Heavy oxygen recycled into the lithospheric mantle

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Mags in volcanic arcs have geochemical and isotopic signatures that can be related to mantle metasomatism due to fluids and melts released by the down-going oceanic crust and overlying sediments, which modify the chemistry and mineralogy of the mantle wedge. However, the effectiveness of subduction-related metasomatic processes is difficult to evaluate because the composition of arc magmas is often overprinted by interactions with crustal lithologies occurring during magma ascent and emplacement. Here, we show unequivocal evidence for recycling of continental crust components into the mantle. Veined peridotite xenoliths sampled from Tallante monogenetic volcanoes in the Betic Cordillera (southern Spain) provide insights for mantle domains that reacted with Si-rich melts derived by partial melting of subducted crustal material. Felsic veins crosscutting peridotite and the surrounding orthopyroxene-rich metasomatic aureoles show the highest \(^{18}\)O/\(^{16}\)O ratios measured to date in upper mantle assemblages worldwide. The anomalously high oxygen isotope compositions, coupled with very high \(^{87}\)Sr/\(^{86}\)Sr values, imply the continental crust origin of the injected melts. Isotopic anomalies are progressively attenuated in peridotite away from the veins, showing \(^{18}\)O isotope variations well correlated with the amount of newly formed orthopyroxene. Diffusion may also affect the isotope ratios of mantle rocks undergoing crustal metasomatism due to the relaxation of \(^{18}\)O isotope anomalies to normal mantle values through time. Overall, the data define an O isotope “benchmark” allowing discrimination between mantle sources that attained re-equilibration after metasomatism (>5 Myr) and those affected by more recent subduction-derived enrichment processes.

Mantle wedges at destructive plate margins are significantly heterogeneous in chemical and isotopic compositions due to the reaction of the original mantle mineralogy with fluids and/or melts from the subducted slab1–7. Dehydration and/or melting of material from the subducted slab produce H\(_2\)O- and CO\(_2\)-rich metasomatizing agents, which in turn may trigger partial melting in the asthenospheric mantle wedge responsible for arc magmatism8–11. Sub-continental lithospheric mantle interacts similarly with percolating fluids or melts released by the subducting lithosphere12–18. Evidence of these processes is found in the chemical and isotopic compositions of subduction-derived magmatic rocks worldwide8,13,19. In several cases, however, especially in continental settings, shallow-level crustal contamination can also modify the composition of the erupted magmas, making it difficult to discriminate between processes occurring within the mantle source and those affecting the magmas en route to the surface17,18,20.

Oxygen isotope investigations provide evidence for recycling within the mantle of fluids/melt derived from the subducted oceanic crust21–23. The limited oxygen isotope fractionation at mantle temperatures and the narrow O isotope compositional variations in “typical” mantle rocks (\(\delta^{18}\)O\(_{\text{O}}\) = 5.18 ± 0.28‰; \(\delta^{18}\)O\(_{\text{Opx}}\) = 5.69 ± 0.28‰; \(\delta^{18}\)O\(_{\text{Cpx}}\) = 5.57 ± 0.36‰)24 make oxygen isotopes a powerful tool for identifying recycled crustal material in the mantle23,25. It is difficult, however, to define the specific (oceanic vs. continental) nature of the subducted components, and evidence for recycling of continental crust is generally rare and elusive26. Moreover, as highlighted above, high \(\delta^{18}\)O values recorded in erupted subduction-related lavas can also (and often) be due to crustal contamination, and it is frequently difficult to unequivocally discriminate between the two processes27.

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In this study, we determined the O isotope compositions, coupled with new Sr and Nd isotope data, on primary minerals from peridotite mantle xenoliths and felsic veins in composite mantle xenoliths from Tallante monogenetic volcanoes, Betic Cordillera, southern Spain. The host lavas were erupted in a post-collisional tectonic setting (cf. Supplementary Paragraph 1), exhuming abundant ultramafic mantle xenoliths (cf. Supplementary Paragraphs 2 and 3), which likely represent portions of a supra-subduction mantle wedge. Therefore, the studied samples provide an almost unique opportunity to directly study the effect of mantle metasomatism without any possible influence of shallow-level crustal contamination.

**Extreme Oxygen Isotope Variability in Mantle Minerals from Tallante**

The peridotite mantle xenoliths from Tallante display proto-granular textures and a mineralogy composed of orthopyroxene (opx), olivine (ol), clinopyroxene (cpx), spinel (sp) and occasional plagioclase (pl). In some composite xenoliths, centimetre- to millimetre-sized felsic veins crosscut the peridotite (Fig. 1). These veins mainly consist of plagioclase and orthopyroxene with accessory amphibole (amph), phlogopite, quartz, apatite, monazite/huttonite, rutile, and zircon (see also Supplementary Paragraph 2). In situ U-Pb dating of paragenetic zircons yields ages between 2.2 and 6.8 Ma, suggesting a close link to the Tertiary subduction process, which ultimately led to the formation of the Betic Cordillera.

To schematise, the studied xenoliths are divided into three broad groups representing different portions of the lithospheric mantle under the Betic region: (i) anhydrous peridotite xenoliths, sometimes containing plagioclase; (ii) orthopyroxene-rich, amphibole- and plagioclase-bearing xenoliths; and (iii) composite xenoliths with felsic veins showing clear evidence of reaction with percolating silica-rich melts. Group ii is interpreted as transitional between the unveined and veined mantle domains represented by group i and group iii, respectively.

Oxygen isotope compositions ($\delta^{18}O = \left[ R_{\text{sample}} / R_{\text{ref}} - 1 \right] \times 1000; R = ^{18}O/^{16}O$) were measured on distinct mineral phases of the three groups of Tallante xenoliths delineated above (Supplementary Paragraph 4 and Supplementary Table 1). The largest variability of $\delta^{18}O$ values is shown in the composite xenoliths (group iii) crosscut by felsic veins (Fig. 1a). The minerals forming the veins preserve the highest $\delta^{18}O$ values (sample TL112: $\delta^{18}O_{\text{opx}} + 9.84\%o$,
δ18Opl + 10.56‰; sample TL5: δ18Opl + 9.63‰, δ18Oopx + 8.02‰). These δ18O values are among the highest ever recorded in mantle phases (see Supplementary Material). Orthopyroxene from the vein/peridotite reaction domains still shows anomalously high O isotope compositions (δ18Oopx = 7.32–8.38‰), whereas the anomalies are less pronounced in the surrounding peridotite matrix. Plagioclase within smaller felsic veinlets shows lower δ18O values (sample TL117: δ18Opl = 7.33‰; sample TL347: δ18Opl = 7.58‰) than that from thicker veins, yet these values are still higher than those of the surrounding peridotite domains, suggesting that the larger the vein is, the higher the δ18O values of orthopyroxene and plagioclase contained therein.

The isotopic anomalies persist, although to a lesser extent, in unveined anhydrous peridotite xenoliths (group i) that range in composition from harzburgites to lherzolites (Supplementary Paragraph 4), especially in samples containing plagioclase. The δ18O values in minerals from these samples are still greater than typical mantle values (5.19‰ ≤ δ18Opl ≤ 5.78‰; 5.68‰ ≤ δ18Oopx ≤ 6.47‰; 5.03‰ ≤ δ18Oopx ≤ 6.62‰) and similar to those measured in O-enriched sub-arc mantle peridotite9,22,25, showing large δ18O variabilities within single mineral phases, which correlate well with the modal contents of the constituent phases (Supplementary Paragraph 5).

Overall, our samples define a broad picture where δ18O decreases away from the metasomatic veins through the reaction zones and in the surrounding peridotite (Fig. 1a,b); within this framework, the orthopyroxene-rich, amphibole- and plagioclase-bearing harzburgite xenolith (TL23) coherently represents a distal portion of the reaction zone triggered by felsic veining, having δ18O values (δ18Opl = 6.99‰, δ18Oopx = 7.33‰, δ18Oopx = 7.02‰) similar to those of the orthopyroxene found in the reaction zone of the veined xenoliths.

**Nature and Origin of the Percolating Melts Producing the Veins**

The nature of orthopyroxene-rich mantle domains is widely debated36–39. Partial melts of subducted material injected into pre-existing supra-subduction mantle domains have been found to produce secondary orthopyroxene9,40 when SiO2-rich percolating melts react with peridotite9,40.

The occurrence of rare quartz crystals within orthopyroxene-plagioclase veinlets of composite mantle xenoliths further constrains the silica-oversaturated nature of the percolating melts and their plausible derivation from partial melting of subducted material41. New 87Sr/86Sr and 143Nd/144Nd values (Supplementary Paragraph 4 and Supplementary Table 2) obtained in plagioclase and clinopyroxene crystals from the veins of the composite xenoliths provide further clear evidence (together with the extreme δ18O values) for a crustal, subduction-related origin of the metasomatizing agent. Indeed, plagioclase crystals from the thicker felsic vein are characterised by highly radiogenic Sr (87Sr/86Sr = 0.71266) and non-radiogenic Nd isotope compositions (143Nd/144Nd = 0.51260) that can be attained only if the percolating melt originated from subducted continental crust material. This material could have been recycled in the subcontinental mantle through slab delamination processes occurring during the Betic continental collision and may be represented by meta-sedimentary xenoliths exhumed in the same volcanic centre as the studied mantle xenoliths35. These metasedimentary xenoliths, which equilibrated under P-T conditions similar to those of the co-existing mantle xenoliths (0.7 GPa, 1050 °C), have silica/alumina-rich bulk compositions and consist mainly of quartz, plagioclase, garnet, spinel, and ilmenite ± orthopyroxene ± sillimanite ± graphite.

Plagioclase and clinoxyroxene from smaller (millimetre-sized) veinlets are characterised by lower radiogenic Sr (87Sr/86Sr = 0.70286–0.70409) and higher Nd (143Nd/144Nd = 0.51328–0.51318), which are similar to the values in clinopyroxene from the surrounding peridotite matrix. The observed variability in Sr and Nd isotopes (Supplementary Table 2) suggests that vein and veinlet formation occurred through metasomatic reactions between the primary mantle minerals and melts of variable composition and involved different melt/wall rock proportions. Due to an extreme chemical potential gradient, percolating metasomatic melts are highly reactive; thus, their initial compositions are difficult to assess. Any melt would interact extensively with the peridotite of the mantle wedge, given its alkali-rich and silica-rich nature42,43, and would equilibrate with mantle minerals44. Orthopyroxene oversaturation is achieved during melt evolution after olivine is completely consumed by the melt-peridotite reaction9,36,45,46. In this scenario, the minerals in the felsic veins preserve orthopyroxene and plagioclase in the reaction zone are produced by metasomatism according to the following reactions36,45,47:

\[
\text{oil} + \text{SiO}_2-\text{rich melt}_1 = \text{opx} + \text{melt}_2
\]

and

\[
\text{cpx} + \text{sp} + \text{SiO}_2 - \text{rich melt}_1 = \text{pl} + \text{opx} + \text{quartz} + \text{melt}_2
\]

Orthopyroxene from the boundary surrounding the vein still shows anomalous O isotope compositions, which are significantly lower than those of the mineral phases within the vein. This contrast is consistent with the metasomatic reactions described above, where most of the oxygen in the newly formed orthopyroxene derives from the unmodified peridotite, and only a subordinate amount is instead inherited from the percolating melt.

In addition, a positive covariation trend between modal contents of orthopyroxene and δ18Oopx is observed in the vein-free ultramafic xenoliths (groups i and ii; Fig. 2), which is accompanied by concomitant crystallisation of plagioclase and approximately positive covariation trends between orthopyroxene/clinoxyroxene and...
Implications for Magma Generation in the Betic Post-Collisional Setting

The complex processes revealed by our data are synthesised in the cartoon of Fig. 4, which illustrates the possible recycling of continental crust slivers during late-stage subduction processes of the continental collision in the Betic area. The process generates inter-layering of mantle and (low solidus) crustal lithotypes, i.e., the formation of crust-mantle melanges that are sometimes observed in orogenic peridotite massifs (Supplementary Paragraph 3).

18O values, \( \delta^{18}O \), of samples with mineral phases showing typical crustal oxide values, on one hand, and of samples with mineral phases showing typical crustal oxide values, on the other hand, suggests that the silica-rich metasomatic melt was progressively consumed and that it evolved during reaction with wall rock peridotite.

The metasomatic orthopyroxene-rich domains enveloping the veins subsequently equilibrated with the surrounding peridotite, acting as an armour against exotic material. Accordingly, the metasomatic reaction may be explained as an initial reactive porous flow reaction, followed by diffusion-assisted re-equilibration. Indeed, further oxygen isotope heterogeneities are likely derived from incomplete O isotope equilibration towards mantle-like values due to limited intra-crystalline diffusion, which is affected by the age of exotic melt injection into the peridotite, the initial oxygen isotope composition of the contaminant, the occurrence of fluid phases, and the chemical-physical characteristics of the mineral assemblage forming the peridotite wall rock. We can use oxygen isotope diffusion data to calculate the temporal variation in \( \delta^{18}O \) and the time required for complete re-equilibration. Note that the time required to physically digest exotic crustal material under mantle conditions clearly differs from that required to partly or completely obliterate the oxygen isotope signature. Oxygen diffusion at mantle temperatures is thought to be rapid enough to erase disequilibrium among minerals on a million-year time scale\(^4,49\). It follows that if the \( \delta^{18}O \) values of orthopyroxene in the veins represent the initial values of the mineral phase crystallised in the mantle, we can calculate the compositional variations due to O isotope diffusive re-equilibration with the surrounding mantle. Using the empirical oxygen isotope geothermometer of Matthews et al.\(^50\), the temperature of equilibration based on the \( \Delta^{18}O_{\text{opx}} \) is estimated at 930°C. This result is consistent with those of previous studies\(^41\), as the temperature of equilibration in the felsic veins estimated based on the compositions of the plagioclase-amphibole pair constrains the temperature of vein to above 850°C, whereas the equilibration temperature of the peridotite domains (based on the compositions of the orthopyroxene-clinoxyroxene pair) is in the range between 830 and 1030°C. At these temperatures, model calculations predict a rapid decrease in \( \delta^{18}O_{\text{opx}} \) values over the first 5–6 Myr (Fig. 3 and Supplementary Fig. 3). After this timespan, the orthopyroxene O isotope composition shows small variation with time, and the average \( \delta^{18}O \) value remains slightly higher than 6‰. These values are similar to the values measured in some anhydrous unveined peridotite mantle xenoliths (open circles in Fig. 2 and Supplementary Fig. 9), indicating that the local sub-continental lithospheric mantle includes portions completely re-equilibrated after earlier metasomatic events. On the other hand, other portions of such mantle, represented by the veined and the orthopyroxene-rich, amphibole- and plagioclase-bearing xenoliths, still preserve isotopic disequilibrium, thus implying that metasomatism continued up until shortly before the xenolith were entrained and exhumed, in agreement with the available U-Pb zircon dating\(^45\). Upon melting, such a mantle could have generated magmas with high \( \delta^{18}O \), even before any possible modification due to shallow-level crustal contamination during magma ascent.

**Figure 2.** Relationships between modal orthopyroxene amount and the relative oxygen isotope composition in unveined peridotite mantle xenoliths from Tallante (southern Spain). Anhydrous xenoliths (group i) are subdivided into plagioclase-free (open circles) and plagioclase-bearing (grey filled circles), whereas orthopyroxene-rich, amphibole- and plagioclase-bearing xenoliths (group ii) are recorded as black circles.
sources and that their isotope signature depends on the time interval between metasomatism and partial melting of the mantle source and eventually on crustal contamination during magma ascent to the surface. According to this hypothesis, $\delta^{18}O_{\text{Opx}}$ values of 6.2‰ would be the maximum that can be expected in the Betic magmas produced by partial melting of equilibrated mantle domains (where the time lapse between metasomatism and magma genesis exceeds 5 Myr). Higher $\delta^{18}O_{\text{Opx}}$ values necessarily imply nearly contemporaneous source veining/metasomatism and magma genesis or have to be attributed to crustal contamination during magma ascent.

**Figure 3.** Oxygen isotope diffusion model calculating the time necessary to reset the isotopic heterogeneities induced by the $^{18}$O-rich veining metasomatic agents. The blue ribbon delineates the expected temporal variation of the oxygen isotopic composition, assuming the diffusion parameters proposed by Ingrin et al.\textsuperscript{51} for starting $\delta^{18}O_{\text{Opx}}$ values of 9.84 and 8.28‰. See Supplementary Material and Supplementary Table 3 for further details.

**Figure 4.** (a) Cartoon showing a cross-sectional sketch of crustal recycling during continental collision, after which oceanic lithosphere is completely subducted. Note that the model invokes crust-mantle interlayering (melanges). Partial melting of the crustal domains generates felsic melts that percolate through the peridotite domains and react with them. (b) The crustal melts react with the surrounding peridotite and freeze to form the metasomatic veins, recycling heavy oxygen into the mantle. (c) Such a process is recorded in the composite mantle xenoliths (e.g., TL112) erupted at Tallante.
References
1. Defant, M. J. & Drummond, M. S. Derivation of some modern arc magmas by melting of young subducted lithosphere. Nature 347, 662–665 (1990).
2. Keppler, H. Constraints from partitioning experiments on the composition of subduction-zone fluids. Nature 380, 237–240 (1996).
3. Scaillet, B. & Prouteau, G. Oceanic slab melting and mantle metasomatism. Sci. Prog. 84, 335–354 (2001).
4. Maiaee, S. The dunite bodies, websterite and orthopyroxenite dikes of the Leka Ophiolite complex, Norway. Mineral. Petrology 85, 163–204 (2005).
5. Kawamoto, T. Hydrous phases and water transport in the subducting slab. Rev. Mineral. Geochem. 62, 273–289 (2006).
6. Hermann, J., Spandler, C., Hack, A. & Korsatov, A. V. Aqueous fluids and hydrous melts in high-pressure and ultra-high pressure rocks: Implications for element transfer in subduction zones. Lithos 92, 399–417 (2006).
7. Kessel, R., Schmidt, M. W., Ulmer, P. & Peritek, T. Trace element signature of subduction zone fluids, melts and supercritical liquids at 120–180 km depth. Nature 437, 724–727 (2005).
8. Elliott, T., Plank, T., Zindler, A., White, W. & Bourdon, B. Element transport from slab to volcanic front at the Mariana arc. J. Geophys. Res. Solid Earth 102, 14991–15019 (1997).
9. Rapp, R. P., Shimizu, N., Norman, M. D. & Applegate, G. S. Reaction between slab-derived melts and peridotite in the mantle wedge: experimental constraints at 3.8 GPa. Chem. Geol. 160, 335–356 (1999).
10. Milde, K., Kawamoto, T., Matsukage, K. N., Fei, Y. & Ono, S. Slab melting versus slab dehydration in subduction-zone magmatism. PNAS 108, 8177–8182 (2011).
11. Avanzinelli, R. et al. Combined 238U–230Th and 235U–231Pa constraints on the transport of slab-derived material beneath the Mariana Islands. Geochim. Cosmochim. Acta 92, 308–328 (2012).
12. Conticelli, S. & Peccerillo, A. Petrology and geochemistry of potassic and ultrapotassic volcanism in central Italy: petrogenesis and evolution of the mantle sources. Lithos 28, 221–240 (1992).
13. Plank, T. & Langmuir, C. H. Tracing trace elements from sediment input to volcanic output at subduction zones. Nature 362, s739–743 (1993).
14. Plank, T. & Langmuir, C. H. The chemical composition of subducting sediment and its consequences for the crust and mantle. Chem. Geol. 145, 325–394 (1998).
15. Plank, T. & Conticelli, S. Constraints from thorium/lanthanum on sediment recycling at subduction zones and the evolution of the continents. J. Petrol. 46, 921–944 (2005).
16. Bebout, G. E. Metamorphic chemical geodynamics of subduction zones. Earth Planet. Sci. Lett. 260, 373–393 (2007).
17. Conticelli, S., Avanzinelli, R., Poli, G., Bracchi, E. & Giordano, G. Shift from lamproite-like to leucititic rocks: Sr–Nd–Pb isotope data from the Monte Cimino volcanic complex vs. the Vico stratovolcano, Central Italy. Chemical Geology 353, 246–266 (2013).
18. Conticelli, S., Avanzinelli, R., Ammannati, E. & Casalini, M. The role of carbon from recycled sediments in the origin of ultrapotassic igneous rocks in the Central Mediterranean. Lithos 232, 174–196 (2015).
19. Elliott, T. Tracers Of The Slab. Geophysical Monograph-American Geophysical Union 138, 23–46 (2003).
20. Peccerillo, A., Dallas, L., Frezzotti, M. L. & Kempdon, P. D. Sr–Nd–Pb–O isotopic evidence for decreasing crustal contamination with ongoing magma evolution at Alicudi volcano (Aeolian arc, Italy): implications for style of magma–crust interaction and for mantle source compositions. Lithos 78(1–2), 217–233 (2004).
21. Bindeman, I. N. et al. Oxygen isotope evidence for slab melting in modern and ancient subduction zones. Earth Planet. Sci. Lett. 235, 480–496 (2005).
22. Liu, C. Z. et al. A hidden 18O-enriched reservoir in the sub-arc mantle. Sci. Rep. 4, 4232 (2014).
23. Eller, J. M., Schiano, P., Calvani, J. W., Kita, N. T. & Stolper, E. M. Oxygen-isotope and trace element constraints on the origins of silica-rich melts in the subarc mantle. Geochim. Geophys. Geosyst. 8, Q09012 (2007).
24. Mathey, D., Lowery, D. & Macpherson, C. Oxygen isotope composition of mantle peridotite. Earth Planet. Sci. Lett. 128, 231–241 (1994).
25. Eller, J. M., Mclnnes, B., Valley, J. W., Graham, C. M. & Stolper, E. M. Oxygen isotope evidence for slab-derived fluids in the sub-arc mantle. Nature 393, 777–781 (1998).
26. Daniels, L. R. M., Gurney, J. J. & Harte, B. A crustal mineral in a mantle diamond. Earth Planet. Sci. Lett. 153, 156–156 (1996).
27. Dallas, L., Freda, C. & Gaeta, M. Oxygen isotope geochemistry of pyroclastic clinopyroxene monitors carbon contributions to Roman-type ultrapotassic magmas. Contributions to Mineralogy and Petrology 148(2), 247–263 (2004).
28. Arai, S., Shimizu, Y. & Gervilla, F. Quartz diorite veins in a peridotite xenolith from Tallante, Spain: implications for reaction and survival of slab-derived SiO2-oversaturated melt in the upper mantle. Proc. Japan Acad. 79, 145–150 (2003b).
29. Shimizu, Y., Arai, S., Morishita, T., Yurimoto, H. & Gervilla, F. Petrochemical characteristics of felsic veins in mantle xenoliths from Tallante (SE Spain): an insight into activity of silicic melt within the mantle wedge. Trans. Royal Soc. Edinburgh, Earth Sci. 95, 265–276 (2004).
30. Beccaluva, L., Bianchini, G., Bonadiman, C., Siena, F. & Vaccaro, C. Coexisting anorogenic and subduction-related metasomatism in mantle xenoliths from the Betic Cordillera (southern Spain). Lithos 75, 67–87 (2004).
31. Bianchini, G., Beccaluva, L., Nowell, G. M., Pearson, D. G. & Siena, F. Mantle xenoliths from Tallante (Betic Cordillera): insights into multi-stage evolution of the south Iberian lithosphere. Lithos 124, 308–318 (2011).
32. Rampone, E., Vissers, R. L. M., Poggio, M., Scambelluri, M. & Zanetti, A. Melt Migration and Intrusion during Exhumation of the Alboran Lithosphere: the Tallante Mantle Xenolith Record (Betic Cordillera, SE Spain). J. Petrol. 51, 295–325 (2010).
33. Conticelli, S. et al. Trace elements and Sr–Nd–Pb isotopes of K-rich, shoshonitic, and calc-alkaline magmatism of the Western Mediterranean Region: genesis of ultrapotassic to calc-alkaline magmatic associations in a post-collisional geodynamic setting. Lithos 107, 68–92 (2009).
34. Martelli, M., Bianchini, G., Beccaluva, L. & Rizzo, A. Helium and argon isotopic compositions of mantle xenoliths from Tallante and Calatrava, Spain. J. Volcanol. Geotherm. Res. 200, 18–26 (2011).
35. Bianchini, G., Braga, R., Langone, A., Natali, C. & Tiepolo, M. Metasedimentary and igneous xenoliths from Tallante (Betic Cordillera, Spain): Inferences on crust–mantle interactions and clues for post-collisional volcanic magma sources. Lithos 220–223, 191–199 (2015).
36. Kelemen, P. B., Hart, S. R. & Bernstein, S. Silica enrichment in the continental upper mantle via melt/rock reaction. Earth Planet. Sci. Lett. 164, 387–406 (1998).
37. Tamura, A. & Arai, S. Harzburgite-dunite-orthopyroxenite suite as a record of supra-subduction zone setting for the Omanophiolite mantle. Lithos 90, 43–56 (2006).
38. Morishita, T., Dilek, Y., Shallo, M., Tamura, A. & Arai, S. Insight into the uppermost mantle section of a maturing arc: the Eastern Mirdita ophiolite, Albania. Lithos 124, 215–226 (2011).
39. Giovanardi, T., Morishita, T., Zanetti, A., Mazzucchelli, M. & Vannucci, R. Igneous sapphiren as a product of melt-peridotite interactions in the Finero Phlogopite-Peridotite Massif, Western Italian Alps. J. Volcanol. Mineral. 25, 17–31 (2013).
40. Rapp, R. P., Watson, E. B. & Miller, C. F. Partial melting of amphibolite/eclogite and the origin of Archean trondhjemites and tonalites. Precamb. Res. 51, 1–25 (1991).
41. Bali, E. et al. A Quartz-bearing Orthopyroxene-rich Websterite Xenolith from the Pannonian Basin, Western Hungary: Evidence for Release of Quartz-saturated Melts from a Subducted Slab. J. Petrol. 49, 421–439 (2008).
42. Kepezhinskas, P. K., Defant, M. J. & Drummond, M. S. Na metasomatism in the island arc mantle by slab melt-peridotite interaction: evidence from mantle xenoliths in the north Kamchatka arc. *J. Petrol.* **36**, 1505–1527 (1995).
43. Hack, A. C., Thompson, A. B. & Aerts, M. Phase relations involving hydrous silicate melts, aqueous fluids, and minerals. *Rev. Mineral. Geochem* **65**, 129–185 (2007).
44. Prouteau, G., Scaillet, B., Pichavant, M. & Maury, R. Evidence for mantle metasomatism by hydrous silicic melts derived from subducted oceanic crust. *Nature* **410**, 197–200 (2001).
45. Sen, C. & Dunn, T. Experimental modal metasomatism of a spinel lherzolite and the production of amphibole-bearing peridotite. *Contrib. Mineral. Petrol.* **119**, 422–432 (1995).
46. Piccardo, G. B., Zanetti, Z. & Muntener, O. Melt/peridotite interaction in the Southern Lanzo peridotite: field, textural and geochemical evidence. *Lithos* **94**, 181–209 (2007).
47. Kelemen, P. B., Dick, H. J. B. & Quick, J. E. Formation of harzburgite by pervasive melt/rock reaction in the upper mantle. *Nature* **358**, 635–641 (1992).
48. Rosenbaum, J. M., Kyser, T. K. & Walker, D. High temperature oxygen isotope fractionation in the enstatite-olivine-BaCO3 system. *Geochim. Cosmochim. Acta* **58**, 2653–2660 (1994).
49. Perkins, G. B., Sharp, Z. D. & Selverstone, J. Oxygen isotope evidence for subduction and rift-related mantle metasomatism beneath the Colorado Plateau–Rio Grande rift transition. *Contrib. Mineral. Petrol.* **151**, 633–650 (2006).
50. Matthews, A., Goldsmith, J. R. & Clayton, R. N. Oxygen isotope fractionations involving pyroxenes: the calibration of mineral pair geothermometers. *Geochim. Cosmochim. Acta* **47**, 631–644 (1983).
51. Ingrin, J., Pacaud, L. & Jaoul, O. Anisotropy of oxygen diffusion in diopside. *Earth Planet. Sci. Lett.* **192**, 347–361 (2001).

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**Author Contributions**

L.D. and G.B. designed the research study, L.D. performed isotope measurements; L.D., G.B., C.N., R.A. and S.C. participated in the discussion of data and in the writing of the paper.

**Additional Information**

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**Competing Interests:** The authors declare no competing interests.

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