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Supplementary Materials for

Highly oxidized intraplate basalts and deep carbon storage

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Supplementary Text

Supplementary Section 1

Geological Setting and samples

Cenozoic intraplate basalts in eastern China are widely distributed along the coastal provinces and adjacent offshore shelf extending over 4000 km. Representative Cenozoic intraplate basalts from eight localities in eastern China were analyzed for $Fe^{3+}/\Sigma Fe$ value in this study. In a total alkali vs silica (TAS) diagram, studied samples ranges from nephelinite to basaltic andesite (Fig. S1). Their FeO_{total} range from 9.7 to 14.5 wt% (77-82).

Datong volcanic field (DVF) is located in the northern part of the Trans-North China Orogen. The DVF erupted at 0.74 Ma and 0.4 Ma (*83, 84*). Eighteen fresh samples analyzed herein are porphyritic olivine basalts, where phenocrysts are olivine, plagioclase and clinopyroxene, and the groundmass is composed of plagioclase, clinopyroxene and needle-shaped Fe–Ti oxide (*77*). These samples range from tholeiitic basalt, alkaline trachybasalt to basanite (*77*), with their major, trace element and Mg-Zn isotopic compositions reported in Wang and Liu (*77*).

Hannuoba basaltic plateau is located along the northern margin of the Trans-North China Belt. Hannuoba basalts have K-Ar ages of 14-22 Ma (78). Five samples from Hannuoba analyzed in this study are porphyritic alkaline basalts (78). They have rare and small fresh olivine phenocrysts with a groundmass of plagioclase, clinopyroxene, olivine, and opaque minerals (78). Their major and trace elements have been studied by Qian et al. (78), and Mg isotopic compositions were reported in Li et al. (16).

Shandong basaltic field is located in the North China carton. The Cenozoic alkaline magmatism in Shandong took place during two periods: 24.0-10.3 Ma and 8.7-0.3 Ma (15, 85). The early magmatism was voluminous and characterized by large volcanoes densely distributed in a narrow area near the Tan-Lu Fault. Most samples are fresh except a few samples from Fangshan and Mashan, whose olivine phenocrysts are partially altered to iddingsite (79). All samples have minor olivine as phenocrysts in a groundmass of olivine, Ti-magnetite, nepheline, and glass (79). These samples are classified as basanite and nephelinite (79). Their Fe³⁺/ Σ Fe have been analyzed by Sheng et al. (86), and our duplicated analyses of Fe³⁺/ Σ Fe for a selective set of samples agree well within 3% with those reported in Sheng et al. (86) (Table S1). Comparison of Fe³⁺/ Σ Fe values between unaltered and slightly altered samples suggests that iddingsitization does not have an impact on the bulk-rock Fe³⁺/ Σ Fe (86). Their major and trace element compositions were reported by Zeng et al. (15) and Zeng et al. (79), and their Mg-Zn isotope were reported in Zeng et al. (79) and Wang et al. (87).

Pingmingshan – Anfengshan is located in the Sulu orogenic belt. Pingmingshan and Anfengshan basalts have K-Ar ages of 7.3-12.3 and 4.0-6.4 Ma, respectively (85). Five samples from Pingmingshan and three samples from Anfengshan were analyzed

in this study. Most of the studied samples are fresh, except for 13AFS9 and 13AFS10, whose olivine phenocrysts were partially altered to iddingsite. These samples are porphyritic basanite (80), where phenocrysts consist predominantly of olivine in the Anfengshan basalts and olivine, clinopyroxene, and plagioclase in the Pingmingshan basalts (80). Their groundmass mainly consists of plagioclase, olivine, augite, nepheline, magnetite and glass. Their major and trace element compositions have been studied by Huang et al. (80). Their Mg-Zn isotopic compositions were reported in Li et al. (16) and Liu et al. (39).

Jiaozhou is located in Jiaolai basin in the North China carton. Jiaozhou basalts have K-Ar ages of 71.9 Ma (*81*). Four samples studied in this study are porphyritic basanites (*81*), where phenocrysts consist of fresh pyroxene and olivine and groundmass mainly consists of plagioclase, olivine, pyroxene and Fe-Ti oxide (*81*). Their major, trace element and Sr-Nd isotopic compositions have been studied by Meng et al. (*81*). The Mg isotope compositions of four samples were reported in Li et al. (*16*).

Fangshan is located in the northeast of the South China Block. Fangshan basalts were dated at 2.9-3.5 Ma by K-Ar method (80). Five fresh samples analyzed in this study are porphyritic trachybasalt (80), where phenocrysts consist of olivine and clinopyroxene and the groundmass mainly consists of plagioclase, olivine, augite, nepheline, magnetite and glass. Their major, trace element and Mg-Zn isotope compositions were reported in Huang et al. (80) and Liu et al. (39).

Longyou is located in the east of the South China Block. Longyou basalts were dated at 9.4-9.0 Ma by K-Ar method (80). They are porphyritic basanites, and phenocrysts consist of olivine and clinopyroxene. Their groundmass mainly consists of plagioclase, olivine, augite, nepheline, magnetite and glass. Two samples from Longyou are analyzed in this study. Sample 10LYSK13 is fresh, whereas 10LYSK11 is slightly altered with olivine phenocrysts partially replaced by iddingsite. These two samples show very similar Fe³⁺/ Σ Fe values of 0.33 and 0.34, respectively, supporting that iddingsitization does not change the bulk-rock Fe³⁺/ Σ Fe (Table S1). Their major, trace element and Mg-Zn isotope compositions were reported in Li et al. (*16*) and Liu et al. (*39*).

Niutoushan is located in the southeast of the South China Block. Niutoushan basalts were dated at 19.2-11.7 Ma by K-Ar method (82). An alkaline basalt sample from Niutoushan was analyzed in this study. This sample has fresh olivine and pyroxene as phenocrysts in a groundmass of plagioclase and pyroxene (82). Its major and trace element compositions were reported by Yang (82) and Mg isotopic compositions were reported in Li et al. (16).

Supplementary Section 2

Fe³⁺/∑Fe correction for crystal fractionation

Different degree of crystal fractionation prior to eruption may cause the Fe³⁺/ Σ Fe variation, although this effect is thought to be minimal (88). Here, we corrected Fe³⁺/ Σ Fe data to the primary magma composition, following the method of Sossi et al. (89). Since all of our studied basalts have MgO > 6 wt%, it is assumed that olivine is the only crystal phase removed from or added to the melts (89). Olivine in

equilibrium with melt is calculated using $K_{D \, Ol-Melt}^{Fe-Mg} = 0.3$ (defined as the molar

Fe²⁺/Mg of the liquid divided by Fe/Mg of coexisting olivine (90)), and it is added or subtracted at a step of 1 wt% until Mg#_{melt} = 0.72, equilibrium with mantle olivine at Fo₉₀. Considering that olivine in an oxidized mantle may have a lower Fo content than the normal mantle (91), we did another set of correction to equilibrate the melt with mantle olivine at Fo₈₅. The MgO and FeO composition of the olivine crystallizing is given by:

$$\left(\frac{Fe}{Mg}\right)_{Ol} = K_{DOl-Melt}^{Fe-Mg} \left(\frac{Fe}{Mg}\right)_{Melt}$$

where Fe = FeO (wt%)/71.845 and Mg = MgO (wt%)/40.3. The composition of the olivine is iterated every 1%, and the composition of the melt + olivine mixture is given by mass balance:

$$M_{Melt}^{F_n} = \left(1 - (F_n - F_{n-1})\right) M_{Melt}^{F_{n-1}} + (F_n - F_{n-1}) M_{Ol}^{F_n}$$

M refers to the concentration of an element, and *F* is the fraction of olivine, which ranges from $F_1, F_2 \dots F_n$, where *n* is the number of iterations. The modelling results show that olivine fractional crystallization or accumulation may have shifted Fe³⁺/ Σ Fe data by no more than 0.08, and the corrected Fe³⁺/ Σ Fe for melts equilibrated with Fo₉₀ or Fo₈₅ olivines agree with each other within 24% (Fig. S7).

Supplementary Section 3

Partial melting models

A non-modal batch melting model is used to evaluate the distribution of Fe²⁺ and Fe³⁺ during partial melting. Initial modal abundances of olivine, clinopyroxene, orthopyroxene, and garnet are assumed to be 0.53, 0.27, 0.18, and 0.02, respectively (92). Melting reactions of partial melting of garnet peridotite were taken from Walter et al. (92). Garnet and clinopyroxene in peridotite were modeled to be exhausted at 10% and 23% degree of melting. Partition coefficients for Fe²⁺ ($D_{Fe^{2+}}$) and Fe³⁺ ($D_{Fe^{3+}}$) of mantle minerals are from Wang et al. (93). The bulk partition coefficient (P) of the melt and solid are calculated using the partition coefficients of melt and minerals (D_{l-j}) and the relative proportion of a given mineral in the melting reaction (r_i):

$$P = \sum_{j=1}^{n} [r_j * D_{l-j}]$$

The element abundance in the melt C_i^l can be calculated using the equation of

$$C_{i}^{l} = \frac{C_{i}^{0}}{D_{0} + (1 - P)F}$$

where F is degree of partial melting, C_i^0 is the initial element abundance, and D_0 is the melt-solid partition coefficient at the onset of melting.

We also used a fractional melting model to determine the Fe^{2+} and Fe^{3+} content in the melts for comparison:

$$C_i^l = C_i^0 \times \frac{1}{D_0} (1 - \frac{PF}{D_0})^{(\frac{1}{P} - 1)}$$

Our modelling shows that the Fe³⁺/ Σ Fe value of melts does not differ significantly between batch melting and fractional melting (Fig. S8). Partial melting of a peridotitic mantle source with a normal-mantle Fe³⁺/ Σ Fe of 0.036 (28) cannot produce the high-Fe³⁺/ Σ Fe value observed in EC basalts (Fig. S8). In order to produce the high Fe³⁺/ Σ Fe as high as 0.6 in EC basalts, the Fe³⁺/ Σ Fe of the mantle source must be elevated to, for example, ~0.30 if 3% partial melting degree is assumed (Fig. S8).

Supplementary Section 4

Mixing model calculation

We calculate the amount of subducted carbonate required to produce the observed high- δ^{66} Zn and low- δ^{26} Mg endmember for the HOME using a mixing model of subducted oceanic crust and carbonate. Experimental studies have shown that with increasing pressure during subduction, the stable carbonate mineral changes from calcite, to calcite/dolomite, and to dolomite/magnesite (e.g. 94). Therefore, dolomite/magnesite was taken as an endmember in the mass balance calculations. The subducted oceanic crust is assumed to be a mixture of carbonate minerals and MORB. The modelling results are plotted in Fig. S10.

Our modelling suggests that involving small amounts of dolomite and magnesite in the melting reactions would lead to a significant deviation of the Mg-Zn isotopic compositions of the melt from the normal mantle range, and different carbonate species have different effects on the Mg-Zn isotopic compositions of resulting melts due to the distinct elemental contents and initial isotopic compositions of dolomite and magnesite. Overall, in order to produce the observed high- δ^{66} Zn and low- δ^{26} Mg HOME, 10-20% of carbonates are needed in the melting reaction during the partial melting of carbonated oceanic crust (Fig. S10A). The Mg-Zn isotopic variations observed in the EC basalts can be explained by a mixture of the HOME (15% carbonate + 85% MORB) and asthenospheric peridotite (Fig. S10B). Modelling parameters are provided in Supplementary Table 7.

Supplementary Section 5

Computational details of the melt-diamond density crossover at mantle depth

We performed first-principles molecular dynamics (FPMD) simulations based on density functional theory (DFT) using the Vienna ab initio simulation package (VASP). The local density approximation (LDA) and projector augmented wave method were adopted for the exchange-correlation functional. The energy cutoff was 600 eV. The gamma point was used for Brillouin zone summations over the electronic states. Previous studies found that LDA works better than the generalized gradient approximation (GGA) in predicting many properties of silicates including equation of state and elasticity (95-97). Single-particle orbitals were populated based on the Fermi-Dirac statistics. All spin-polarized FPMD simulations were performed in the NVT (constant number of atoms N, volume V, and temperature T) thermodynamic ensemble with a fixed temperature controlled by a Nosé thermostat. The time step was set to 1 fs. We focus on three types of silicate melts with mid-ocean ridge basalt (MORB) compositions, Mg₆Ca₆Fe₅Si₂₇Al₁₀Na₃O₈₈ (dry MORB), Mg₆Ca₆Fe₅Si₂₇Al₁₀Na₃H₁₈O₉₇ (MORB with 4.9 wt.% water), and Mg₆Ca₆Fe₅Si₂₇Al₁₀Na₃C₄O₉₆ (MORB with 5.3 wt.% CO₂) to model the water- and carbon-bearing basaltic melts (Table S5). We did not introduce a Hubbard U correction for Fe atoms, as Caracas et al. (98) found that a +U correction does not significantly improve the calculated properties. The initial melt configurations at different volumes were prepared by melting the structures at 6000 K and down to 3000 K for 10 ps, and then, we ran NVT simulations at 1700 K for at least 40 ps. Pressures at different volumes were derived by averaging the pressure for each time step after the equilibration. The calculated results together with the chemical compositions were listed in Table S6.

Our calculated results show that at 1700 K, the density of dry basaltic melt increases from 3.046 g/cm³ at 2.2 GPa to 3.461 g/cm³ at 7.5 GPa. A linear interpolation suggests a density of ~ 3.35 g/cm³ at 6 GPa, which is higher than the measured values (3.23 g/cm³) at 5.9 GPa and 1673 K using the sink-float method (99). This is typical for the LDA, which underestimates the volumes of silicate minerals and hence overestimates their densities (96). A pressure correction of ~ +1.5 GPa is required to bring the LDA results into agreement with the experimental data. In contrast, the GGA underestimates the density of silicate minerals, and it was suggested that the pressure correction should be at least -2.5 GPa to match the literature data (100).

The density of MORB melt with 4.9 wt.% water ranges from 2.902 g/cm³ at 2.2 GPa to 3.638 g/cm³ at 13.5 GPa, 1700 K. Compared with dry MORB melt, the density of this hydrous MORB melt is lowered by ~ 0.18 g/cm³, corresponding to a decrease

of 0.037 g/cm³ per 1 wt.% H₂O. Recently, Drewitt et al. (*100*) conducted FPMD simulations on MgO-SiO₂-H₂O melts using GGA and found that the incorporation of 1.0 wt.% water can reduce the density of MgSiO₃ melt by ~0.043 g/cm³, which is similar to our results.

The density of MORB melt with 5.3 wt.% CO₂ is lower than that of dry MORB melt but higher than that of MORB melt with 4.9 wt.% H₂O (Table S6). The incorporation of CO₂ into MORB melt also decreases its density, the CO₂ effect on is weaker than the H₂O effect. In comparison, the density of MORB melt only decreases by ~0.015 g/cm³ per 1 wt.% CO₂. Such a magnitude is similar to the CO₂ effect on the density of pyrolite melt at 3000 K calculated by FPMD simulations using GGA (*101, 102*).

Our simulations together with previous studies on diamond show that diamond is always denser than MORB deeper than the bottom of upper mantle (~12-14 GPa). As the density of silicate melt increases with Fe content but decreases with H₂O and CO₂ contents, the intersection of the density lines of diamond and silicate melt could be changed by 1-2 GPa. This variation caused by the chemical composition does not change the conclusion that diamonds formed in deep-sourced carbon-bearing silicate melts via the redox reaction will descend to the bottom of melt and the residual melt, if it is separated from diamonds, would be enriched in Fe³⁺.

Supplementary Section 6

The amount of carbon storage

In order to estimate the area of Cenozoic basalt exposed on the land of eastern China, Chen et al. (51) utilized a digital-image processing program to extract the distribution information of Cenozoic basalts by pixel from the geological map, and overlaid on the high-precision geomorphologic map. The specific methods are as follows.

The geological and geomorphic map of eastern China attached in GeoMapApp are drawn by Mercator projection. The ratio of basalt eruption area S1 to the Earth surface area S of the region is equal to the ratio of basalt image area P1 in the Mercator projection graph to the image area P of the region, within the latitude of 1 °, between a certain longitude.

$$\frac{S_1}{S} = \frac{P_1}{P}$$

The image area in the Mercator projection graph can be calculated by photoshop software. The Earth surface area S between latitude λ_1 to latitude λ_2 ($\lambda_2 = \lambda_1 + 1$) and longitude ϕ_1 to longitude ϕ_2 ($\phi_2 > \phi_1$) can be obtained by spherical calculation formula:

$$S = 2\pi R^2 (\sin \lambda_2 - \sin \lambda_1) \times \frac{(\phi_2 - \phi_1)}{360}$$

Therefore, the basalt eruption area S_1 can be calculated as

$$S_{1} = \frac{P_{1}}{P} 2\pi R^{2} (\sin \lambda_{2} - \sin \lambda_{1}) \times \frac{(\phi_{2} - \phi_{1})}{360}$$

where *R* represents Earth's radius, with an average value of 6371 km. The total area of basalt in a certain area (S_{total}) is the sum of the areas in each latitude.

$$S_{total} = S_1 + S_2 + S_3 + \cdots S_n$$

The results show that the total area of Cenozoic basalts in eastern China is 78525 \pm 3141 km² (51). The carbon stored at the bottom of the BMW, *C_{storage}*, can be calculated according to

$$C_{storage} = S_{total} \times h \times \rho \times C^{4+}$$

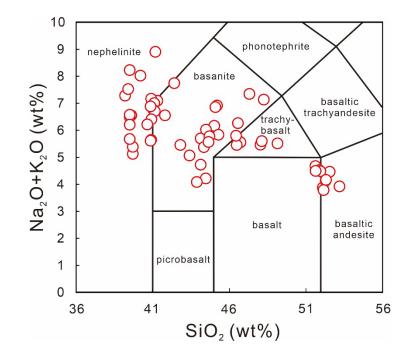
where h is thickness of EC basalt, ρ is the density of basalt, and C⁴⁺ is the amount of carbon required to elevate the average Fe³⁺/ Σ Fe value of MORBs to what is observed in EC basalts via reaction of $4Fe^{2+} + C^{4+} \rightarrow 4Fe^{3+} + C^0$. We assume that the FeO_{total} content of EC basalt is 12 wt%, the density of basalt is 2.9 g/cm³, and the thickness of EC basalt is ~10 km. To elevate the melt's Fe³⁺/ Σ Fe from a MORB-like value 0.14 (*18*) to 0.35, the average of studied EC basalts (< 50 Ma), the C_{storage} is roughly estimated to be 2400 Gt, which is four times of pre-industrial atmospheric carbon budget (Fig. S11). Note that the measured Fe³⁺/ Σ Fe of EC basalts may represent a minimum value, because Fe³⁺/ Σ Fe of EC basalts may be lowered as they ascended and percolated across the redox melting frontline (~250 km) through the redox melting reaction (4Fe³⁺ + C⁰ \rightarrow 4Fe²⁺ + C⁴⁺).

Supplementary Section 7

The data sources of HIMU lavas (St. Helena and Cook-Austral) used in Fig. 1 in the main text are listed in data file S1.

The arc basalt data used in Fig. 3 in the main text are taken from GEOROC (http://georoc.mpch-mainz.gwdg.de/georoc/Entry.html), with data sources listed in data file S2.

The best estimated 'most parental' $Fe^{3+}/\Sigma Fe$ values for OIB from each hotspot location used in Figs. 3 and 4 are from Brounce et al. (19), with original data from Hartley et al. (103), Shorttle et al. (24) (Iceland), Helz et al. (104), Brounce et al. (105), Moussallam et al. (32) (Hawaii), Moussallam et al. (20) (Erebus), Moussallam et al. (2) (Canaries and Cape Verde), Brounce et al. (19) and Gaborieau et al. (106) (Reunion). Elemental data source of OIB are provided in data file S3. In order to minimize crystal fractionation/accumulation effects, OIB data are filtered by using lavas with MgO between 8% and 16%.





Total alkali (Na₂O + K₂O) vs SiO₂ diagram for Cenozoic intraplate basalts from eastern China.

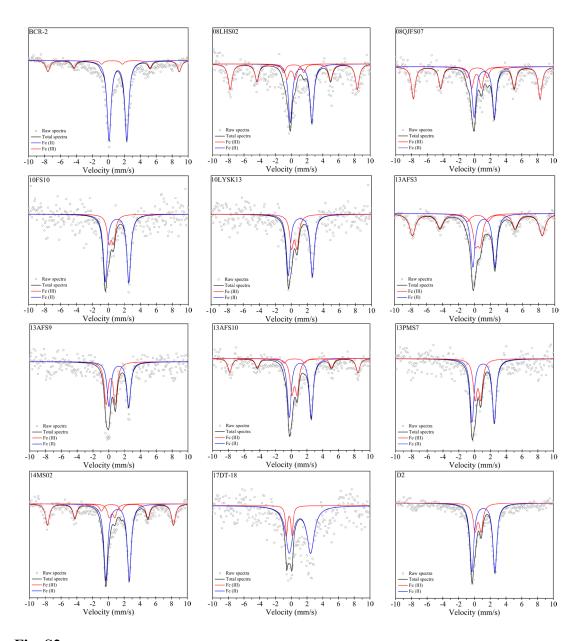


Fig. S2. Mössbauer spectra measured at 12 K on all analyzed samples.

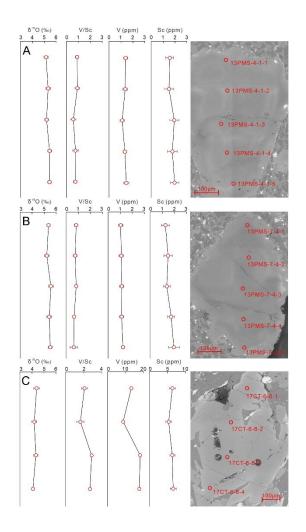


Fig. S3.

 δ^{18} O values, V/Sc ratios, V and Sc content of different positions in olivine phenocrysts for Cenozoic intraplate basalts from eastern China. Data are reported in Table S4.

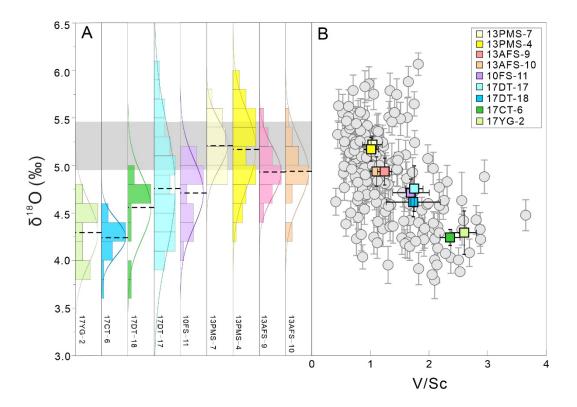


Fig. S4.

All analyzed olivine δ^{18} O and V/Sc in this study. (A) Probability distribution plots of oxygen isotope composition of olivine grains in each individual sample. The black dashed lines represent average δ^{18} O values for each probability distribution plot. Grey band represents the normal-mantle δ^{18} O value (5.18 ± 0.28 ‰) (21). (B) Covariation diagram of δ^{18} O versus V/Sc in olivine (n=198). Squares represent the average value of different samples. Error bars represent 2 s.e. Data are from Table S4.

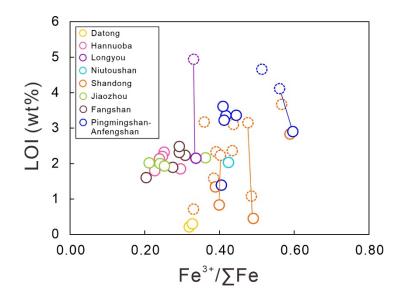


Fig. S5.

Measured Fe³⁺/ Σ Fe versus Loss of Ignition (LOI) for Cenozoic intraplate basalts from eastern China in different locations. The iddingsitized samples are shown in dashed outline. Fresh and iddingsitized samples from the same location are connected by lines. Note that the absence of correlation between Fe³⁺/ Σ Fe and LOI, and no significant difference between fresh and iddingsitized samples, suggest that surface weathering (*e.g.*, iddingsitization) does not have a large impact on the bulk rock Fe³⁺/ Σ Fe values.

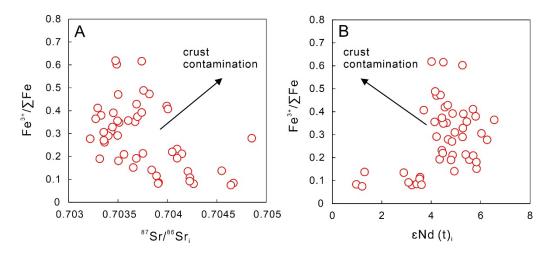


Fig. S6.

Corrected Fe³⁺/ Σ Fe values versus ⁸⁷Sr/⁸⁶Sri (A) and ϵ_{Nd} (t)i (B) for Cenozoic intraplate basalts from eastern China (EC). Sr-Nd isotopic compositions were reported in Wang and Liu (77) and Li et al. (16) and references therein. The relationships preclude crustal contamination or assimilation and fractional crystallization (AFC) processes as the cause of elevated Fe³⁺/ Σ Fe for the EC basalts.

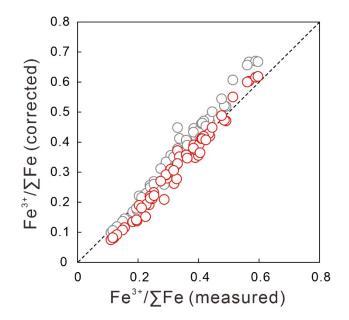


Fig. S7.

Olivine fractional crystallization or accumulation correction of $Fe^{3+}/\Sigma Fe$ for Cenozoic intraplate basalts from eastern China compared with the measured $Fe^{3+}/\Sigma Fe$ value. Data are from Table S1. Samples equilibrium with mantle olivine at Fo₉₀ are shown in red circles, and samples equilibrium with mantle olivine at Fo₈₅ are shown in grey circles. Correction details are in the Supplementary Section 2.

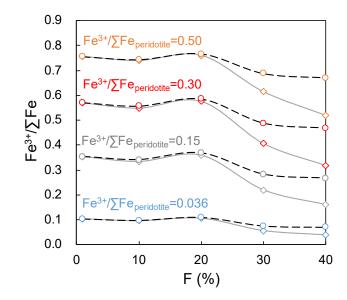


Fig. S8.

The Fe³⁺/ Σ Fe of melts generated by batch (black dashed line) and fractional (grey solid line) partial melting of peridotites with different Fe³⁺/ Σ Fe. The peridotite sources are assumed to have initial Fe³⁺/ Σ Fe of 0.036 (normal-mantle value) (28), 0.15, 0.30 and 0.50, respectively.

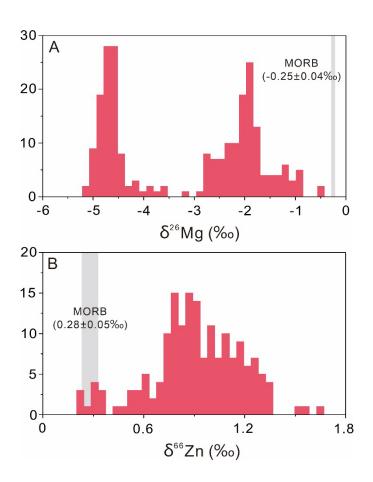


Fig. S9.

Magnesium (A) and Zinc (B) isotopic compositions of sedimentary carbonates compared to those of average MORB. δ^{26} Mg of sedimentary carbonates are compiled from Pokrovsky et al. (107), Geske et al. (108), Higgins and Schrag (109-111), Fantle and Higgins (112) and Blättler et al. (113). δ^{66} Zn of sedimentary carbonates are compiled from Pichat et al. (114), Liu et al. (115) and Sweere et al. (116). δ^{26} Mg and δ^{66} Zn of MORB shown in grey bar are from Teng et al. (41) and Chen et al. (117), respectively.

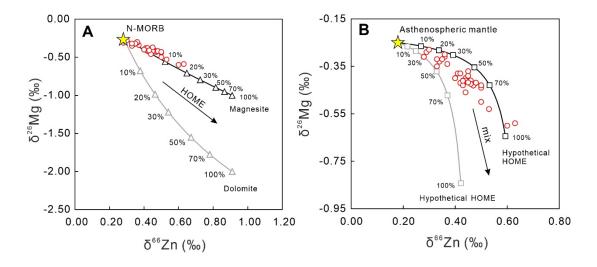


Fig. S10.

Plots of δ^{26} Mg against δ^{66} Zn for the intraplate basalts from eastern China, together with MORB-carbonate mixing (A) and asthenospheric mantle-HOME mixing model (B). Two carbonate species including magnesite (black lines) and dolomite (grey lines) are considered. Hypothetical HOME in (B) is formed by hybridization of 15% carbonate and 85% N-MORB. Modelling parameters are provided in Supplementary Table 7.

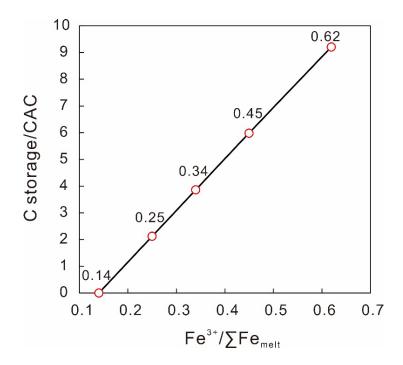


Fig. S11.

The total amount of carbon storage ($C_{storage}$) relative to the current atmospheric carbon (CAC) as a function of assumed average $Fe^{3+}/\Sigma Fe$ in Cenozoic intraplate basalts from eastern China. Computation details are in the Supplementary Section 6.

Legends for Table S1 to S7

Table S1. Wet-chemical Fe³⁺/Fe_{total} ratios for Cenozoic basalts from eastern China.

Table S2. Wet-chemical determination of FeO content in geological standards.

Table S3. Mössbauer spectroscopic measurements on samples at ~12 K and comparison with wet-chemical measurements.

Table S4. Oxygen isotope and V/Sc ratio of olivine in intraplate basalts from eastern China.

Table S5. The chemical compositions of modeled basaltic melts compared with those of molten basalt investigated by experiments and mid-ocean ridge basalt.

Table S6. The calculated density of three basaltic melts.

Table S7. Parameters used for mixing model.

Legends for data files S1 to S3

Data File S1 Data sources of HIMU lavas.

Data File S2 Data sources of arc basalts compiled from GEOROCK.

Data File S3 Data sources of OIB lavas from each hotspot locations.

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