W. E. Gall, J. Cowman, Eds. (Wiley, New York, 1987), pp. 21–56.
9. Slice preparation, intracellular and extracellular solutions, data acquisition, model fitting, and three-dimensional (3D) reconstructions were as in (7). The model iterations use at least two frequencies, five responses, and the RTR. Membrane potentials were not corrected for ~9-mV junction potential.
10. Recordings were discarded because of access resistance changes, membrane instabilities, and synaptic responses below 60 μV and 1.5 pA.
11. $[Cl^-]_{out}$ = 133.5 mM and $[Cl^-]_{in}$ = 20 mM; −50.4 mV (Nernst potential); +9 mV (junction potential), expected reversal potential (V_{rev}), −41.4 mV.
12. Morphometric analysis (NeuroExplorer, MicroBrightField, Colchester, VT): Only contacts by axonal boutons within 0.37 μm were counted. Light microscopic estimates without electron microscopic confirmation can be misleading [H. Markram, J. Lübke, M. Frotscher, A. Roth, B. Sakmann, *J. Physiol.* **500**, 409 (1997)].
13. G. Tamas, E. H. Buhl, P. Somogyi, *J. Physiol.* **500**, 715 (1997).
14. Pilot studies indicated that RTR of 500 ms is optimal for separation of potentially different degrees of residual facilitation and depression.
15. Superperfusate (10 min) 0.75 mM $[Ca^{2+}]$ and 2.25 mM $[Mg^{2+}]$.
16. E. L. White, W. Weinfeld, D. L. Lev, *Somatosens. Mot. Res.* **14**, 34 (1997).
17. P. Somogyi, Z. F. Kisvarday, K. A. C. Martin, D. Whitteridge, *Neuroscience* **10**, 261 (1983).
18. Sholl analysis of the axon was used to produce a histogram of the number of axon segments found in regions progressively further away from the somata; see D. A. Sholl, *J. Anat.* **87**, 387 (1953). ASD, median in the histogram of intersections. ASL, mean interbranch length.
19. Z. F. Kisvarday, K. A. C. Martin, D. Whitteridge, P. Somogyi, *J. Comp. Neurol.* **241**, 111 (1985).
20. C. Martinotti, *Ann. Freniatr. Sci. Affini.* **1**, 314 (1889); Y. Kawaguchi and T. Shindou, *J. Neurosci.* **18**, 6963 (1998).
21. M. L. Feldman and A. Peters, *J. Comp. Neurol.* **179**, 761 (1979).
22. Possibly the same as in J. DeFelipe and A. Farien, *Brain Res.* **244**, 9 (1982).
23. M. Steriade, I. Timofeev, N. Durmuller, F. Grenier, *J. Neurophysiol.* **79**, 483 (1998).
24. Y. Kawaguchi, *J. Neurosci.* **15**, 2638 (1995).
25. J. F. Storm, *Nature* **336**, 379 (1988).
26. On the basis of methods of data sampling as well as anatomical and electrophysiological binning, the 95% confidence intervals (CIs) for the number of classes that would result if the same methods were repeated are [*11, 17*]. CI was calculated as number of classes ± 1.96 SD among 10,000 bootstrapped data sets sampled with replacement, each categorization with the identical procedure to generate a classification binning scheme [B. Efron and R. Tibshirani, *Science* **253**, 390 (1991)].
27. A Monte Carlo permutation test was applied to 10,000 shufflings of the synaptically classified cells to determine their expected distribution among 14 anatomically or physiologically defined categories. Chi-square analysis of type occurrences across categories [M. Siegel and N. J. Castellan Jr., *Nonparametric Statistics for the Behavioral Sciences* (McGraw-Hill, New York, ed. 2, 1988)] yielded $P = 3.1 \times 10^{-9}$, indicating that the probability of obtaining the observed synapse mapping randomly is negligible.
28. Model fitting of IPSCs at different voltages across V_{rev} yielded essentially identical synaptic parameters, indicating that local changes in $[Cl^-]$ do not contribute to synaptic dynamics. Model fitting of IPSPs at different membrane potentials yielded similar parameters, indicating negligible contribution of dendritic saturation and activation of nonlinearities. Near identical synaptic dynamics of divergent connections in different PCs, despite differences in IPSC/IPSP amplitudes, also indicated negligible contribution of nonlinear processes.
29. A. Gupta, Y. Wang, H. Markram, data not shown.
30. We thank E. White, Y. Yaari, I. Segev, R. Malach, and P. Goodman for comments on the manuscript. This study was supported by grants from the Office of Naval Research, the Human Frontier Science Program, the Minerva Foundation, the Israel Science Foundation, and the Nella and Leon Benziyo Center for Neurosciences. A.G. is a Minerva Fellow.

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Rutile-Bearing Refractory Eclogites: Missing Link Between Continents and Depleted Mantle

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A mass imbalance exists in Earth for Nb, Ta, and possibly Ti: continental crust and depleted mantle both have subchondritic Nb/Ta, Nb/La, and Ti/Zr, which requires the existence of an additional reservoir with superchondritic ratios, such as refractory eclogite produced by slab melting. Trace element compositions of minerals in xenolithic eclogites derived from cratonic lithospheric mantle show that rutile dominates the budget of Nb and Ta in the eclogites and imparts a superchondritic Nb/Ta, Nb/La, and Ti/Zr to the whole rocks. About 1 to 6 percent by weight of eclogite is required to solve the mass imbalance in the silicate Earth, and this reservoir must have an Nb concentration ≥ 2 parts per million, Nb/La ≥ 1.2, and Nb/Ta between 19 and 37—values that overlap those of the xenolithic eclogites. As the mass of eclogite in the continental lithosphere is significantly lower than this, much of this material may reside in the lower mantle, perhaps as deep as the core-mantle boundary.

The elements Ti, Zr, Nb, Ta, and rare earth elements (REE) are refractory and lithophile and therefore should exist in chondritic relative abundances in the silicate Earth. Continental crust and depleted mantle (DM) [mid-ocean ridge basalt (MORB) source] generally are assumed to be geochemically complementary reservoirs within the Earth. However, both reservoirs have subchondritic Nb/La (*1–4*). A similar observation is made about Nb/Ta ratios. These elements share the same valence state (+5) and have matching atomic radii (*5*), and they are thought to be geochemically inseparable. However, recent analyses (*6*) have demonstrated that Nb/Ta ratios are subchondritic in MORB and near-ridge seamounts (*7–9*), ocean island basalts (OIB) (*7, 10*), and the upper continental crust (*11, 12*). Because Nb is more incompatible than Ta in clinopyroxene during mantle melting (*13*), the DM and the source of OIB should have even lower Nb/Ta ratios. A third element ratio that also may not mass balance in Earth is Ti/Zr. The continental crust, MORB, and OIB have Ti/Zr ratios below 115, the chondritic ratio (*1*). However, because Zr is more incompatible than Ti (*13*), partial melts should have lower Ti/Zr than their source regions and the mass imbalance in this case is not clear. The DM and OIB sources could have chondritic or even superchondritic Ti/Zr [as massif peridotites do (*14*)]. Nevertheless, the subchondritic Ti/Zr in MORB and continental crust suggests that another reservoir exists that is Ti enriched relative to Zr.

The above observations require the existence of an additional reservoir that contains appreciable Nb, Ta, and Ti with superchondritic Nb/La, Nb/Ta, and Ti/Zr—features that, until now, have not been observed in common igneous and metamorphic rocks (*15*). McDonough (*1*) suggested that refractory, rutile-bearing eclogite may satisfy the mass balance requirements for Ti, Nb, and Ta in the silicate Earth. Here we show that eclogites, sampled in xenoliths from cratonic kimberlites, do indeed have the requisite trace element compositions to satisfy this mass imbalance.

Rutile (TiO_2) is a common accessory phase in metamorphic rocks and it can have

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high concentrations of high field strength elements, particularly Nb and Ta. For this reason, rutile has been considered by some to be the phase that is responsible for the marked Nb and Ta depletions seen in arc magmas (*16*). Rutiles from continental crustal rocks (*17, 18*) have Nb contents greater than 100 parts per million (ppm) with Nb/Ta ratios that generally cluster about the chondritic ratio of 17.4 ± 0.5 (*19*) or lower (*20*) (Fig. 1A). Metasomatic rutiles from cratonic peridotites (*21, 22*) are characterized by high Nb contents (0.3 to 0.5 weight %) and chondritic Nb/Ta ratios. In contrast, rutiles from eclogite xenoliths carried in kimberlite pipes from Siberia (*23*) and western Africa (*24, 25*) have more variable Nb contents and Nb/Ta ratios and many have Nb/Ta ratios that are chondritic to strongly superchondritic; the population forms a log-normal distribution and has a geometric mean value of 24 ($n = 19$) (*26*).

Although rutile is an accessory phase in the eclogites (*27*), it dominates the budget of Nb and Ta (*28*). Thus, the Nb/Ta ratio of the whole rock eclogite equals that of the rutile, and we can conclude that, on average, the xenolithic eclogites have superchondritic Nb/Ta ratios.

Determining the Nb/La ratio of the eclogites is more difficult. Whole rock data are unreliable because of variable degrees of large-ion lithophile element (*29*) enrichment produced by interaction with the host kimberlite (*30*). Thus, the preentrainment eclogite compositions must be calculated from primary mineral compositions and modes (*31*). This requires relatively precise knowledge of the modal abundance of rutiles, which cannot be determined from point-counting these coarse-grained rocks. We therefore calculated modal rutile from Ti mass balance (*32*), which yields proportions of 0.1 to 0.9% by weight, with a relative error of ≤10%. The resulting Nb/La of all but five of the reconstructed eclogites are superchondritic, with a geometric mean Nb/La of 2.7 ($n = 17$) (*26*) (Fig. 1B).

In a similar fashion we calculated the Ti/Zr ratio of the bulk eclogites. All but one of our samples have superchondritic ratios (Fig. 1C). These eclogites are thus distinct from MORB, continental crust, and OIB, which have subchondritic Ti/Zr ratios. Interestingly, this feature is a result of Zr (and Hf) depletion in the eclogites rather than Ti enrichment; that is, on mantle-normalized plots, Ti is not anomalous relative to REE of similar incompatibility such as Eu and Gd, but Zr and Hf are distinctly depleted (relative to Sm and Eu).

The above data demonstrate that xenolithic eclogites have, on average, superchondritic Nb/Ta, Nb/La, and Ti/Zr ratios and thus support the contention that refractory, rutile-bearing eclogites may be important in the mass balance of Nb, Ta, and Ti in Earth. The mass of this reservoir is not easily constrained from the trace-element compositions of the eclogites, given the rather large standard deviations of Nb/Ta, Nb/La, and Ti/Zr observed for these samples. We have therefore calculated its mass as a function of the mass fraction of DM by

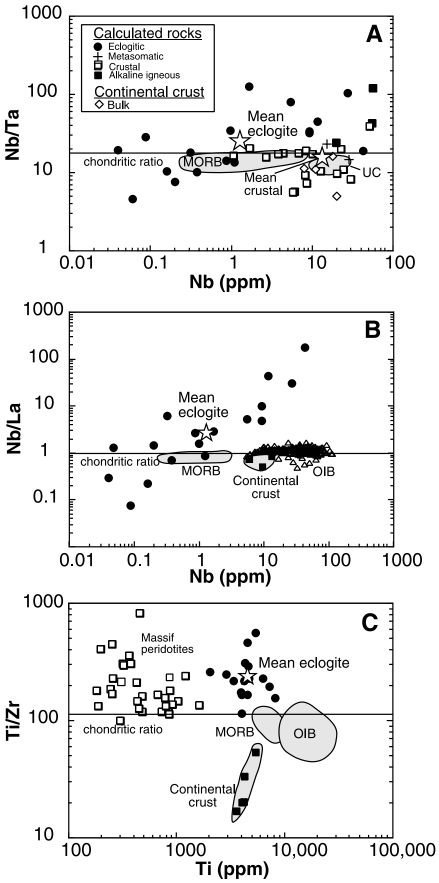

Fig. 1. (**A**) Nb versus Nb/Ta for a variety of rock types and model compositions: xenolithic eclogites (black dots), crustal igneous and metamorphic rocks (open squares), and metasomatic peridotite xenoliths from Tanzania (pluses). Stars represent geometric mean (*26*) for the eclogitic and crustal populations. Field of MORB from (*9*). Diamonds, various estimates of bulk crust composition (*2*); UC, field of upper crust derived from GLOSS (*12*), loess, and PAAS (*11*). Only three crustal rutile samples have Nb/Ta significantly above the chondritic ratio and two of these are from a carbonatite complex (Magnet Cove, Arkansas) (*20*); the third is from a South Carolina beach sand deposit of unknown provenance. Eclogite whole rock compositions are calculated from modal mineralogy (*32*); crustal and metasomatic mantle whole rock compositions are calculated assuming that rutile makes up 0.5% of the rock and is the sole contributor of Nb and Ta to the whole rock budget. (**B**) Nb versus Nb/La for reconstructed whole rock eclogites (solid circles), field of MORB, average continental crust (black squares on gray field), and OIB (triangles). Data sources are as listed for (A) and from the literature. Star, geometric mean of the eclogite population. (**C**) Ti versus Ti/Zr for reconstructed eclogites (solid circles), field of MORB, continental crust, OIB, and Massif peridotites (open squares). Data sources are as listed for (A) and from the literature. Star, geometric mean of the eclogite population.

using the Al_2O_3 contents of continental crust (*2*), primitive mantle (*33*), median worldwide eclogite (*34*), and DM, assuming that the DM contains between 80 and 95% of the Al_2O_3 present in the primitive mantle. Al_2O_3 was chosen for this calculation because it is the only major element that meets all of the following criteria: (i) its concentration is well defined in the continental crust, (ii) its concentration is markedly different between DM and eclogites, and (iii) it exhibits a relatively narrow range of variability in eclogites (*34*). An Al_2O_3 deficit exists in Earth if the DM is 40% or more of the mantle (Fig. 2A), a likely minimum proportion based on the concentrations of incompatible

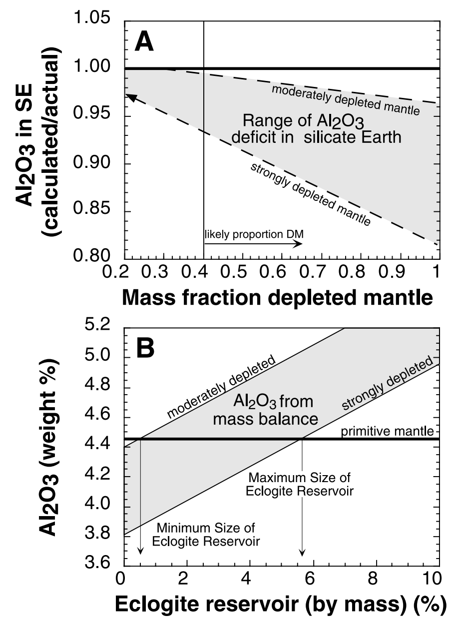

Fig. 2. (**A**) Gray field shows the deficit in Al_2O_3 that exists in the silicate Earth as a function of the proportion of DM. Calculated Al_2O_3 composition of the silicate Earth is derived from the sum of Al_2O_3 contributed from the DM, continental crust (CC), and primitive mantle (PM) (mantle that has not differentiated $= 1 - M_{CC} - M_{DM}$, where M is mass fraction). Continental crust is assumed to contain 2% of the Al_2O_3 in the silicate Earth ($0.0057 \times 15.8/4.45$); there is little variation in this value for different published estimates (*2*). The DM composition, which is more poorly constrained, is allowed to vary from a moderately depleted composition with 95% of the Al_2O_3 of the primitive mantle to a strongly depleted composition, containing 80% of the Al_2O_3 of the primitive mantle. Primitive mantle composition is from (*33*). (**B**) Gray field shows range of Al_2O_3 contents in the silicate Earth needed to eliminate the Al_2O_3 deficit shown in (A), calculated from mass balance as a function of the mass of a refractory eclogite reservoir. In this calculation, the mass of the DM is allowed to vary between 50 and 80% of the silicate Earth. Moderately depleted and strongly depleted mantle compositions are as defined above. Intersection of the gray field with the Al_2O_3 content of the primitive mantle defines the upper and lower bounds on the mass of eclogite that might exist in the Earth—that is, between 0.5 and ~6% by mass, if it accounts for the missing Al_2O_3.

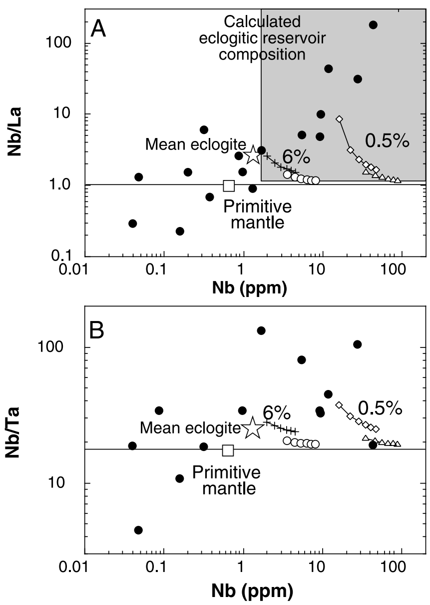

Fig. 3. Composition of refractory eclogite reservoir, calculated from mass balance (*39*), compared with the range of eclogite compositions reported here. Solid circles, individual eclogites; stars, geometric mean of xenolithic eclogite population (*26*); curves, end member outcomes of the mass balance calculations; circles and pluses, results assuming the eclogite reservoir represents 6% by mass of the silicate Earth; triangles and diamonds, results assuming the eclogite reservoir represents only 0.5% by mass of the silicate Earth. A range of DM compositions were assumed (Nb in DM = 0.12 to 0.35 ppm), corresponding to the range of Nb contents calculated for the DM from representative MORB compositions, assuming 5 to 10% batch melting and bulk *D* values of 0.0005 and 0.00028 (*13*). Other elements in the DM were calculated assuming Nb/La = 0.9 (*3*) and Nb/Ta = 15.5 (*7*). Pluses and diamonds, moderately depleted mantle with 0.35 ppm of Nb (about half the concentration of the PM); circles and triangles, more strongly depleted mantle with 0.12 ppm of Nb (about 20% of the PM). Because the continental crust has a Nb/La ratio significantly smaller than either DM or PM, the mass balance calculation for Nb/La (**A**) is very sensitive to the mass of the crust. Increasing the crust's mass from 0.57 to 0.60% of the silicate Earth, results in a factor of 2 increase in the Nb/La calculated for the refractory eclogite reservoir. For this reason, minimum bounds are shown for this reservoir by the gray box, which is considered the only robust constraint that can be placed on its Nb/La composition [that is, the Nb/La could be significantly higher than that depicted by the curves in (A) but not lower]. Because the Nb/Ta ratio of the crust is not significantly different from the DM, the Nb/Ta calculations shown in (**B**) do not depend on crustal mass.

Table 1. Parameters used to calculate refractory eclogite composition from mass balance. Numbers in plain type are input parameters for mass balance calculations; numbers in italics are derived from mass balance calculations.

	Mass fraction of silicate Earth	Al_2O_3 (weight %)	Nb (ppm)	La (ppm)	Ta (ppm)	Nb/La	Nb/Ta
DM	0.4–0.9	3.6–4.2	0.12–0.35	0.13–0.38	0.007–0.022	0.91	15.5
Continental crust (*2*)	0.0057	15.8	8.6	18	0.7	0.48	12.3
Primitive mantle (*33*)	0.03–0.59	4.45	0.658	0.648	0.037	1.01	17.5
Refractory eclogite reservoir*	*0.005–0.06*	15.8	*>1.6**	*>0.75**	*>0.04**	*>1.18**	*19–37*

*Concentrations of Nb and the Nb/La ratio in the eclogite reservoir are highly sensitive to the mass of the continental crust because of its relatively high concentrations and large fractionation of Nb/La relative to other reservoirs. For example, increasing the crustal mass by 5% causes a factor of 2 increase in the Nb/La ratio in the eclogite reservoir in some cases.

elements present in the continental crust (*2*). The mass fraction of eclogite needed to compensate for this deficit ranges between 0.5 and 6% of the silicate Earth, equal to or greater than the mass of the continental crust and approximately equivalent to the mass of oceanic crust subducted through time (*1, 35*) (Fig. 2B). This mass overlaps that of the continental lithospheric mantle (1.5 to 2.5% of silicate Earth) (*1, 36*) and, although these and other eclogite samples originate from the lithospheric mantle, population studies of xenocrysts and xenoliths in kimberlites demonstrate that eclogite is a minor component of the continental lithosphere, probably below 1 to 2% by volume (*37*). Thus, our estimates suggest that much of this eclogitic reservoir exists at deeper levels of the mantle, possibly in the lower mantle (*38*).

Given the mass of refractory eclogite calculated above, some constraints on its trace element composition can also be obtained from mass balance calculations (*39*) (Fig. 3A). The mean eclogite lies near the low end of the Nb concentration range of the calculated eclogitic reservoir and within its range of Nb/La. In view of the large spread in concentrations and ratios observed in the eclogites, this agreement is good. Likewise, the range in Nb/Ta ratios for the eclogites is large, but the mean eclogite falls within the range of Nb/Ta calculated for the missing reservoir (Fig. 3B).

We propose that the eclogite reservoir forms a missing link between continental crust and DM. We envisage that fractionation of Nb from La and Ta (and possibly Ti from Zr) is produced as altered oceanic crust transforms to eclogite, giving up a melt or fluid phase during subduction. During the Archean [when the eclogites we examined here are likely to have formed (*40*)] higher mantle temperatures resulted in a thicker and more mafic oceanic crust that underwent dehydration melting upon subduction (*41*). The major and trace element compositions of xenolithic eclogites are consistent with them being residues of tonalite-trondhjemite-granodorite production from a higher MgO oceanic crust (*42*). As Earth cooled, dehydration melting of slab basalts in subduction zones may have given way to dehydration only. Because the partitioning of Nb and Ta between fluid and rutile is extremely low (*43*), dehydration should not fractionate Nb from Ta. Thus the Nb/Ta ratio of rutiles in Phanerozoic eclogites reflects that of their protolith. For example, if the rutiles are in metamorphosed MORB, their Nb/Ta should be low (*7–9*).

Finally, a relevant question is whether the refractory eclogite reservoir, once transported into the deep mantle, is ever seen again. A number of persuasive arguments have been made for incorporation of recycled oceanic crust into the source regions of OIB (*44*). Although some OIB [particularly the HIMU family (*45*)] exhibit high Nb/La, they apparently do not have elevated Nb/Ta (*10*). This observation suggests that the amount of refractory eclogite in the OIB source is small. For example, if OIB are derived from sources that are mixtures of refractory eclogite and peridotite (DM or primitive mantle), ≤10% eclogite is able to dominate the Nb and Ta contents of the mixture, giving rise to superchondritic Nb/Ta in the source. However, because recycled oceanic lithosphere is likely to contain both oceanic crust (now eclogite) and sediment, which will have high concentrations of Nb and Ta and low Nb/Ta (*11, 12*), one expects to see a range of Nb/Ta in OIB, depending on the amount and nature of the recycled component in their source (one would predict HIMU to have high Nb/Ta and EM I (*45*) to have low Nb/Ta). Therefore, a search for systematics in Nb and Ta contents of well-characterized OIB offers an additional test of the importance of recycled oceanic lithosphere in the source regions of OIB (*46*).

References and Notes

1. W. F. McDonough, *Philos. Trans. R. Soc. London* **335**, 407 (1991).
2. B. L. Weaver and J. Tarney, *Nature* **310**, 575 (1984); S. R. Taylor and S. M. McLennan, *The Continental Crust: Its Composition and Evolution* (Blackwell Scientific Publications, Oxford, 1985), p. 67; R. L. Rudnick and D. M. Fountain, *Rev. Geophys.* **33**, 3 (1995); K. H. Wedepohl, *Geochim. Cosmochim. Acta* **59**, 1217 (1995).
3. A. W. Hofmann, *Earth Planet. Sci. Lett.* **90**, 297 (1988); S.-S. Sun and W. F. McDonough, in *Magmatism in the Ocean Basins*, A. Saunders and M. Norry, Eds. (Geological Society, London, special edition, 1989), vol. 42, pp. 313–345.
4. MORB are depleted in Nb relative to La, and because Nb is more incompatible than La during mantle melting (*13*) it follows that the source region of MORB, the so-called DM, must have even lower Nb/La.

5. Both are 0.064 nm for octahedral coordination [R. D. Shannon, *Acta Crystallogr*. **32**, 751 (1976)].
6. We consider here only data from high-precision techniques where both elements are analyzed simultaneously, such as inductively coupled plasma mass spectrometry (ICP-MS) [S. M. Eggins *et al*., *Chem. Geol*. **134**, 311 (1997)] and multichannel spark source mass spectrometry [K.-P. Jochum *et al*., *J. Anal. Chem*. **359**, 385 (1997)].
7. K.-P. Jochum, J. Pfander, J. E. Snow, A. W. Hofmann, *Eos* **78**, F805 (1997).
8. T. Plank and W. M. White, *Eos* **76**, F655 (1995).
9. Y. Niu and R. Batiza, *Earth Planet. Sci. Lett*. **143**, 471 (1997).
10. A. W. Hofmann and K.-P. Jochum, *J. Geophys. Res*. **101**, 11831 (1996); K.-P. Jochum, A. W. Hofmann, A. J. Stolz, *Eos* **77**, F785 (1996).
11. M. G. Barth, W. F. McDonough, R. L. Rudnick, *Chem. Geol.*, in press.
12. T. Plank and C. H. Langmuir, *Chem. Geol*. **145**, 325 (1998).
13. C. C. Lundstrom, H. F. Shaw, F. J. Ryerson, Q. Williams, J. Gill, *Geochim Cosmochim. Acta* **62**, 2849 (1998), and references therein.
14. F. A. Frey, C. J. Suen, H. W. Stockman *Geochim. Cosmochim. Acta* **49**, 2469 (1985); E. Takazawa, thesis, Massachusetts Institute of Technology, Cambridge, MA (1996); O. Muetner, thesis, Swiss Federal Institute of Technology (1997).
15. To date, superchondritic Nb/Ta has been observed only in some high K island arc lavas [A. J. Stolz, K.-P. Jochum, B. Spettel, A. W. Hofmann, *Geology* **24**, 587 (1996); T. Elliott, T. Plank, Z. Zindler, W. White, B. Bourdon, *J. Geophys. Res*. **102**, 14991 (1997); C. Münker, *Chem. Geol*. **144**, 23 (1998)], which can have Nb/Ta up to 33. However, these lavas are volumetrically minor and share the low Nb/La typical of other convergent margin magmas. Therefore, they do not appear to derive from a source with the necessary chemical composition to achieve the mass balance. Similarly, some OIB have superchondritic Nb/La but not Nb/Ta (*10*) or Ti/Zr ratios (*1*). Superchondritic Ti/Zr is observed in massif peridotites, but these have strongly subchondritic Nb/Ta and Nb/La (*14*).
16. F. J. Ryerson and E. B. Watson, *Earth Planet. Sci. Lett*. **86**, 225 (1987), and references therein.
17. Supplementary material is available at www.sciencemag.org/feature/data/1044137.shl (Web table 1).
18. Major and minor elements, including Al_2O_3, Cr_2O_3, MgO, ZrO_2, and Nb_2O_5 were determined with a Camebax MBX electron microprobe operated at 15 kV and a 30-nA beam current, using a rastered spot of 100 μm. Trace elements were determined by laser ablation ICP-MS with a home-built excimer laser that operates in the deep ultraviolet at 193 nm. This laser is coupled to a VG Plasmaquad 2+ ICP-MS, which has sensitivity in solution mode of $\sim 1 \times 10^8$ cps/ppm at mass 115. Details of the laser system are in (I. Horn, R. L. Rudnick, W. F. McDonough, *Chem. Geol*., in press) and can also be viewed at http://www-eps.harvard.edu/people/faculty/rudnick/la-icp-ms.html. Data reduction follows the procedure outlined in [H. Longerich, S. E. Jackson, D. Günther, *J. Anal. Atom. Spectrom*. **11**, 899 (1996)]. For the rutile analyses, ^{49}Ti was used as the internal standard and NIST 610 glass was used for the calibration standard. Excellent agreement exists between electron microprobe and LA-ICP-MS data for elements analyzed by both techniques (Al, Fe, Cr, Zr, and Nb).
19. K.-P. Jochum and A. J. Stolz, *Meteoritics Planet. Sci*. **32**, Suppl. 67 (1997).
20. The only exception to this generalization are rutiles from the Magnet Cove carbonatite complex and a rutile from a South Carolina beach sand of unknown provenance.
21. Supplementary material is available at www.sciencemag.org/feature/data/1044137.shl (Web table 2).
22. The two rutiles occur in veins in harzburgite xenoliths carried in volcanoes of the eastern African Rift: Labait and Pello Hill. In the Labait sample (LB-17) the rutile is associated with secondary zircon, sulfide, orthopyroxene, chromite, and minor phlogopite [R. L. Rudnick *et al.*, in *Proc. Seventh International Kimberlite Conference*, Cape Town, South Africa, J. J. Gurney and S. R. Richardson, Eds. (Red Barn, Cape Town, South Africa, 1999)]. In the sample from Pello Hill (PEL-40), rutile occurs in a phlogopite vein that also contains abundant sulfide.
23. Siberian eclogites come from the Udachnaya pipe courtesy of Z. Spetsius and N. Sobolev.
24. D. V. Hills and S. E. Haggerty, *Contrib. Mineral Petrol*. **103**, 397 (1989).
25. The western African eclogites come from the Koidu kimberlite pipe, Sierra Leone, and constitute the low MgO suite of (*24*). They are essentially bimineralic rocks with accessory sulfides and rutile. Kyanite, coesite, graphite, and diamond also occur as accessory phases. See (*24*) for a complete description.
26. The Nb/Ta, Nb/La, and Ti/Zr ratios of the eclogites follow log-normal distributions. We have therefore chosen the geometric mean as the value most representative of the population.
27. Rutile occurs in the eclogites as equant grains, from 100 μm to several millimeters in diameter. The rutiles generally occur interstitial to altered garnet and omphacite, but occasionally they occur fully included in omphacite. They typically show exsolution of ilmenite ± spinel at 90° angles. Some rutiles show thin (several micrometers) rims of ilmenite with variable MgO and MnO contents. Rims were not measured in laser ablation analyses. Metasomatic rutile is distinguished by highly heterogeneous Nb and Ta contents and occasionally by a skeletal texture. Based on textures, trace element homogeneity, and evidence for equilibrium between rutile and primary silicates, all rutiles reported in Web table 2 (*21*) are considered primary phases.
28. Unpublished data show that garnets and omphacites in rutile-bearing samples have Nb and Ta concentrations generally below detection limits, which vary as a function of spot size. For the spot sizes used in this study (50 to 100 μm), detection limits of 10 to 400 ppb are typical for both Nb and Ta. In contrast, garnet and omphacite contain significant Nb and Ta concentrations in rutile-free eclogites. About 70% of the low MgO eclogites from Koidu are rutile bearing.
29. Large ion lithophile elements include light weight REE, K, Rb, Cs, Sr, and Ba.
30. E. Jagoutz, J. B. Dawson, S. Hoernes, B. Spettel, H. Wanke, *Proc. 15th Lunar Planet. Sci. Conf.*, 395 (1984); Neal *et al*., *Earth Planet Sci. Lett*. **99**, 362 (1990); T. R. Ireland, R. L. Rudnick, Z. Spetsius, *Earth Planet Sci. Lett*. **128**, 199 (1994). In addition, the western African whole rock powders were ground in a tungsten carbide mill, which has led to significant Ta contamination. This is reflected by the good correlation between W and Ta values and very low Nb/Ta ratios (down to 1) in the whole rocks.
31. E. A. Jerde, L. A. Taylor, G. Crozaz, N. V. Sobolev, V. N. Sobolev, *Contrib. Mineral. Petrol*. **114**, 189 (1993); B. L. Beard *et al*., *Contrib. Mineral. Petrol*. **125**, 293 (1996).
32. The weight percent of rutile in the eclogites was determined from Ti mass balance by using the measured Ti contents of garnet and omphacite and their modal abundances [both given in (*24*)] to calculate their contribution to the whole rock Ti budget. Because both garnet and omphacite have lower TiO_2 than the bulk rock, this invariably led to a Ti deficit, which was made up by assuming that the remaining Ti was present in rutile. For the two samples lacking bulk rock TiO_2 concentrations, the TiO_2 content of the whole rock was calculated by assuming it has no Ti anomaly (that is, Ti is not depleted or enriched relative to elements of similar incompatibility such as Eu). The methodology described above yields the maximum amount of rutile in the sample, because it does not account for any Ti that is in secondary phases such as amphibole (0.5 to 2.5 weight % TiO_2) and phlogopite (1.6 to 4 weight % TiO_2). However, the overestimation is small and within the errors of the estimate. For example, sample KEC 81-18 has the highest measured bulk K_2O content of 1 weight %. If all this K_2O is contained within phlogopite, it corresponds to 11% phlogopite in the whole rock by weight, which in turn corresponds to only 0.03 weight % of the bulk rock's TiO_2 content. Decreasing the whole rock TiO_2 content by this amount leads to an estimated rutile abundance of 0.61% compared with 0.64% if the phlogopite is ignored. We thus conclude that our estimates of rutile proportions are accurate to within ±0.05% absolute or 10% relative uncertainty.
33. W. F. McDonough and S.-S. Sun, *Chem. Geol*. **120**, 223 (1995); C. J. Allegre, J.-P. Poirier, E. Humler, A. W. Hofmann, *Earth Planet. Sci. Lett*. **134**, 515 (1995).
34. The Al_2O_3 contents of xenolithic eclogites are derived from a literature compilation of major element compositions for 77 samples normalized to 100%, anhydrous. The population follows neither a log-normal nor a normal distribution but is skewed to high values. We therefore adopt the median Al_2O_3 content of xenolithic eclogites (15.8 weight %) as best representative of the population. Further statistics: average = 17.6% ± 5.9% (1σ), minimum = 7.4%, maximum = 31%.
35. A minimum estimate of the amount of oceanic crust subducted though Earth history is 1.3×10^{26} g, or 3.3% of the silicate Earth by mass. This is derived by assuming the present mass of oceanic crust (5.3×10^{24} g) is subducted every 100 million years for the last 2.5 billion years (Ga). This estimate is nearly identical to that commonly assumed in recycling models for OIB generation (*44*). We consider this estimate a minimum bound because subduction may well have operated before 2.5 Ga, the ocean basins may have been larger than at present (if the mass of the continents has increased with time), and the mantle was hotter in the Archean, which would produce a greater thickness of oceanic crust at a faster rate.
36. W. F. McDonough, *Earth Planet. Sci. Lett*. **101**, 1 (1990).
37. D. J. Schulze, *J. Geophys. Res*. **94**, 4205 (1989); P. H. Nixon, Ed. *Mantle Xenoliths* (Wiley, New York, 1989). However, in rare occurrences, eclogite may dominate some areas of the lithospheric mantle, see [N. V. Sobolev, E. S. Yefimova, D. M. DeR. Channer, P. F. N. Anderson, K. M. Barron, *Geology* **26**, 971 (1998)] and references therein.
38. S. Kaneshima and G. Helffrich, *Science* **283**, 1888 (1999); R. D. van der Hilst, S. Widiyantoro, E. R. Engdahl, *Nature* **386**, 578 (1997).
39. La, Nb, and Ta contents of the eclogitic reservoir were calculated from mass balance assuming that the silicate Earth (SE) is made up of four components: DM, continental crust (CC), primitive mantle (PM), and a refractory eclogite reservoir (EC). The concentration of an element in the eclogite reservoir is $X_{EC}{}^i = (X_{SE}{}^i - M_{CC}X_{CC}{}^i - M_{DM}X_{DM}{}^i - M_{PM}X_{PM}{}^i)$, where $X_{zz}{}^i$ is the concentration of element *i* in reservoir zz and M_{zz} is the mass fraction of the reservoir relative to the total silicate Earth. The mass fraction of the reservoirs and the range in concentrations used in the calculations are given in Table 1.
40. D. G. Pearson *et al*., *Nature* **374**, 711 (1995); M. G. Barth, R. L. Rudnick, R. W. Carlson, I. Horn, W. F. McDonough, *Eos* **80**, F1192 (1999).
41. H. Martin, *Geology* **14**, 753 (1986).
42. T. R. Ireland, R. L. Rudnick, Z. Spetsius, *Earth Planet. Sci. Lett*. **128**, 199 (1994); R. L. Rudnick, in *Extended Abstracts 6th International Kimberlite Conference* (1995), p. 473; H. Rollinson, *Nature* **389**, 173 (1997).
43. J. M. Brenan, H. F. Shaw, D. L. Phinney, F. J. Ryerson, *Earth Planet. Sci. Lett*. **128**, 327 (1994); R. Stalder, S. F. Foley, G. P. Brey, I. Horn, *Geochim. Cosmochim. Acta* **62**, 1781 (1998).
44. A. W. Hofmann, *Nature* **385**, 219 (1997) and references therein.
45. See [A. Zindler and S. R. Hart, *Annu. Rev. Earth Planet. Sci*. **14**, 493 (1986)] for a lexicon of OIB end members.
46. A. N. Halliday, *Nature* **399**, 733 (1999).

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