Oxygen isotope ($\delta^{18}O$, $\Delta^{17}O$) insights into continental mantle evolution since the Archean

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Oxygen isotopic ratios are largely homogenous in the bulk of Earth’s mantle but are strongly fractionated near the Earth’s surface, thus these are robust indicators of recycling of surface materials to the mantle. Here we document a subtle but significant ~0.2‰ temporal decrease in $\delta^{18}O$ in the shallowest continental lithospheric mantle since the Archean, no change in $\Delta^{17}O$ is observed. Younger samples document a decrease and greater heterogeneity of $\delta^{18}O$ due to the development and progression of plate tectonics and subduction. We posit that $\delta^{18}O$ in the oldest Archean samples provides the best $\delta^{18}O$ estimate for the Earth of 5.37‰ for olivine and 5.57‰ for bulk peridotite, values that are comparable to lunar rocks as the moon did not have plate tectonics. Given the large volume of the continental lithospheric mantle, even small decreases in its $\delta^{18}O$ may explain the increasing $\delta^{18}O$ of the continental crust since oxygen is progressively redistributed by fluids between these reservoirs via high-$\delta^{18}O$ sediment accretion and low-$\delta^{18}O$ mantle in subduction zones.
Earth’s peridotitic mantle is the predominant reservoir of the planet, largely controlling elemental and isotopic mass balances of lithophilic elements and their isotopes planet-wide. Furthermore, the temporal evolution of the mantle may exhibit large impacts on the lithosphere, hydrosphere, and atmosphere however this topic remains unexplored.

The formation of the mantle is due to the accretion of Earth from different types of meteorites and planetesimals at 4.56 Ga, followed by its quick segregation from the iron-rich core. Perhaps the late and most significant episode of Earth’s accretion was the Giant Impact at 4.44 Ga when a Mars-sized object Thea collided with a differentiated Earth to expel material in the close gravitational proximity of the Earth forming the moon. The composition of Thea with respect to its major elements and isotopes (e.g., oxygen) was not dramatically different from that of the Earth.

The magma oceans that followed the collision further homogenized the mantles of both the Earth and the moon. Their subsequent geologic histories, however, were dramatically different as the moon is a smaller body that underwent pervasive hydrothermal exchange with seawater, which interacted with rocks on the surface. This difference can be seen, for example, in the δ18O values, centers around the initial difference and the degree of mixing between Thea, moon, and the Earth after the Giant Impact.

It is abundantly clear that the surface of the Earth was covered by oceans since the 4.4 Ga. As the basaltic crust was largely submarine, it interacted with seawater both at low and high temperatures. Oxygen isotopes may be the best and most straightforward tool in addressing the effects of water-rock interaction and recycling of surface-exposed materials. In the modern world, oceanic crust, created at mid-ocean ridges (MOR), undergoes pervasive hydrothermal exchange with seawater, leading to heavy δ18O (+7–13‰) at the top in pillow basalts and lower δ18O (+2–5‰) at the bottom in gabbros and peridotites. Olivine with higher and lower δ18O than the average olivine phenocrysts from mantle-equilibrated MOR basalts has been found in many island arcs around the world and attributed to the dehydration or melting of this altered oceanic crust during subduction. Eclogites that represent metamorphosed basalts in subducting slabs display a similar range of δ18O values, suggesting that hydrothermally altered slabs were subducted in the past at least since 2.5 Ga and perhaps as early as 3.0–3.2 Ga, a time window when eclogitic diamonds became prevalent over peridotite.

The higher temperature of the Hadean and early Archean mantle leads to a higher degree of mantle melting and precludes modern-style plate tectonics from a physical point of view, with its subduction and crustal recycling driven by the transformation of basaltic crust into dense eclogites. The time of initiation of plate tectonics on Earth is a topic of current debate. The transition likely happened in the mid-to-late Archean but the style of the earliest Archean tectonics may have been very different from that of today. It could have been on-off, with limited subduction surrounding big mantle swells or dominated by “sagduction” or vertical lithospheric delamination due to the predominance of plume-related activity. In such regimes, progressive accretion of basaltic lavas on the surface and delamination of the deep lithosphere results in a limited amount of recycling of the surface-altered material (e.g., with respect to δ18O and other proxies) into the convecting mantle. Shallow flat subduction or plate stacking would also result in limited exchange.

With documented evidence of accretion of the first supercontinent, Kenorland by 2.5 Ga, comes evidence of large lateral continental migrations and continental collisions, and modern-style subduction under the continents. Subduction is capable of accreting sediments and efficient delivery of surface-altered materials via melts and/or fluids, with both low- and high-δ18O, into the mantle and directly under the continental lithosphere. It follows, therefore, that the early Archean subcontinental mantle could have been less affected by subducting slabs, i.e., be more similar to lunar rocks, thus more closely reflecting the BSE. Finally, the earliest CLM (at least pre-3.8 Ga) may not be preserved because the Earth’s earliest lithosphere went through a major resurfacing process in Eoarchean as indicated by Hf isotopes in zircons.

Of independent and particular importance is the question of potential differences between the Earth’s earliest mantle, represented by xenoliths (fragments) of Archean age in volcanic rocks, and younger mantle samples. As the Archean mantle was 100–200 °C hotter than today, degrees of shallow mantle melting were greater (up to 40%) leaving behind extremely depleted harzburgites. As these highly refractory residues were Fe-depleted, they were less dense and accumulated to form the rigid and stagnant keels of buoyant Archean continental lithosphere. This difference can be seen, for example, in the distinct composition (e.g., olivine Mg#, defined as Mg/(Mg+Fe)) of Archean and modern peridotites. Formation and subsequent growth of the CLM and continental keels involve imbrication upon collisions of depleted and buoyant subducted oceanic lithosphere (including melt depletion directly at subduction settings followed by slab delamination) and thickening by compression around existing continental margins or subarc settings. It can thus be expected that CLM rocks, like Earth’s surface rocks, have different ages and details of chemical and isotopic composition related to their age and mode of origin. However, only recently have we started paying attention to this heterogeneity with respect to many elements and isotopic systems. Oxygen, the most abundant element on Earth should in theory reflect these changes.

Nonetheless, for the past ~30 years, the δ18O values of peridotite xenoliths from many tectonic settings have been inferred to be roughly uniform (within analytical error ~±0.1‰) irrespective of age, tectonic setting, bulk composition, and mineralogy (e.g., spinel vs garnet facies, fertile vs. refractory) ever since new laser
fluorination methods to generate an expansive dataset of global peridotites were first employed\textsuperscript{15}. Later studies of even strongly metasomatized, hydrous (amphibole-bearing) peridotites reported values within the canonical mantle ranges\textsuperscript{33}. Previous studies, including those employing secondary ionization mass spectrometry (SIMS) (within \( \pm 0.2\% \) precision), found a range from 5.0 to 5.5\% for olivine from different peridotite xenoliths, attributed to a subtle diversity of depletion/enrichment processes, but detected no covariation of \( \delta^{18} \text{O} \) with modal or chemical composition, settings, or age\textsuperscript{34,35}.

Laser fluorination, with its error on the order of 0.01–0.08\%, continues to be the most precise method to resolve small 0.1–0.3\% differences in \( \delta^{18} \text{O} \). The analytical effort and a dataset presented here for 104 individual mantle xenoliths spans 13 years but are based on a single set of standards, analytical methodologies, and normalization procedures (Supplementary Table 1) in a single lab of the University of Oregon thus avoiding inter-laboratory standardization/analytical \( \delta^{18} \text{O} \) corrections that are important to recognize small trends. We report data for all samples that came to the lab without selection bias. These are well-characterized xenoliths with available modal, petrographic, and chemical data pertinent to the depletion/enrichment events (Mg\#, Al\textsubscript{2}O\textsubscript{3}, CaO) as well as equilibrium temperatures\textsuperscript{36–41}, and references in the supplementary). These samples are not uniformly distributed geographically, because of explosive volcanic eruptions: kimberlites and alkali basalts that can fragment the CLM and can carry mantle xenoliths to the surface require volatile-rich magmas. These, however, span many tectonic settings and regions on Earth, and occur above hot spots, at continental plate boundaries, and rift zones where explosive eruptions rapidly carry pieces of the mantle to the surface at rates of meters per second (e.g. ref. \textsuperscript{42}). This rapid transport prevents extensive chemical and isotopic exchange between the host melt and the xenoliths, especially for major elements including oxygen.

Finally, CLM fragments are much easier to collect than loose pyroclastic facies of volcanic eruptions than in magmas. These, however, span many tectonic settings and regions on Earth, and occur above hot spots, at continental plate boundaries, and rift zones where explosive eruptions rapidly carry pieces of the mantle to the surface at rates of meters per second (e.g. ref. \textsuperscript{42}). This rapid transport prevents extensive chemical and isotopic exchange between the host melt and the xenoliths, especially for major elements including oxygen.

Importantly, the differences between the Archean and Proterozoic olivine are observed not only globally but also in two kimberlite pipes in Siberia (Udachnaya and Obnazhennaya) (Fig. 1a)\textsuperscript{37,40}. Olivine modal abundance in our predominantly harzburgitic dataset stays nearly constant at 76 ± 6\% from 3 Ga to 2 Ga. Mg\# in our dataset displays an overall decrease from 0.93 to 0.94 in the Archean-early Proterozoic to ≤0.92 after that, consistent with greater melting degrees and pressures for the ancient mantle\textsuperscript{20,29}. The last equilibration temperatures estimated with the Ca-in-Opx thermometer are lower for the higher-\( \delta^{18} \text{O} \) Archean cratonic xenoliths than for off-craton ones but display no trend vs. age (Supplementary Table 1). Different temperatures of storage do not have any \( \delta^{18} \text{O} \) effect on the bulk, but colder peridotites would have lower \( \delta^{18} \text{O}_{\text{Olivine}} \) and higher \( \delta^{18} \text{O}_{\text{Opx}} \) values (greater \( \Delta^{18} \text{O}_{\text{Opx-Olv}} \), Fig. 3). The lower temperature should result in lower (not higher) \( \delta^{18} \text{O}_{\text{Olivine}} \) values of olivine at identical \( \delta^{18} \text{O}_{\text{Opx}} \) at identical \( \delta^{18} \text{O}_{\text{Olv}} \) for the Archean olivine commonly stored in colder conditions of thicker continental roots, and further decrease it for hotter recent samples, amplifying the temporal trend for olivine.

To explore the complexity of the recovered trends further, we performed thermodynamic calculations of the effects of melt depletion during mantle melting and its effects on residual harzburgite assemblage (Fig. 3).

**Mantle melting and \( \delta^{18} \text{O} \) value of the starting peridotite.** Performed modeling of bulk, fractional, and fluxed melting of original tholeiitic peridotite reveals small associated oxygen isotopic effects on coexisting minerals, melt, and remaining residue bulk solid (Fig. 3). As the basaltic melt is 0.4–0.7\% higher in \( \delta^{18} \text{O} \) than the bulk\textsuperscript{15}, due to the predominant removal of higher \( \delta^{18} \text{O} \) pyroxenes upon basalt production during peridotite melting, fractional melting with the removal of 30\% of melt leads to a 0.12\% decrease in the remaining bulk harzburgitic residue \( \delta^{18} \text{O} \) values. The 45\% melt removal and production of dunite residue, carries its 0.19\% \( \delta^{18} \text{O} \) depletion. In addition, the noticeable and counter-intuitive feature of the peridotite melting process that has not been discussed previously to our knowledge is that the \( \delta^{18} \text{O}_{\text{Olivine}} \) value increases during the formation of these melting residues (harzburgite and dunites), as \( \delta^{18} \text{O}_{\text{Olivine}} \)
**Fig. 1** Evolution of oxygen isotopes in lithospheric continental mantle (CLM). Temporal trends of $\delta^{18}O$ olivine (a, b), orthopyroxene and bulk (b), and CLM corrected for melt depletion (b, c) in studied mantle nodules. Bulk is computed based on modal mineral abundances and $\delta^{18}O$ values of olivine and orthopyroxene (T Supplementary Table 1). Zircon from the Archean Kaapvaal cratonic mantle is from ref. 50, and zircon and basalts from the moon are from refs. 12, 51, lunar mantle estimate is based on zircon, olivine, and basalts (see the text). Notice decreasing trends (95% conf. interval error envelope in line fit) and inbox diagrams.

**Fig. 2** Locality-averaged $\delta^{18}O$ values for the studied samples of olivine (Ol), bulk, and reconstructed original undepleted peridotite (see Fig. 3). Line fit statistics indicate decreasing trends.
becomes closer to the bulk values while its modal proportion increases. This simple behavior of oxygen isotope repartitioning during peridotite melting accounts for small 0.05–0.1‰ corrections due to the melt removal effects allowing reconstruction of the original peridotitic bulk before melting. This estimation of approximate melt depletion is given in Supplementary Table 1 and is based on Al₂O₃, MgO, and Mg# by using the experimental data of ref. 29. It leads to ~45% melt extraction estimates for dunites and lowest-Al (<0.5) harzburgites, 40% for low-Al, high-Mg# (>0.952) harzburgites, 30–40% for Proterozoic harzburgites with 0.5–1% Al₂O₃, 20–25% for moderate-Al harzburgites, 30% to all Cenozoic Avacha harzburgites (28% to those with 0.8% Al₂O₃). Although estimates of the melting degrees are likely accurate to ±5–7%, we consider them sufficiently robust because associated effects on δ¹⁸O reveal to 6.1–7.3‰ in equilibrium with the ambient assemblage. The upper bound of the melt fractionation triangle is computed by assuming decreasing δ¹⁸O from 7.3‰ to 6.1‰, while the lower bound assumes that the hydrous melts maintain a constant high δ¹⁸O= 7.3‰. Notice that melt depletion results in lowering bulk δ¹⁸O, but it also results in higher modal olivine and the δ¹⁸O values which are higher (closer to the bulk), while δ¹⁸O_Opx is also higher; Δ¹⁸O_Opx-Ol are constant. b Effect of melt depletion along the melting path shown in (a) for δ¹⁸O_{Opx} and δ¹⁸O_{bulk}. Notice the nearly linear change. Upon melt extraction, δ¹⁸O_{dunite} < δ¹⁸O_{harzburgite} < δ¹⁸O_{Lherzolite}. Cooling will not affect δ¹⁸O_{bulk} (blue horizontal lines) but will increase Δ¹⁸O_{mineral-mineral} fractionation as is shown. c Thin sections of samples showing enriched and depleted harzburgites that lost melt, and the final residual assemblage is olivine-richer. The horizontal width is 3 cm.

Comparison with other datasets. The decreasing olivine δ¹⁸O trend that we observed made us search for similar trends in other published datasets, of which ref. 13 is the most comprehensive and done in the same lab. When assigning ages to their xenolith suites, based on studies of similar xenoliths from the same or analogous age and tectonic provinces (Supplementary Table 3), which has not been done before, we observe a trend similar to ours (Fig. 1 and Supplementary Fig. 2): decreasing δ¹⁸O_{Olivine} and δ¹⁸O_{Bulk} values and constant or even decreasing δ¹⁸O_{Opx} values.

We experimented with an alternative age assignment to the samples studied here and to the dataset in ref. 13, by simply using model formation ages of the host lithosphere (e.g., ref. 46 and Supplementary Figs. 1 and 2). This results in similarly decreasing trends, signifying the conclusion that the obtained: subtle temporal trends are not fortuitous results of age assignments.

The average for δ¹⁸O_{Olivine} in our entire datasets (5.224 ± 0.120, s.d., n = 174) is heavier by 0.04‰ than that for data presented in ref. 13, which we attribute to different sample suites and small differences in standardization. The computed average bulk values of 5.34 ± 0.13‰ are identical to ref. 13. We thus consider the average values of the two datasets as compatible and provide the best current estimates of the δ¹⁸O in the average lithospheric.
mantle (Supplementary Table 4). Below we further consider its evolution.

The 5.37‰ value for Archean olivine and 5.44‰ bulk value for mean Archean refractory peridotite of our dataset with the average 79% modal olivine and 16% modal orthopyroxene enables correction for a decrease in δ18O due to prior melt depletion as is explained in Fig. 3a, b. Translating this harzburgitic bulk into a typical original lherzolitic assemblage of 56% olivine and 26% orthopyroxene30 leads to a 0.12‰ increase in the value of the original lherzolitic bulk peridotite. We thus obtain a value of 5.57‰ as the best estimate of the primary mantle source (Fig. 1c) that characterizes the original BSE prior to melting in the Eocene. The olivine δ18O value of 5.37 ± 0.07‰ (1 s.d., n = 20) recorded in the Archean olivine would stay the same and may thus reflect the best estimate for olivine in the BSE.

### Triple oxygen isotopes

Triple oxygen isotope analyses of a selection of olivines (Fig. 4 and Supplementary Table 2) yield an overlap in values: Δ17O, bulk = −0.047 ± 0.011‰ (n = 9) for Archean vs −0.051 ± 0.010‰ (n = 12) for the early-Paleoproterozoic samples. The value for San Carlos Olivine run as standard, likely sampling younger off-craton Phanerozoic (≤1.8 Ga) mantle of N America46, measured in the University of Oregon and two other labs are −0.051‰17. Vein orthopyroxenes with minor amphibole from the Kamchatka arc, most likely formed due to subduction fluid/melt percolation48, yield a mantle-like value of −0.052 ± 0.005‰. Modeling demonstrates that fluxing with fluids with any reasonable δ18O (0 to +10‰) or Δ17O (+0.02 to −0.02‰) values will have a far greater impact on δ18O than on Δ17O, resulting in largely constant mantle-like Δ17O. Our data confirm the recent result in ref. 49 on limited Δ17O mantle ranges.

### Earth and Moon initial δ18O values: BSE = BSM

Significant attention has been recently paid to recognizing small Δ17O differences between the Earth and the moon, pertinent to the original Δ17O composition of Thea and the degree of homogenization of magma ocean, as well as the late-veenere Δ17O composition3–6,49. However, the δ18O value of the earth’s mantle and its predominant rock on earth, peridotite has not been revisited since 199413. This work fills this gap in an attempt to reconstruct the original BSE oxygen isotopic values, and we show here that it is higher than commonly assumed and is closer to that of the moon at 5.57‰ (Fig. 2).

Constraining δ18O for mantle older than 3.0–3.5 Ga is hampered by the lack of dated peridotites and unaltered olivine, formed at the time. Here, we use crustal zircon as a proxy for mantle olivine, since zircons of such age exist in mantle-derived crustal rocks, survive alteration, and because zircon-olivine O isotope fractionation at mantle temperatures is very small and is well-constrained (0.1 ± 0.1‰50, see below). For example, Kaapvaal craton zircons of the ~3.2 Ga Archean age exhibit the range of 5.32 ± 0.17‰12. Lunar zircon of presumably 4.4–4.5 Ga age has δ18O of 5.61‰12, these values are 0.3‰ heavier than typical terrestrial mantle zircons (5.3%30,51), most of which are Phanerozoic. The δ18O composition of typical 4.3–3.8 Ga lunar basalts and zircons can be used to estimate the δ18O value of the lunar (and coeval terrestrial) mantle by a simple isotopic mass balance approach involving computing the CIPW mineral norm of basalts, taking a weighted average of δ18O(CIPW mineral – zircon fractions) using published fractionation factors (14,15,50 at assumed temperatures, see Fig. 3). Such computation results in Δ18O(lunar basalt-peridotite) of 0.02 to 0.12‰ at 1400–1450°C by targeting common lunar basaltic magma types with lower values being characteristic for high-Ti and higher for low-Ti basalts. As lunar zircons are lighter by 0.08–0.09‰ than lunar basalts12, the Δ18O(lunar zircon-peridotite) is 0.01–0.02‰, indicating essentially that δ18O(lunar zircon) is identical to δ18O(peridotite). Therefore, the lunar zircon plotted in Fig. 1 serves as a very good proxy for the lunar (and perhaps terrestrial) mantle at 4.3–3.8 Ga.

Another way to resolve these small but important differences in lunar and terrestrial peridotites is to directly consider terrestrial and lunar basalts derived from their respective mantles. Typical 4.3–3.8 Ga low-Ti lunar basalts are 5.69‰, 0.12‰ heavier than the mode of modern terrestrial MORB (5.57‰, ref. 12). There are no coeval and unaltered 4.3–3.8 Ga terrestrial basalts to precisely compare with lunar basalts, but lunar basalts can be used to suggest that coeval terrestrial basalts of an equivalent degree of mantle melting of the Hadean age, were also higher in δ18O.

The higher δ18O values for lunar zircons and basalts directly support the conclusion of our present study that mantle peridotites (parental to basalts) evolved temporally to lower δ18O values, and thus the signature of basalts is directly inherited from peridotites. Both planets had magma oceans after the Giant impact of 4.44 Ga and thus likely had initially similar upper mantles, and basaltic upper crusts with respect to major element oxygen5. Triple oxygen isotopic effort to find differences between the earth and the moon resulted in almost complete overlap6.

As the Moon has not had plate tectonics, it thus provides a benchmark for the pre-plate tectonics on Earth since both planets
re-accreted after the Giant Impact (4.44 Ga) and had contemporaneous magma oceans\(^1\). These heavier values agree with our extrapolated estimates of \(\delta^{18}O_{\text{BSE}} = 5.57\%\pm0.07\%\) (based on peridotites with propagated errors) very well.

Our estimate of the \(\delta^{18}O_{\text{BSE}}\) is of course related to the timing of initiation of plate tectonics, which is a matter of significant debate\(^2\). If significant subduction started much earlier than 3 Ga, and TRD ages were also reset, then the pre-plate tectonic \(\delta^{18}O_{\text{CLM}}\) would have been slightly higher than we estimate here. For example, extrapolation of the linear trend for CLM in Fig. 1 would result in 5.61\% at 3.8 Ga and 5.63\% at 4.1 Ga, but within error of our measured Archean estimate of 5.57 \(±0.07\%\). We notice, however, that the temporal change in \(\delta^{18}O\) in the Archean samples from 3.0 to 2.6 Ga is less steep than the change between the Archean and Proterozoic and Archean vs all post-Archean samples (Fig. 1c), and so extrapolation \(\delta^{18}O\) value is less than the above estimates. Slab dehydoration on early Earth would likely happen under shallower conditions (24) and the oxygen isotope effects that we describe below, were likely less prominent. Perhaps more importantly, the oldest peridotite samples in our collection are \(-3\) Ga and worldwide there are no CLM peridotite xenoliths with robust bulk-rock Re-Os ages significantly more than 3 Ga\(^3\). This perhaps reflects that there may not be much left of surviving earliest Eoarchean and Hadean CLM as it was recycled back into the convecting mantle immediately after the Hadean (9.11, 24), annihilating the effects of early subduction (if any) on crust-CLM oxygen isotope repartition. Thus, if the plate tectonic started at 3.8–4.1 Ga (the earliest suggested estimates\(^2,24\)) the \(\delta^{18}O\) of the CLM was not significantly changed.

**Origin of decreasing \(\delta^{18}O\) trend in mantle peridotites.** It should be noted that most of the samples in the peridotite collection brought up by basalts and kimberlites in this work represent not the entire Earth’s convecting mantle (difficult to sample through time) but only its more or less melted residues of the Earth’s upper boundary layer of different age, which form 100–200-km-thick continental lithospheric mantle. The decreasing \(\delta^{18}O\) trend that we first observed by assigning age to studied collections (Figs. 1 and 2 and Supplementary Figs. 1 and 2) is not due to melting, cooling, or variable effects related to melt depletion (Fig. 3). We demonstrated that accounting for greater melt depletion in the Archean only enhances the temporal trend to 0.2\%. The only terrestrial reservoir that is lower in \(\delta^{18}O\) than the mantle is the terrestrial hydrosphere, and thus the most parsimonious interpretation of the trend is that of putatively accumulated effects of water–rock interaction.

Thus, we next consider the possible mechanisms for an external low-\(\delta^{18}O\) hydrospheric fluid interaction with the peridotites and their time-integrated effects, as well as recycling of hydrothermally altered lithospheric materials (Fig. 5) and describe likely processes that were in operation.

First, direct hydrothermal alteration (serpentinization and chloritization) of the shallow mantle in areas accessible to seawater percolation occurs today, in Cenozoic ophiolites (ref. 14 and in the geologic history at mid-ocean ridges, as well as, importantly, in areas where plates bend in front of subduction trenches\(^2,23\)). Any such hydrothermal interaction at \(T > 200^\circ\text{C}\), plausible in terms of typical sub-Moho temperature gradients, would generate lower-\(\delta^{18}O\) peridotites\(^1,15\). Subsequent deserpentinization reaction and restoration of the olivine and orthopyroxene would preserve the original low-\(\delta^{18}O\) birthmark\(^4\). These low-\(\delta^{18}O\) peridotites could have accreted under the continents upon initiation of horizontal motion.

Second, such low-\(\delta^{18}O\) portions of subducted slabs expel low-\(\delta^{18}O\) fluids and thus modify the \(\delta^{18}O\) of the overlying mantle wedge peridotites. Given the \(\delta^{18}O\) distribution in the altered oceanic crust and sediments on it, which ranges from high-\(\delta^{18}O\) at the top to low-\(\delta^{18}O\) in the chloritized and serpentinized interior\(^1,14,15,53\), upon subduction and slab heating the high-\(\delta^{18}O\) fluid will be lost first at the shallow fore-arc, while dehydoration of the low-\(\delta^{18}O\) interior of the slab would occur deeper into the peridotitic mantle wedge as the slab geotherm progressively increases\(^34\). The modern analogs to Archean subduction are modern “hot” subduction zones, such as the Central American Arc. Eiler et al.\(^53\) argued that the subtly low-\(\delta^{18}O\) value of the magmas in the central part of this arc results from low-\(\delta^{18}O\) fluids, and greater (2–4%) addition of such fluids corresponded to greater (15–25%) degree of mantle melting. Our sample collection has two Phanerozoic arc-related xenolith suites: harzburgites from the Kamchatka\(^48\) and the West Bismarck arcs\(^45\). Both occupy the low-\(\delta^{18}O\) end of our sample array, supporting the proposed scenario of fluxing by low-\(\delta^{18}O\) fluids. In other, shallower areas of the arc, fluids can be high-\(\delta^{18}O\) and normal (mante-like)\(^39\), contributing to higher \(\delta^{18}O\) values of accretionary sediments and the crust. Besides these two localities studied in this work, strongly re-worked mantle peridotites elsewhere with deformed and modally metasomatized at high temperature and pressure textures, show shifts to lower (not higher) \(\delta^{18}O\) values (down by 1\%\(^33\)). The pre-entrainment metasomatism is invoked to occur by deep subduction fluids shortly before magmatic entrainment, which thus also appears low-\(\delta^{18}O\).

**Discussion**

Here reported a temporal decrease in \(\delta^{18}O\) value of peridotites, dominated by continental harzburgite, is likely due to a billion-year record of seawater-peridotite interaction in areas of spreading and plate bending, and the subduction-accretion of these materials to the CLM (Fig. 5). If we consider the entire 100 km-thick section of such mantle, at present subduction length of 62 Km and rates of 8 cm/yr it would take 2 Gyr to lower the value of peridotite by 0.15\%. This computation assumes that the remaining 1–2 wt% of H\(_2\)O is released from the upper 10 km of the slab into the overlying peridotite as a low-\(\delta^{18}O\) fluid (0 to

![Fig. 5](https://example.com/f5.png) A cartoon that explains the cooling of the Earth and rehydration of the mantle by low-\(\delta^{18}O\) fluids in spreading centers\(^1,15\), plate bending zones\(^52\), and subduction zones\(^53,56\), generating progressively lower \(\delta^{18}O\) (and overall heterogeneous) continental lithospheric mantle (darker blue) after initiation of plate tectonics. \(\Delta^{17}O\) is not significantly modified by these processes (Fig. 4). Color code: yellow: low-\(\delta^{18}O\) peridotites, red: high-\(\delta^{18}O\) sediments, basalts, and eclogites, green: primitive mantle plumes, light blue: oceans. a Early Earth and moon regimes: degassed mantle, plume tectonics, rudimentary subduction around plumes, and intense hot mantle convection. The \(\delta^{18}O\) of the original peridotites is 5.57 \(±0.07\%\) and Bulk Silicate Earth=Bulk Silicate Moon. b Modern plate tectonics regime: rehydration of mantle, plate accretion, and imbrication, lower-\(\delta^{18}O\) peridotites in the subcontinental lithospheric mantle samples by studied xenolith suites.
due to the breakdown of serpentine and chlorite ~100–200 km below the mantle wedge. This estimate is likely robust within a factor of 2–3 depending on the choice of water content, its isotopic composition, and the total volume of the mantle affected. Perhaps more importantly, only a certain fraction of the mantle under volcanic fronts may be affected, compared to neighboring areas, or by different fluids. Besides subduction, as is mentioned above, direct seawater-peridotite interaction at spreading and plate bending zones, followed by plate stacking and imbrication would potentially produce a range of δ18O for xenoliths from a single locality. This depends on the mechanisms and timescales of fluid migration/fluid-rock reaction and subsequent recrystallization of fluid peridotites. This explains resolvable δ18O heterogeneity observed among xenoliths from a single kimberlite pipe (Udachnaya and Obnazhennaya (Fig. 1a) or xenoliths from variously flushed mantle wedges in the Phanerozoic Kamchatka or West Bismarc arcs. This is an important observation that can also explain moderate degrees of δ18O diversity in basaltic melts of a single locality that we call “natural δ18O noise” generated from a moderately laterally diverse δ18O shallow (continental mantle-derived) mantle source.

The trend established here for the isotopic composition of a major element, oxygen, supports a temporal oxygen isotopic separation between the upper mantle and the crust via gradual cumulative and putative effects of accreting low-density, high-δ18O sediments, and upper basaltic portions of the subducting slabs at shallow crustal levels, and supplying low-δ18O peridotitic material and fluids into the CLM. We here suggested that the described process of δ18O separation may also explain the contemporaneous increase of δ18O in the continental crust (Fig. 6) and the remaining hydrosphere, as documented by surface sedimentary archives and ref therein), a long-standing controversy in Earth sciences. Although not considered in this work, sunken slabs with residual water and predominantly low-δ18O values would additionally transfer more 18O-depleted oxygen into the predominant volume of the convecting mantle (Fig. 5), working in the same direction of contributing to the overall increase in δ18O of the crust, hydrosphere, and surface materials. Described low-δ18O unidirectional flux from the surface to the shallow and deeper mantle is likely firmly linked to the intensity of plate tectonics. As it mostly comes with water, low-δ18O flux is correlative to mantle rehydration, which was suggested earlier to explain the secular drop in the sea level contributing to continental emergence after the Archean. Given that the mass of the CLM is 10–20× that of the continental crust, a decrease by ~0.2‰ in δ18O of the CLM on a Ga time scale that we documented here, would suggest an increase of up to 4‰ in the crust (Fig. 6) by a simple crust-CLM mass balance, without taking into account unidirectional loss of the subduction-affected materials (both low and high-δ18O, hydrous and anhydrous, e.g., Fig. 5) to the deeper convecting mantle. Such a calculation assumes that most of the oxygen isotope mass balance proceeds via surface tectonics and fluid transfer (hydration–dehydration) and is mostly contained within lithospheric plates of 100–250 km. A similar approach for other chemical and isotopic systems that record interaction with the hydrosphere may serve to test the above conclusion and better quantify its mechanisms as well as the onset of mantle fluxing and rehydration of the mantle after the beginning of modern-style plate tectonics.

Methods

Analytical methods for δ18O. Oxygen isotope measurements for δ18O relied on 1–1.5 mg of material, predominantly single crystals of olivine, and were performed by laser fluorination and gas-source mass spectrometry (MAT253) at the University of Oregon, and the effort spanned 13 years (Supplementary Table 1). Coexisting orthopyroxenes, clinopyroxenes, and garnets were also analyzed in many samples. We used purified BrF5 as a reagent and boiling Hg diffusion pump to get rid of excess F2 gas, then converted purified O2 into CO2 and run it in a dual-inlet mode on MAT253 mass spectrometer, integrated with the vacuum line, as this method is most precise for δ18O determination. Samples yields were measured in a calibrated volume using a Baratron gauge and were >90%, and when plotted vs δ18O demonstrated no correlation. San Carlos Olivine (δ18O = 5.25‰), UWG2 garnet, 5.80‰, and an indoor UOG garnet standard (δ18O = 6.52‰) calibrated relative to the other two were used to calibrate the data on VSMOW scale. Each session included analyses of 4–6 standards, and correction for day-to-day variability was 0 to 0.2‰. Standard CO2 gas was used as a working standard and it was periodically rerun against OZTECH CO2 gas. Errors for standards in individual
sessions ranged from ±0.01 to ±0.11% and on average are ±0.06%, 1 s.d. Samples from sessions with worse precision on standards were rerun and most data reported in Supplementary Table 1 represents duplicates with some triplicates/quintuplicates run in different sessions and are averaged with shown 2 s.e. on replicate measurements. Using δ18O values for the same samples run on different sessions is a preferred way to recognize differences between samples.

**Triple oxygen isotopic methods.** For triple oxygen isotope analyses, generated gas was run as O2 in sessions with NCO standard ($\Delta^{17}O = -0.052\%_\text{O}$) utilizing a triple O continuous flow line constructed for the most precise triple O measurements49,57 at the University of Oregon. The generated O2 gas was put through the 8 ft long gas chromatographic column at room temperature for its purification from NCO compounds. Generated gases were additionally frozen on a 3 zeolite and then released into the bellow of the mass spectrometer by LN2–ethanol mix over 10 min. GC and zeolite traps were degassed with flowing He at 200 °C for 15–20 min between each sample. The purified O2 gas was run five times eight cycles in a dual-inlet mode, against a well-calibrated VSMOW University of Washington oxygen gas standard on a MAT253 isotope ratio mass spectrometer. Triple O isotope values for δ18O and δ17O are reported in Supplementary Table 2.

**Statistical handling of data.** Data handling included a statistical analysis that was performed by simple linear trends fitting (with error envelopes and line fit statistics) of the entire dataset and split (location-based) sub-datasets (Figs. 1 and 2). No data were excluded from the analyses, and we report all data accumulated over 13 years. We performed T tests when comparing data of δ18O and $\Delta^{17}O$ for periods of different ages (Supplementary Tables 3 and 5) and used P value as criteria to accept or reject the difference.

**Data availability**

The Oxygen isotopic data generated in this study are provided in the Supplementary Information/Source Data file.

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The authors declare no competing interests.

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