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Formation of the world's largest REE deposit through protracted fluxing of carbonatite by subduction-derived fluids

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Rare Earth Elements (REE) are essential to modern society but the origins of many large REE deposits remain unclear. The U-Th-Pb ages, chemical compositions and C, O and Mg isotopic compositions of Bayan Obo, the world's largest REE deposit, indicate a protracted mineralisation history with unusual chemical and isotopic features. Coexisting calcite and dolomite are in O isotope disequilibrium; some calcitic carbonatite samples show highly varied $\delta^{26}\text{Mg}$ which increases with increasing Si and Mg; and ankerite crystals show decreases in Fe and REE from rim to centre, with highly varied REE patterns. These and many other observations are consistent with an unusual mineralisation process not previously considered; protracted fluxing of calcitic carbonatite by subduction-released high-Si fluids during the closure of the Palaeo-Asian Ocean. The fluids leached Fe and Mg from the mantle wedge and scavenged REE, Nb and Th from carbonatite, forming the deposit through metasomatism of overlying sedimentary carbonate.

Bayan Obo, located at the northern margin of the North China Craton (Fig. 1), is the largest light rare earth element (LREE) deposit in the world (Supplementary Figure S1 and Table S1), the largest niobium (Nb) and thorium (Th) deposit in China^{1–4}, and a major iron (Fe) deposit^{5,6}. The REE deposit is hosted by the H8 dolomitic marble of the Bayan Obo Group (Fig. 1)^{5,7}. In addition to the ore bodies, there are two main types of carbonatite dykes in the Bayan Obo ore district, dolomitic and calcitic, distinguished on the basis of the dominant carbonate mineral^{8,9}. Proposed models for the richness and genesis of the ore include carbonatite magmatism^{5,10–17}, alteration/metasomatism of sedimentary carbonate rocks by hydrothermal fluids^{2,14,18–25}, deposition of carbonates on the sea floor accompanied by simultaneous metasomatism^{6,26}, epigenetic processes related to Palaeozoic plate subduction²⁷, and a polyphase model involving multiple periods of alkaline magmatism, metamorphism and deformation and potentially subsequent infiltration of Caledonian-age fluids derived from subduction-related granitoids^{28–30}. The debate centres on the genetic relationship between the REE and Fe ore bodies and associated carbonatite dykes and sedimentary dolomite. Our new evidence suggests that the Bayan Obo deposit formed through protracted fluxing of carbonatite by fluids released from a subducting slab and their subsequent reaction with sedimentary carbonates.

Results

We have made an integrated geochemical study of key samples from the Bayan Obo ore and its host rocks, including analyses of whole rock chemical compositions and Mg, C and O isotope compositions of calcite and dolomite, *in situ* chemical analyses of minerals, and SHRIMP monazite U-Th-Pb dating of calcitic and dolomitic carbonatites, and ore-bearing dolomite. Major and trace element compositions of carbonatites and ore-bearing dolomite are listed in Supplementary Table S2. Mg, C and O isotopic compositions are listed in Supplementary Table S3.

The analyses show that the dolomitic carbonatite dykes have major and trace element compositions that are essentially the same as those of the ore bodies. In contrast, the calcitic carbonatite dykes have systematically higher REE and Sr contents and a wider range of Si, Fe and Mg contents^{18,19} (Figs. 2, 3a and 4, Supplementary Fig. S2, S3

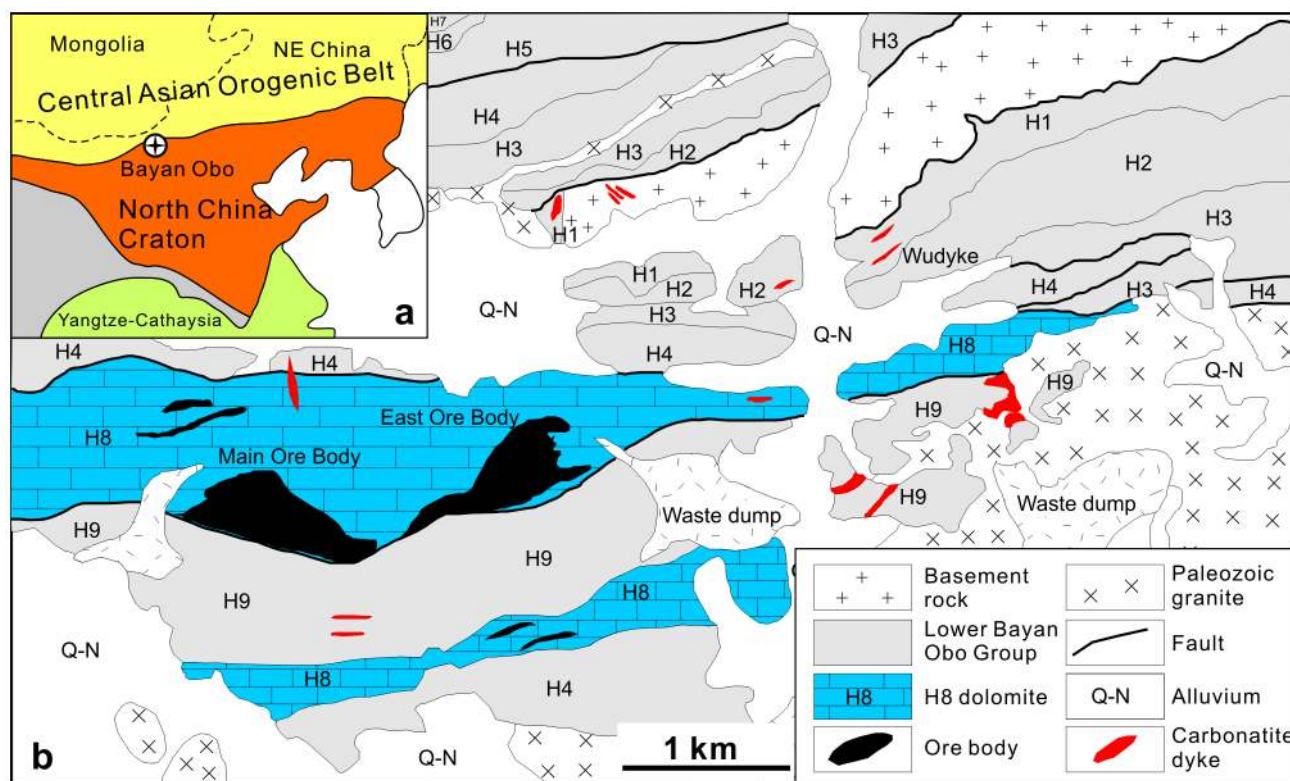


Figure 1 | The location of the Bayan Obo deposit and its geological setting. (a) Simplified map showing the location of the Bayan Obo deposit, the North China Craton, and the Central Asian Orogenic Belt, modified after Jahn *et al.*⁵⁸. (b) Sketch geological map of the Bayan Obo deposit and its tectonic setting, modified after Liu *et al.*³. The Bayan Obo giant REE-Nb-Fe deposit is located at the north margin of the North China Craton, close to the suture between the North China Craton and the Central Asian Orogenic Belt. An ophiolite belt has been identified ca. 50 km to the north of the Bayan Obo deposit.

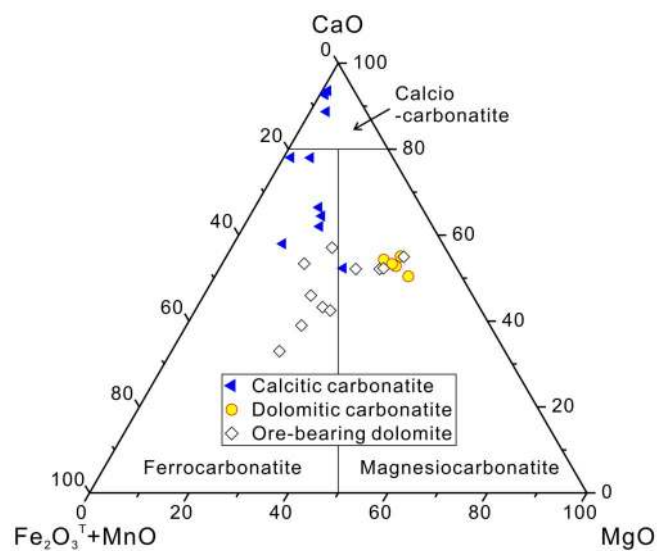


Figure 2 | Carbonatite classification plot of CaO-MgO-FeO + Fe₂O₃ + MnO⁹. Dolomite dykes have a close affinity to the REE ore bodies, both of which have systematically higher Fe and Mg than the calcitic carbonatite samples. Note that more than half of the samples from the calcitic carbonatite dykes plot in the ferrocarbonatite field. Considering that those samples were from the same calcio-carbonatite dykes, we prefer to classify these samples as calcitic carbonatite. Nevertheless, these indicate that the calcitic carbonatite dykes have also been metasomatised by Fe-, Mg-rich fluids, which leached REE, Nb and Th out of the calcitic carbonatite and resulted in ore-forming fluids.

and Table S2). Key element ratios such as Th/U, Nb/U, Th/Nb and Ce/Lu also demonstrate that the REE ore bodies have a closer affinity to the dolomitic carbonatites than to the calcitic carbonatites (Fig. 4).

The same affinity is demonstrated by the Mg isotopic compositions. The $\delta^{26}\text{Mg}$ values for the Bayan Obo ore bodies range from $-0.671 \pm 0.060\text{‰}$ to $+0.283 \pm 0.073\text{‰}$ (Supplementary Table S3, Fig. 3a, b), which is within the compositional range of the upper continental crust (-0.52 to $+0.92\text{‰}$, average -0.22‰)³¹, but distinct from the $\delta^{26}\text{Mg}$ values of sedimentary carbonates and present day seawater (-0.83‰)³². The dolomitic carbonatite dykes have $\delta^{26}\text{Mg}$ values ranging from $-0.195 \pm 0.061\text{‰}$ to $-0.458 \pm 0.073\text{‰}$, which plot within the field of ore body values. Most of the Mg isotopic compositions of the ore bodies can be explained by mixing between mantle-derived material ($-0.25 \pm 0.07\text{‰}$)³³ and calcitic carbonatite, with or without the involvement of upper continental crust (Fig. 3b, Supplementary Table S3).

Several calcitic samples from the same carbonatite dykes plot in the ferro-carbonatite and magnesio-carbonatite fields on the carbonatite classification plot⁹ (Fig. 2); some calcitic carbonatite samples display a negative correlation between Fe and Ce (Supplementary Fig. S3). Consistently, calcitic carbonatite samples with high SiO₂ and MgO contents have $\delta^{26}\text{Mg}$ close to mantle values, whereas those with lower SiO₂ and MgO contents have much lower $\delta^{26}\text{Mg}$ (Fig. 3a, b). The $\delta^{26}\text{Mg}$ values of the calcitic carbonatite dykes range from $-2.277 \pm 0.083\text{‰}$ to $+0.225 \pm 0.061\text{‰}$, distinct from the compositions of the ore bodies and dolomitic carbonatite dykes. Most of the calcitic dyke compositions plot about a mixing line (correlation coefficient -0.89) between the composition of the mantle (average $\delta^{26}\text{Mg} = -0.25 \pm 0.07\text{‰}$)³³ and the calcitic carbonatite sample (No. 07.104-2.5) that has the lowest Mg content and $\delta^{26}\text{Mg}$ value. In simple terms, the binary mixing line can be attributed either to addition of mantle Mg during the formation of carbonatite through recycling of

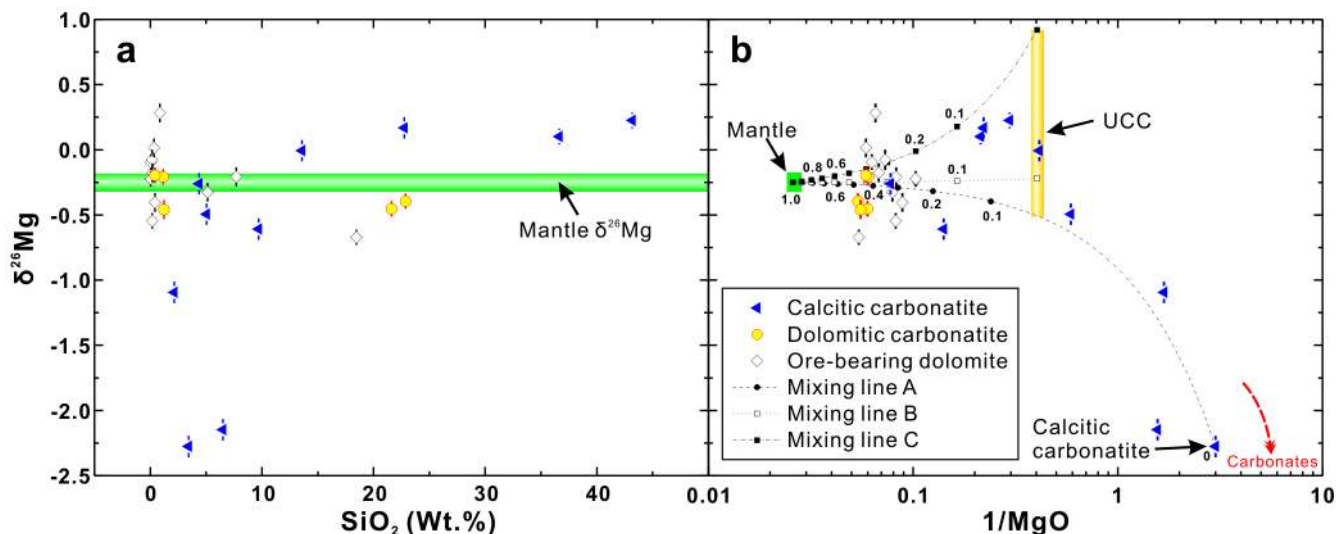


Figure 3 | Diagrams of (a) $\delta^{26}\text{Mg}$ versus SiO_2 , and (b) $\delta^{26}\text{Mg}$ versus $1/\text{MgO}$, for calcitic and dolomitic dykes, and ore bodies of the Bayan Obo deposit. Also shown are the $\delta^{26}\text{Mg}$ ranges of the mantle and the upper continental crust (UCC)^{31,33}. Sedimentary carbonates have $\delta^{26}\text{Mg} = -3.09 \pm 2.66\text{‰}$ ⁵⁹. The calcitic dykes have highly varied $\delta^{26}\text{Mg}$. Samples with high SiO_2 and MgO have $\delta^{26}\text{Mg}$ close to mantle values, indicating addition of SiO_2 and mantle MgO . Most samples plot about a mixing line between the mantle (average $\delta^{26}\text{Mg} = -0.25 \pm 0.07\text{‰}$)³³ and the calcitic carbonatite sample (No. 07.104-2.5) that has the lowest Mg content and $\delta^{26}\text{Mg}$ value. Four of the calcitic carbonatite samples have $\delta^{26}\text{Mg}$ higher than the mantle value, however, which cannot be explained by simple mixing between these two end-members. Material from the upper continental crust may also have been involved.

sedimentary carbonates, or to reaction between a calciocarbonatite with low initial $\delta^{26}\text{Mg}$ and Mg content, and subduction-released fluids with a mantle Mg isotopic composition. The covariation of $\delta^{26}\text{Mg}$ with SiO_2 favours the latter. All these strongly indicate reaction of calcitic carbonatite with Fe-, Mg- and Si-enriched fluids that leached out REE and simultaneously added Fe and Mg to calcitic carbonatite.

Consistent with their similar chemical compositions (Figs. 2 and 4), the ore bodies and dolomitic carbonatite dykes contain calcite and dolomite with similar O and C isotopic compositions, respectively. In contrast, although the calcite and dolomite in the calcitic carbonatite dykes have similar $\delta^{18}\text{O}$ to those minerals from ore bodies, they have systematically lower $\delta^{13}\text{C}$ (Fig. 5, Supplementary Fig. S4 and Table S3). Remarkably, the O isotopes are not in equilibrium between calcite and dolomite; there is a positive correlation between $\Delta^{18}\text{O}_{\text{Dol-Cc}}$ ($\delta^{18}\text{O}_{\text{dolomite}} - \delta^{18}\text{O}_{\text{calcite}}$) and $\delta^{18}\text{O}$ in the dolomite (Fig. 5). There is, however, no correlation between $\Delta^{18}\text{O}_{\text{Dol-Cc}}$ and $\delta^{18}\text{O}$ in the calcite (Supplementary Fig. S4). This is consistent with the disequilibrium being controlled by dolomitic components. Moreover, ankerite (Fe-rich dolomite) is a common REE-rich mineral in the Bayan Obo deposit. Studies of one ankerite grain (Fig. 6) show that its LREE contents range from 10 to more than 3000 times chondritic values. The REE patterns change dramatically from MREE-enriched in the centre to LREE-enriched near the rim (Fig. 6b). This is coupled with changes in the Fe content (Fig. 6c). Such a pattern can best be explained by hydrothermal metasomatism of carbonate by REE- and Fe-enriched fluids.

All these observations point to metasomatism of sedimentary dolomite by REE-, Si-, Mg- and Fe-enriched fluids with mantle $\delta^{26}\text{Mg}$ values, but $\delta^{18}\text{O}$ considerably lower than mantle values (continental origins). The most efficient way to mix sedimentary H8 carbonate with components from the mantle and the continental crust is metasomatism. Additional evidence for metasomatism is provided by the hydrothermal origins of both ore and gangue minerals^{2,21}, the abundant fluid inclusions³⁴ and lack of melt inclusions.

Knowledge of the age of mineralisation at Bayan Obo is essential for understanding its formation. Fifty-seven spots on 31 grains of monazite, an important ore forming mineral, were analysed for U-Th-Pb isotopes by sensitive high resolution ion microprobe

(SHRIMP). The Bayan Obo monazite has extremely low U (most 0.01–5.0 ppm) and low Th (most 1000–8000 ppm) contents, resulting in high to extreme Th/U ratios. As a consequence the measured Th-Pb dates are more precise than the U-Pb dates. The $^{208}\text{Pb}/^{232}\text{Th}$ dates of monazite range from 331 ± 3 to 758 ± 3 Ma, with the main cluster of dates at 440–380 Ma (Fig. 7).

This long mineralisation history coincides in time with the closure of the Palaeo-Asian Ocean³⁵ and is consistent with the presence of multiple generations of minerals^{2,19}. Those U-Pb dates that could be measured with reasonable precision cluster in the range 450–350 Ma, approximately coinciding with the major Th-Pb age group. The ca. 420 Ma peak is close to previously published Th-Pb isochron ages^{22,27} and a pyrite Re-Os isochron age³⁶, all much younger than the zircon U-Pb age of the carbonatite dykes (ca. 1.3 Ga)³⁷ and the Sm-Nd isochron ages of the ore bodies and carbonatite dykes (ca. 1.27 ± 0.10 to 1.34 ± 0.16 Ga)^{38,39}. Considering the very high LREE contents of the calcitic dykes and the very large analytical uncertainties, the Sm-Nd isochrons for the ore bodies are likely to be mixing lines. Mineral inclusions and trace elements in zircon indicate that 1.3 Ga is the age of the carbonatite magmatism.

Discussion

The Bayan Obo deposit is located very close to the Central Asian Orogenic Belt, formed by the closure of the Palaeo-Asian Ocean that started in the Neoproterozoic as indicated by the ages of associated ophiolites^{35,40} (Fig. 1). All the major chemical characteristics of the Bayan Obo deposit can be explained by protracted fluxing of Fe out of the mantle wedge and then REE-Nb-Th out of a calcite carbonatite pluton by subduction-released Si-rich ore-forming fluids that further reacted with sedimentary H8 carbonates, generating the giant mineral deposit (Fig. 8).

A large calcitic carbonatite pluton with high REE contents was emplaced at ca. 1.3 Ga as indicated by dykes that intruded into the Palaeoproterozoic Bayan Obo Group^{38,41,42}. Plate subduction during the closure of the Palaeo-Asian Ocean started in the Neoproterozoic³⁵ and lasted until the Carboniferous/Permian⁴³. Subduction-released fluids first induced serpentinisation as they passed through the uppermost part of the mantle wedge⁴⁴, scavenging Fe and Mg along the way. Subsequently those fluids, with

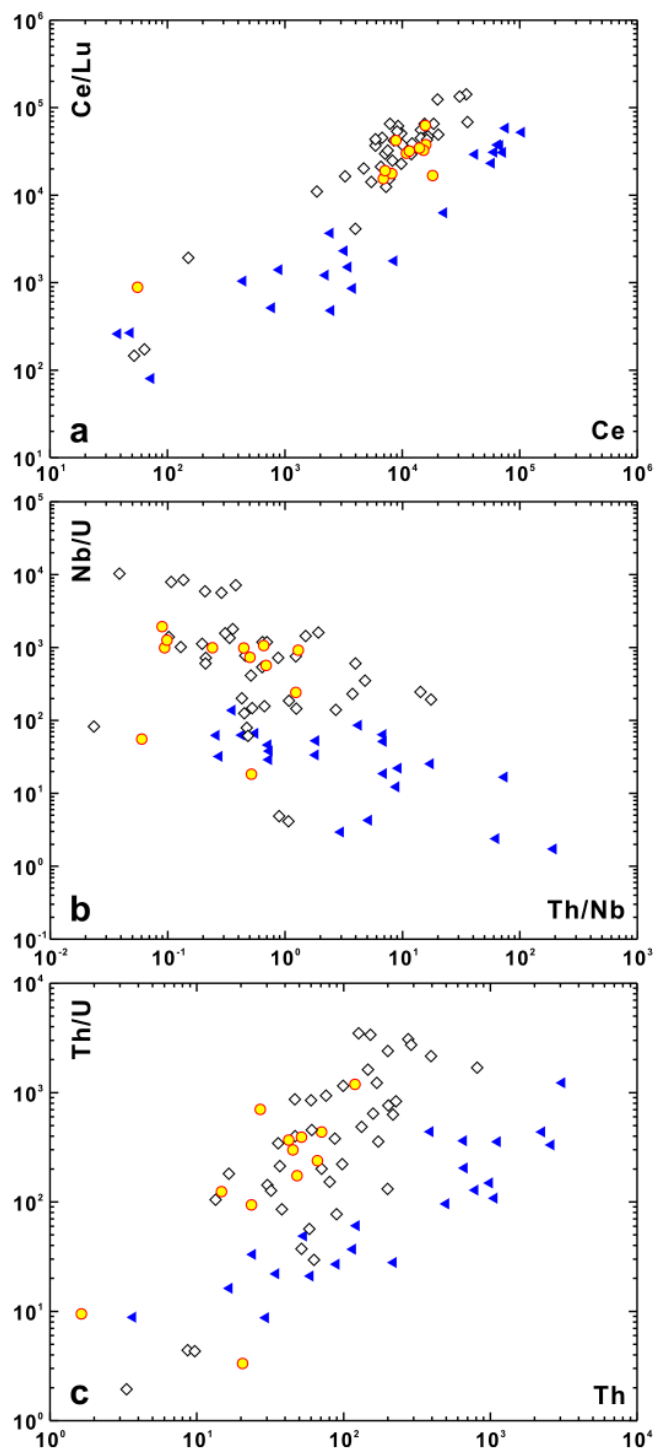
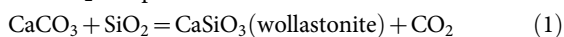


Figure 4 | Trace element discrimination diagrams of carbonates. The dolomitic carbonatite and ore bodies are quite similar to each other in different diagrams, indicating genetic connections. In contrast, the calcitic carbonatites have lower Ce/La and Th/U than the other two types of carbonates, at the same Ce and Th contents, respectively. They also have lower Nb/U ratios.

high Si, Fe and Mg contents, reacted with calcite carbonatite magma (through reactions similar to that illustrated in Equation 1), collecting REE, Nb, Th, and Sr and becoming ore-forming fluids with less SiO₂, but more CO₂ compared to normal subduction released fluids.



The formation of wollastonite (Equation 1) depends on pressure, temperature and XCO₂. For a high-Si fluid with low CO₂, the

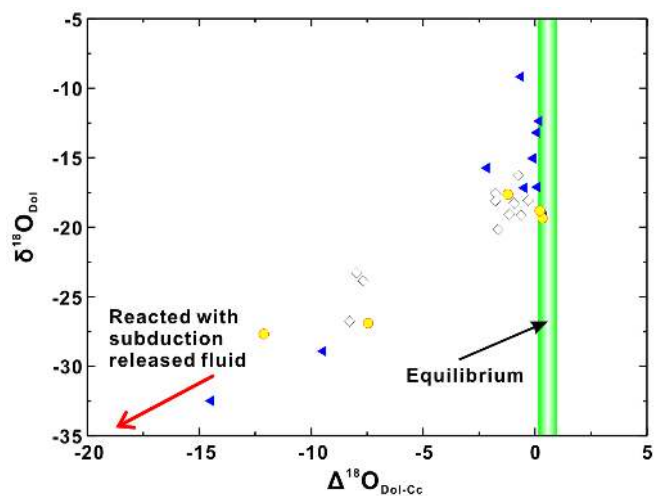
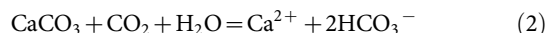


Figure 5 | Diagram of $\delta^{18}\text{O}$ versus $\Delta^{18}\text{O}_{\text{Dol-Cc}}$ in dolomite for calcitic and dolomitic carbonatite dykes, and ore bodies of the Bayan Obo deposit. The “positive correlation” between $\Delta^{18}\text{O}_{\text{Dol-Cc}}$ and $\delta^{18}\text{O}$ in dolomite and lack of correlation in calcite (Supplementary Fig. S4) indicates that the oxygen isotope disequilibrium between dolomite and calcite is controlled by dolomite. The lowest $\delta^{18}\text{O}$ in dolomite is much lower than the mantle value, the most likely candidate for which is subduction released fluids. Also shown is a bar illustrating the equilibrium $\Delta^{18}\text{O}_{\text{Dol-Cc}}$ at temperatures between 200 and 480°C⁶⁰.

reaction starts at ca. 450°C and >500°C, at 100 MPa and 500 MPa, respectively^{45,46}. Once the reaction starts, it releases CO₂, which in turn pushes the reaction temperature higher. CO₂ may also react with carbonate (Equation 2), which favours reaction (1) and the mobility of elements.



According to the regional geology, Bayan Obo was formed at depths of 10–20 km. Fluid inclusions show that the mineralisation temperature (the temperature after “hot” ore-forming fluids passing along fractures reacted with “cool” sedimentary carbonates) was ca. 420–480°C^{47,48}. Hence the ore-forming fluids were probably produced at temperatures considerably higher than 500°C. In this case, the wollastonite reaction (Equation 1) is likely to be the main reaction between subduction-released high-Si fluids and carbonatite that resulted in ore-forming fluids with high REE, Nb, Th and Fe.

Wollastonite has not been reported in the calcite carbonatite dykes however, possibly because those dykes were located at depths similar to the ore bodies and therefore at lower temperature (ca. 420–480°C)^{47,48}. Nevertheless, there is abundant wollastonite at Heinaobao, a dolomite unit to the southeast of the Bayan Obo that is commonly correlated with the H8 dolomite, indicating that the regional temperature was close to 500°C.

Ore-forming fluids transported upward through deep faults further reacted with sedimentary carbonates to form ore bodies with high REE, Nb, Th, Mg, Fe and Sr and caused the alteration (Supplementary Figure S5, e.g., humite, magnesioriebeckite) associated with the ore bodies and wall rocks. Given the high CO₂ in the ore forming fluids⁴⁷, reaction (2) was probably more pronounced than during the leaching process, promoting the channelisation of ore-forming fluids in the sedimentary carbonates and thus favouring mineralisation.

Such a leaching reaction might have started as early as ca. 750 Ma and peaked at 440–380 Ma, with several pulses in between, probably due to changes in subduction regimes. The mineralisation period is coincident with the closure of the Palaeo-Asian Ocean^{43,49}.

The Bayan Obo ore bodies have much higher F contents than the calcite carbonatite dykes, indicating that the ore-forming fluids had

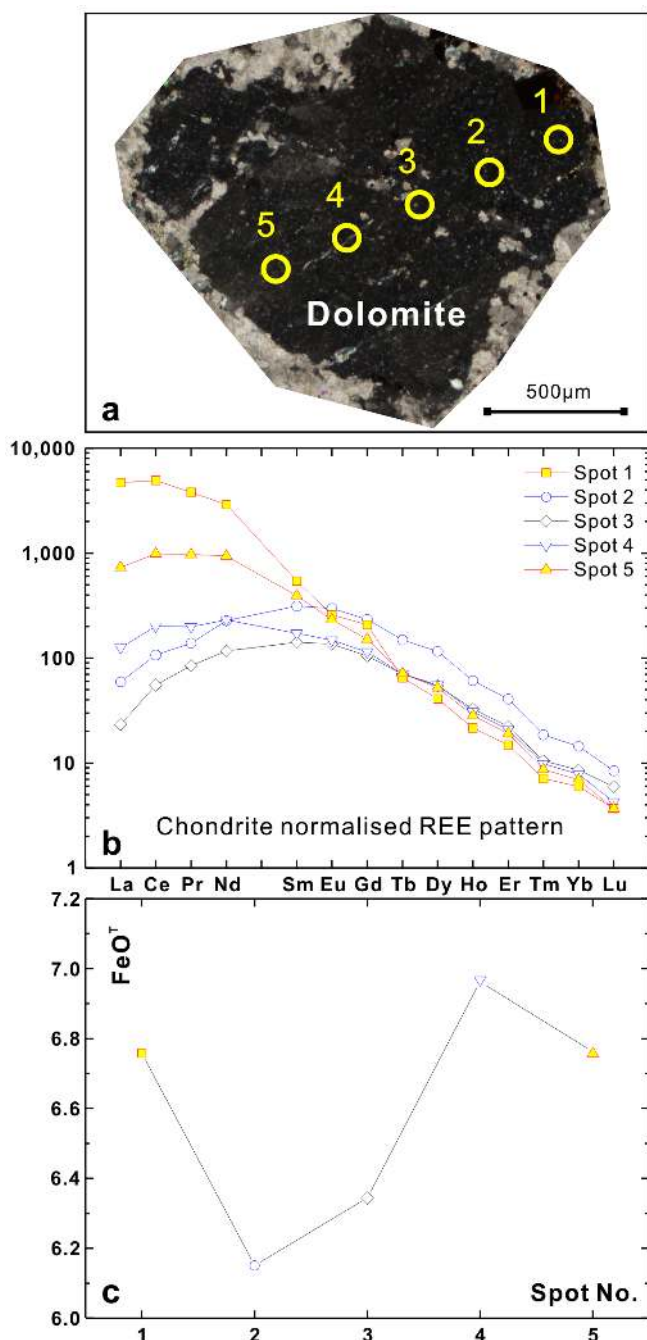


Figure 6 | Iron and REE contents across an ankerite grain from the ore body of the Bayan Obo deposit. Iron and REE contents are lower in the centre. Consistently, REE patterns also change systematically from the rim to the centre. These can plausibly be interpreted as the result of hydrothermal metasomatism of a calcite/dolomite grain by Fe-, Mg-, and REE-enriched fluids.

high F contents. This is consistent with the high F background in the region, as indicated by a fluorite belt in the North China Craton that is roughly parallel to the Central Asian Orogenic Belt. Fluorine is usually enriched in the far field of subduction zones. For example, there is a topaz volcanic belt roughly parallel to the subduction zone in the west of the Americas⁵⁰. This is because F is retained by phengite during plate subduction and transferred to depths up to 300 km, then subsequently released due to phengite decomposition⁵¹. This explains the high F content (as evidenced by abundant fluorite) of the Bayan Obo deposit.

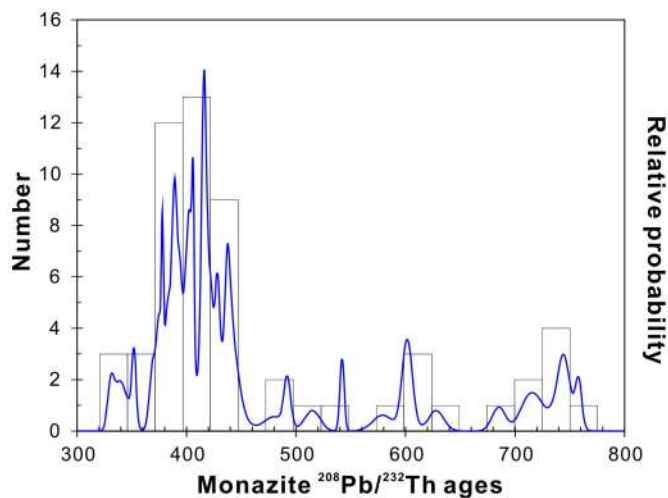


Figure 7 | Cumulative frequency diagram of monazite Th-Pb ages, showing several peaks. The largest peak appears at ca. 420 Ma, with several smaller ones corresponding to 330, 350, 490, 545, 600 and 745 Ma. Such an age spectrum indicates protracted mineralisation at Bayan Obo coincident with the closure of the Palaeo-Asian Ocean^{35,40,43}. Considering that the Bayan Obo deposit is located at the north margin of the North China Craton, and that there is an ophiolite belt ca. 50 km to the north of the deposit, the protracted mineralisation history suggests that the Bayan Obo deposit was related to the closure of the Palaeo-Asian Ocean.

Dolomitic dykes formed due to “leakage” of ore forming fluids out of the sedimentary carbonate, resulting in the dykes and ore bodies having identical geochemical characteristics (Fig. 2 and Supplementary Fig. S2).

This model is strongly supported by the survival of sedimentary structures, the presence of detrital quartz and algal fossil remains in the carbonates, the large distance (16 km) over which the REE ore bodies are distributed, and the hydrothermal origin of the ore and gangue minerals^{2,21} and fluid inclusions³⁴. It is also supported by the C and O isotopic compositions. Previous studies have shown that $\delta^{13}\text{C}$ in the H8 dolomitic marble ranges from -0.31 to -7.98% , with most of the samples having $\delta^{13}\text{C}$ values lower than those of sedimentary rocks. Similarly, the $\delta^{18}\text{O}$ of the H8 marble is very heterogeneous, ranging from near mantle (6.2‰) to sedimentary (25.7‰) values. The combined C and O isotopic compositions of the H8 samples fall in the field between those of mantle fluid and marine facies sedimentary limestone²¹.

Wang and others²⁷ proposed that Caledonian-aged subduction was the key factor that controlled the formation of the Bayan Obo deposit based on Palaeozoic U-Th-Pb ages. Their model has received little attention, however, because it did not consider the carbonatitic nature of the ore bodies. Many other models have attempted to reconcile the sedimentary and carbonatite characteristics of the ore bodies. For example, deposition of carbonates on the sea floor accompanied by simultaneous metasomatism^{6,26}, and metasomatism of sediments by mantle-derived fluids that had connections to carbonatite magmas²¹. The sea-floor deposition model does not explain why the mineralisation is much younger^{27,36} than the Proterozoic Bayan Obo Group⁵ and carbonatite³⁷. The model of sediment metasomatism does not explain the close association between carbonatite and the ore bodies. The carbonatite model is based on the high Sr and Nb/Ta ratios in the ore bodies^{21,52}. It is, however, not supported by the presence of abundant hydrous fluid inclusions and the lack of melt inclusions in the ore bodies⁴⁷. The alternative polyphase model proposed multiple periods of alkaline magmatism, metamorphism and deformation and potentially subsequent infiltration of fluids derived from subduction-related Caledonian granitoids^{28–30}. Our new dating

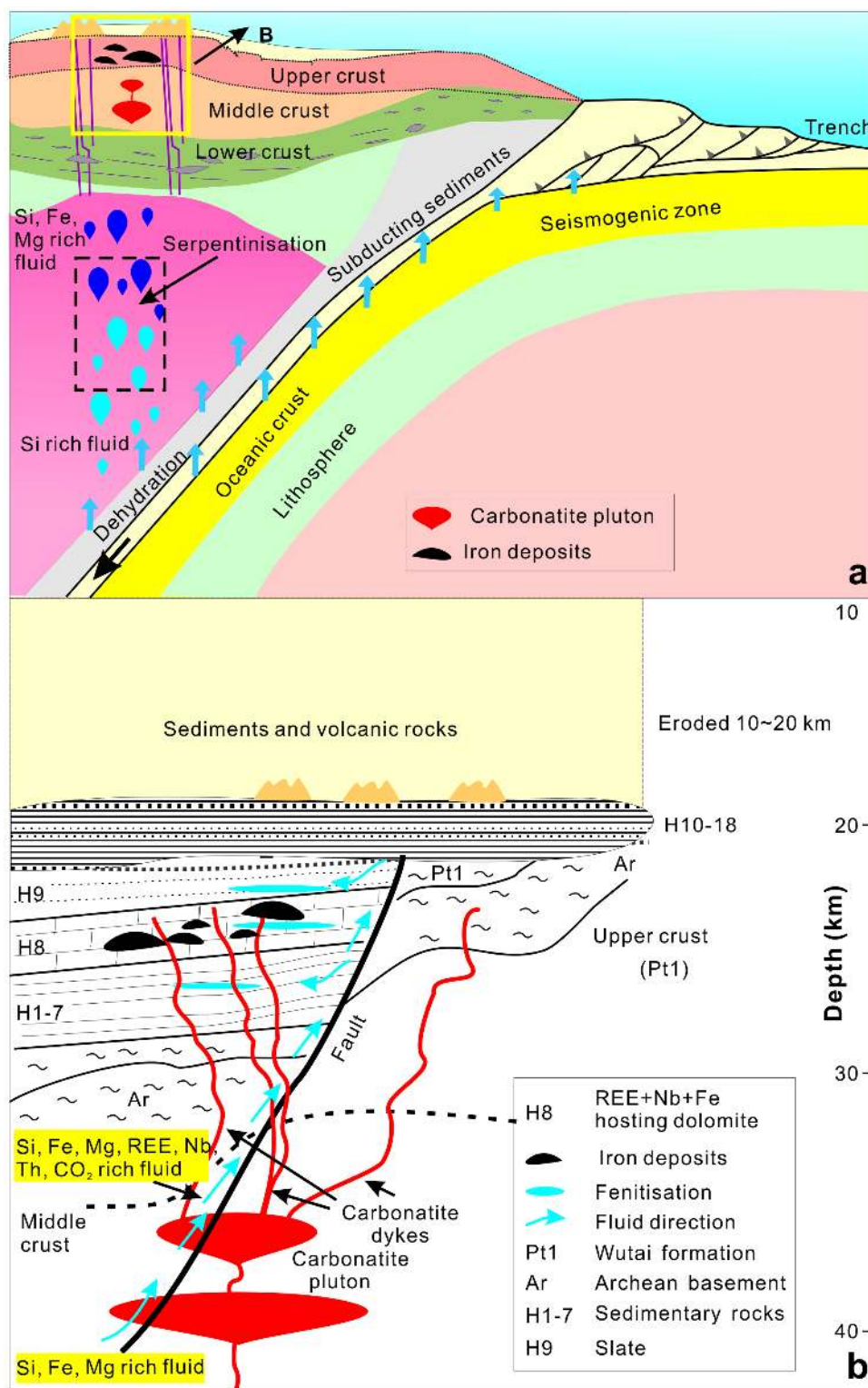


Figure 8 | Cartoon illustrating the fluxing model. Subduction releases high-Si fluids, which leached Fe and Mg from the mantle wedge through serpentinisation at temperatures lower than 720°C⁴⁴ and hydrothermal alteration. These fluids then react with a carbonatite pluton, leaching REE, Nb and Th out of the carbonatite. Finally, the ore-forming fluids ascend along fractures and react with H8 carbonates of the Bayan Obo Group, forming the giant REE, Nb, Th and Fe deposit.

results, however, show that the granitoids in the Bayan Obo region, many of which were previously assumed to be of Caledonian age, are in fact Permian (Supplementary Figure S6), much younger than the mineralisation.

Our model explains all the major, apparently paradoxical, features of the Bayan Obo deposit. Under this model, subduction-released

fluids leached Fe out of the mantle wedge during serpentinisation at shallow depths, which explains the large Fe deposit that is closely associated with the REE deposit. As the fluids ascended, they leached ore-forming elements (REE, Nb and Th) out of a deeply intruded calcitic carbonatite pluton that was highly enriched in LREE, as evidenced by the composition of the calcitic carbonatite dykes.



This process determined the REE patterns and initial Nd isotopic compositions of the ore bodies. As a consequence, the mineralised carbonate rocks have initial Nd isotopic compositions and primitive mantle normalised trace element patterns identical to those of carbonatite dykes^{21,38}.

There are areas within the H8 marble that have much lower REE contents, far below the cut-off grade of the deposit. In those places the REE patterns are typical of sedimentary carbonate²¹ (Supplementary Table S2 and Fig. S2). These areas are remnants of sedimentary carbonate that survived digestion by the ore-forming fluids, and now appear as xenoliths as described by previous authors^{38,53}. Ore-forming fluids reacted with sedimentary carbonate mainly via Equations 1, 2, providing the host structures for the ore bodies. Ore-forming fluids also reacted with other rocks of the Bayan Obo Group, especially along the margins of the ore bodies, due to enhanced release of CO₂ during the mineralisation reaction. These “reaction fronts” produced the features interpreted by previous authors³⁸ as indicating intrusive contacts.

Methods

Magnesium isotopes. Magnesium isotope analyses were carried out at the Isotope Laboratory of the University of Arkansas, Fayetteville, USA. All chemical procedures were carried out in a class 10,000 clean laboratory, equipped with class 100 laminar flow exhaust hoods⁵¹. Optima grade acids or distilled acids and Milli-Q® water with a resistivity of 18.2 MΩ·cm were used throughout the whole chemical process^{51,54}. In order to obtain at least 10 µg of Mg in solution for MC-ICP-MS analysis⁵³, approximately 2–20 mg of whole rock powder was dissolved in Saville screw-top beakers based on the Mg contents, with acid mixtures of concentrated HNO₃-HF (1 : 3, v/v), concentrated HNO₃-HCl (1 : 3, v/v) and concentrated HNO₃ in turn. Magnesium was separated by cation-exchange column chemistry using columns filled with Bio-Rad AG50W-X12 resin and eluted with 12N HCl, and successively AG50W-X8 resin (200–400 mesh) and with 1N HNO₃^{51,54}. The second step of the column chemistry procedure was conducted twice to ensure pure Mg solution recovery. The purified Mg solutions were introduced by a quartz cyclonic spray chamber to the plasma and Mg isotope ratios were determined by a Nu Plasma MC-ICP-MS in a low-resolution mode using a sample-standard bracketing technique in which ²⁶Mg, ²⁵Mg and ²⁴Mg isotopes were measured simultaneously in three separate Faraday cups: H5, Ax and L4, respectively⁵³. Magnesium ratio measurements for all sample solutions were repeated 4 times within a session. The Mg isotopic results are reported in standard δ-notation in per mil relative to DSM3⁵⁵

$$\delta^X \text{Mg} = 10^3 \times \left\{ \frac{\left(\frac{X \text{Mg}/^{24}\text{Mg}}{\text{sample}} \right) - 1}{\left(\frac{X \text{Mg}/^{24}\text{Mg}}{\text{DSM3}} \right)} \right\}, \text{ where X refers to 25 or 26.}$$

Carbon and oxygen isotopes. The δ¹³C and δ¹⁸O of carbonates with coexisting calcite and dolomite were analysed by an online automatic two-step method on a continuous flow Isoprime 100 stable isotope ratio mass spectrometer (IRMS) coupled with a MultiFlow device in the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, CAS. The first step, about 0.1–0.2 mg sample powder was flushed for 300 s by pure He (99.999%), dissolved with excess (5–7 drops) 102% H₃PO₄ in a sample vial at 35°C for 30 min to liberate CO₂ of calcite. The CO₂ was injected into a loop, then separated by a chromatographic column (Poraplot Q, 25 m*0.32 mm, Varian Ltd) at 90°C constantly and dried by Nafion membrane, and finally analysed by IRMS. The CO₂ in the vial was injected into the loop, separated, dried, and analysed three times. The second step, the CO₂ produced by calcite was flushed for 300 s twice by pure He, 3–5 drops of 102% H₃PO₄ was added to dissolve the residue, i.e. dolomite in the sample vial, then the temperature was increased to 90°C for 1 hour to achieve complete reaction and equilibrium. The CO₂ produced by dolomite was analysed in the same way as above. Samples were analysed in duplicate. The δ¹³C and δ¹⁸O results were analysed in standard delta notation (‰ units) relative to the Vienna Pee Dee Belemnite (V-PDB), and corrected to 25°C. Two Chinese isotopic standards GBW04405 and GBW04406 together with an international isotopic standard IAEA-CO-8 were analysed between each 5 samples. A three-point correction method ($r > 0.999$) both for δ¹³C and δ¹⁸O, based on the standards IAEA-CO-8, GBW04405 and GBW04406, was applied in this study, which is better than the two-point correction method⁵⁶ and can greatly reduce the uncertainties in the results. The results of duplicate analysis indicate that the external precision is better than 0.10‰ (1σ) for δ¹³C, and 0.15‰ (1σ) for δ¹⁸O.

In situ trace element analysis. Laser ablation ICP-MS (LA-ICP-MS) was used to analyse trace elements in the minerals. The LA-ICP-MS system consisted of an Agilent 7500a ICP-MS coupled with a Resonetics RESOLUTION M-50 ArF-Excimer laser source (λ = 193 nm). The laser energy was 80 mJ, and the frequency was 10 Hz, with an ablation spot 69 µm diameter. Both a double-volume sampling cell and Squid were used to improve the data quality. The ablated aerosol was carried to the ICP source with He gas. NIST 612 was used as an external calibration standard, and ⁴³Ca as

the internal standard. The detection limits of ICP-MS for trace elements are mostly better than 10 ppb, with uncertainties of 5–10%.

Monazite SHRIMP dating. Monazite grains from dolomite-type ore and aegirine-type ore were extracted at Hebei Institute of Regional Geology and Mineral Resources Survey. After jaw splitting and crushing, coarser grains of carbonatite rock samples were picked out and further crushed to about 250 µm. Monazite was separated using swing mill, followed by magnetic separation by isodynamic separator, and then density separation in tetrabromoethane and methylene iodide, followed by handpicking, then mounted in epoxy and polished down to half sections. The internal textures of the monazite grains were imaged using a light microscope and BSE. BSE investigations were carried out at the Electron Microscope Laboratory at Guangzhou Institute of Geochemistry, CAS, using a JEOL 8100. The working conditions were 15 kV accelerating voltage, 20 nA beam current and 11 mm working distance. Monazite was dated using the sensitive high resolution ion microprobe (SHRIMP II) at the Beijing SHRIMP Centre, Chinese Academy of Geological Sciences. Instrumental conditions and data acquisition procedures for monazite have been described by Williams et al. (1996)⁵⁷.

Whole rock chemical analysis. Major element contents were determined by Rigaku 100e X-ray fluorescence for SiO₂ and by Varian Vista-PRO ICP-AES for the other elements. Trace element concentrations were analysed by Agilent 7500a ICP-MS. Both tests were conducted in the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences.

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Author contributions

W.D.S. designed and initiated the research. Y.L.L., M.X.L., W.D.S., X.Y.Y. and X.D. contributed to the field works. M.X.L. and F.Z.T. analysed the Mg isotopes. M.X.L., L.H.X., W.F.D. and G.J.W. worked on the C and O isotope analysis. Y.L.L. and I.S.W. conducted the monazite Th-Pb dating. M.X.L. completed the other analyses and plotting of all the figures. W.D.S., M.X.L., I.S.W. and F.Z.T. prepared the manuscript.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

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