced by melting of mantle peridotite, namely, mantle-derived, so that their SiO₂ content should be in the range of typical basalt and basaltic andesite composition (45-54 wt.%) based on experimental petrology²⁰. In addition, there are a number of locations where primitive magmas are inferred to be HMAs (SiO₂ = 54-65 wt.%, MgO ≥ 5 wt.% and Mg# ≥ 45)^{15,16}, therefore, samples satisfied with HMA criteria are also retained; (2) They should have reliable formation ages traced by isotopic dating methods (mainly via whole-rock Sm-Nd, Re-Os and magmatic zircon U-Pb isotopic systematics) or limited by geological relationships. Subsequently, data statistics was conducted to these samples based on their rock types, and temporal and

spatial distributions, respectively (Fig. 1,3; Supplementary Fig. 1); (3) Only samples with matched major and trace element data (best to contain the information of V, Ti, La and Nb) are preserved; (4) The least-altered Archean volcanic rocks are reported to have low loss on ignition (LOI, < 6 wt.%) and negligible Ce anomalies ($0.9 < \text{Ce}/\text{Ce}^* < 1.1$, calculated as $\text{Ce}_N / \text{Sqrt}(\text{La}_N \times \text{Pr}_N)$)⁴¹, therefore, the collected basalts and HMAs not satisfied with these criteria are filtrated. Due to their commonly high LOI contents, negligible Ce anomalies is tentatively considered to be the only criterion for komatiites; and (5) Samples affected by significant crustal contamination discussed in the original literatures are also filtrated. After data filtration, this database comprises a total of 2997 samples that cover fourteen ancient cratons (Fig. 1; Supplementary Table 1).

Geochemical characteristics of mantle-derived volcanic rocks. The komatiites were subdivided into Al-depleted (ADKs, N = 90) and Al-undepleted komatiites (AUKs, N = 461) based on $\text{Al}_2\text{O}_3/\text{TiO}_2 < \text{ and } \geq 15.0$, respectively^{5,14}. The ADKs exhibit low $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios (1.76-14.9, average 11.0) and average $(\text{Gd}/\text{Yb})_N$ ratio of 1.50 with nearly flat REE patterns. The AUKs have significantly higher $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios (15.0-40, average 22) but lower average $(\text{Gd}/\text{Yb})_N$ ratio of 1.05, and their REE patterns are more depleted in light rare earth elements (LREEs)^{5,14} (Supplementary Table 1).

B-1 samples (N = 740) predominantly belong to the tholeiitic rock series (Supplementary Fig. 3b,d,f). They are characterized by low SiO_2 contents (45.11-53.91 wt.%, average 50.00 wt.%), variable MgO (3.98-17.50 wt.%, average

8.43 wt.%) and TFeO (6.13-17.51 wt.%, average 12.01 wt.%) contents and other transition metals, for example V contents (102-660 ppm, average 299 ppm), and Mg# values (40-78, average 58) (Supplementary Table 1). They have LREE depleted to nearly flat REE patterns with an average (La/Yb)_N ratio of 1.05, and negligible Nb and Ta anomalies with an average (Nb/La)_{PM} ratio of 0.91 (Supplementary Table 1).

B-2 samples (N = 1393) have similar major oxide features to those of B-1 with SiO₂ (45.00-53.99 wt.%, average 50.55 wt.%), MgO (2.55-17.61 wt.%, average 8.43 wt.%) and TFeO (5.86-18.11 wt.%, average 11.18 wt.%) contents and Mg# values (39-83, average 60). Their V contents (36-586 ppm, average 258 ppm) are slightly lower than those of the B-1 samples (Supplementary Table 1), and in terms of REE ratios they are intermediate between tholeiitic and calc-alkaline rock series, clearly distinct to B-1 samples (Supplementary Fig. 3c,e,g). Most B-2 samples have flat to LREE enriched patterns with an average (La/Yb)_N ratio of 2.79, and they have negative Nb and Ta anomalies with a low average (Nb/La)_{PM} ratio of 0.50 (Supplementary Table 1).

The HMA samples are mainly attributed to calc-alkaline rock series (Supplementary Fig. 3c,e,g), and they have the highest SiO₂ contents (54.00-64.20 wt.%, average 56.13 wt.%) and the lowest MgO (4.50-14.40 wt.%, average 7.08 wt.%), TFeO (4.49-13.52 wt.%, average 8.61 wt.%) and V (50-370 ppm, average 189 ppm) compared to Archean basalts (Supplementary Table 1). Their Mg# values (47-78, average 62) are similar to those of the basalts, but they have fractionated REE patterns with an average (La/Yb)_N ratio of 5.85, and marked relative depletions in Nb and Ta

with the (Nb/La)_{PM} of 0.35 ([Supplementary Table 1](#)).

Estimation of mantle fO_2 by V-Ti redox proxy. V is a redox-sensitive element with variable valence states, whereas Ti is not^{1,3,4,6}. In addition, both of them are generally considered to be immobile during dehydration and melting of oceanic crust (including sediments), and are not strongly enriched in continental crust⁸. Together with their highly incompatible features among most mantle minerals, the V-Ti systematics can ‘see through’ early magmatic differentiation and be used as a stable fO_2 discrimination.

In the mantle fO_2 modelling, the content of trace element i in the instantaneous melt is calculated by $C_{i,m}^{n+1} = \frac{C_{i,r}^n}{D_{i,bulk}^{n+1} + F(1 - D_{i,bulk}^{n+1})}$, where $C_{i,m}^{n+1}$ is the element content in the melt at step $n+1$, $C_{i,r}^n$ is the element content in the residue after melt extraction at step n , $D_{i,bulk}^{n+1}$ is the bulk partition coefficient at step $n+1$, and F is the melt fraction of each step⁸. Element i content in the aggregated melt at step j is calculated by $C_i^{aggr} = \frac{\sum_l C_{i,m}^l M_{melt}^l}{\sum M_{melt}^l}$, where C_i^{aggr} and $\sum M_{melt}^l$ are element i content in the aggregated melt and bulk mass at step j , respectively, $C_{i,m}^j$ and M_{melt}^j are the element i content in the melt and mass at step j , respectively⁸. According to the DM compositions, the initial V and Ti contents are assumed to be 79 ppm and 798 ppm, respectively⁴².

The mineral assemblages of garnet lherzolite (model b) constitute by 52.3% olivine (Ol), 17.4% orthopyroxene (Opx), 26.2% clinopyroxene (Cpx) and 4.1% garnet (Grt) with mineral compositions of Opx Wo# = 4.65 (Wo# = $X_{Wo} / (X_{Wo} + X_{En} + X_{Fs})$), in which X_{Wo} , X_{En} and X_{Fs} are fractions of Wollastonite, Enstatite and Ferrosilite, respectively), Cpx Al^T = 0.21 (Al in the tetrahedron-coordinated site), Opx Al^T =

0.19²⁴. The melting reactions of dry garnet lherzolite at ~3.0 GPa were used for this model²⁴. The melt productivity of 0.23/°C for lherzolite and 0.14/°C for harzburgite were used to calculate the melting degrees and temperatures²⁵. The Kds of V in Ol, Opx and Cpx, and Ti in Opx and Cpx at each melt fraction were calculated by recent empirical equations with variables of mineral compositions and melting P-T conditions⁷. In addition, the Kds of V in Grt and Ti in Ol and Grt are assumed to be constants and collected from <http://earthref.org/GERM/>.

The spinel lherzolite (models a and c) are composed of 57% Ol, 28% Opx, 13% Cpx and 2% Sp with Opx Wo# = 4.38, Cpx Al^T = 0.17, Opx Al^T = 0.15 and Sp Cr# = 10.65 (Cr# = Cr₂O₃ / (Cr₂O₃ + Al₂O₃) on a molar basis.). However, the melting reactions for models a and c are significantly different: the former performed by dry peridotite at 1.5 GPa and the latter by hydrous peridotite at 1.2-2.0 GPa, respectively^{25,26}. The above-mentioned empirical equations were used to calculate the Kds of V in Ol, Opx, Cpx and Sp, and Ti in Opx and Cpx at each melt fraction⁷. During the calculations, the *f*O₂ values varied from FMQ -4 to FMQ +4 at a step of 0.001 log unit until the modelled V and Ti contents may match those of samples with the difference less than 5%. All of the calculations are compiled into a macro document and listed in [Supplementary Table 3](#).

Geochemical modelling for crust recycling. Nb (and Ta) and REEs are generally considered to be incompatible during the partial melting of mantle peridotite but sensitive to subduction-related metasomatism⁴³. Therefore, we perform a series of binary mixing calculations between the possible mantle sources and metasomatic

agents of oceanic crust- and sediment-derived melts, respectively^{42,43} (Fig. 3d-f; Supplementary Fig. 6). The results indicate that the compositional diversity of Archean basalts is most likely related to recycling of oceanic crust materials, rather than the significant crustal contamination. The chemical compositions of oceanic crust-derived melts can be represented by those of average Archean tonalite-trondhjemite-granodiorite (TTG)⁴⁴. The compositions of sediment-derived melts are calculated using batch melting of a ~2.7 Ga metapelite sample from the Yangtze Craton, China, with the fraction (F) of melt ranging from 0.1 to 0.3⁴⁵. The Kds are collected from <http://earthref.org/GERM/>.

Data availability

The authors declare that all data supporting the discoveries of this contribution are available within the article and its Supplementary Information files.

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