Ancient Mantle in a Modern Arc: Osmium Isotopes in Izu-Bonin-Mariana Forearc Peridotites

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Mantle peridotites drilled from the Izu-Bonin-Mariana forearc have unradiogenic $^{187}Os/^{188}Os$ ratios (0.1193 to 0.1273), which give Proterozoic model ages of 820 to 1230 million years ago. If these peridotites are residues from magmatism during the initiation of subduction 40 to 48 million years ago, then the mantle that melted was much more depleted in incompatible elements than the source of mid-ocean ridge basalts (MORB). This result indicates that osmium isotopes record information about ancient melting events in the convecting upper mantle not recorded by incompatible lithophile isotope tracers. Subduction zones may be a graveyard for ancient depleted mantle material, and portions of the convecting upper mantle may be less radiogenic in osmium isotopes than previously recognized.

Rhenium and osmium form a long-lived isotope system based on the β-decay of ^{187}Re to ^{187}Os, with a decay constant $\lambda = 1.666 \times 10^{-11}$ year^{-1} (*1*). These elements display siderophile and chalcophile behavior; rhenium is mildly incompatible (fractionated into the melt) and osmium is compatible during mantle melting. The geochemical behavior of the Re-Os isotope system contrasts markedly with that of all the other commonly used geologic isotope systems, in which the elements are lithophile and both parent and daughter elements are incompatible during mantle melting.

Osmium isotopes therefore provide unique insights into old partial melting events in the residues after melt extraction. Such residues are less dense than fertile mantle and hence are better able to survive the homogenizing effects of mantle convection. The subcontinental lithospheric mantle (SCLM) is isolated from the rest of the mantle, and it preserves a record of regional mantle processes since the stabilization of the overlying crust (*2*). Osmium isotopes correlate well with indicators of melt depletion such as Al_2O_3. On the basis of such correlations, massif peridotites from the Eastern Pyrenees preserve evidence of a melting event 2600 million years ago (Ma) (*3*). Even extensively modal metasomatized peridotites still retain information about ancient melting events (*4*). However, most crust-forming processes involve nonlithospheric mantle, and so the main record of crust formation must be in oceanic peridotites.

Abyssal peridotites, which represent the residues from melting of depleted MORB mantle (DMM) to produce MORB, have been the most difficult peridotites on which to acquire data. Extensive seawater alteration and the presence of manganoan coatings, which contain substantial amounts of radiogenic Os, make it difficult to determine the true Os isotopic value of these peridotites. So far only 10 abyssal peridotites have been analyzed that are believed to record their mantle values; these yield an average $^{187}Os/^{188}Os$ ratio of 0.1246 [range of 0.1222 to 0.1270 (*5*)]. By contrast, the limited data for peridotite xenoliths from subduction zones indicate that some samples have elevated $^{187}Os/^{188}Os$ ratios, which have been interpreted as the result of recent addition of radiogenic Os from subducted oceanic crust and sediments (*6*).

Mantle peridotites are uncommon in subduction zone systems. However, ultramafic rocks are commonly exposed within the inner trench wall of nonaccreting subduction zones, although their origins have remained contentious (*7*). We studied the Re-Os isotope systematics of ultramafic rocks from two serpentinite seamounts in the Izu-Bonin-Mariana (IBM) subduction system, the world's largest intraoceanic arc (Fig. 1). The rocks were obtained from Conical Seamount and Torishima Forearc Seamount during Ocean Drilling Program (ODP) Leg 125. The seamounts are spatially associated with boninitic lavas, and the whole forearc terrane has been suggested to have formed during the initiation of subduction around 48 Ma with the production of extensive boninitic magmatism along the whole length of the forearc (*8*). Recent geochemical work indicates that the Conical Seamount peridotites are accreted Pacific plate mantle that then reacted with ingressing melts to generate the boninitic lavas, whereas the Torishima Forearc Seamount peridotites are interpreted as the residues from melting in an arc system (*9, 10*).

We studied a suite of highly depleted spinel-harzburgites from the two serpentinite seamounts (*11*). The present-day Os isotopic compositions of the Leg 125 peridotites (Table 1) vary over a wide range ($^{187}Os/^{188}Os$ = 0.1193 to 0.1273). Two of the samples have $^{187}Os/^{188}Os$ ratios close to that of chondritic mantle; one of these samples contains amphibole, is oxidized, and has a markedly different rare earth element (REE) pattern from that of the other peridotites (*12*). These features may indicate that its Os isotope composition has been modified by a radiogenic component ultimately coming from the subducted slab (*6, 13*). By contrast, the other five samples have $^{187}Os/^{188}Os$ ratios of 0.1193 to 0.1223, which are more unradiogenic than abyssal peridotites and overlap the range of values for some recently described xenoliths from the Kerguelen Islands (*14*). These values make the Leg 125 samples some of the most unradiogenic oceanic peridotites sampled. The Re content of the peridotites is negligible (<10 parts per trillion), yielding low $^{187}Re/^{188}Os$ ratios. For five of the samples, there is a good positive correlation between Al_2O_3 (a monitor of melt depletion) and $^{187}Os/^{188}Os$, although the spread in Al_2O_3 contents is rather small compared with data for continental lithospheric mantle samples (Fig. 2) (*15*).

Linear relations between Al_2O_3 and the $^{187}Os/^{188}Os$ ratios have been used to extract

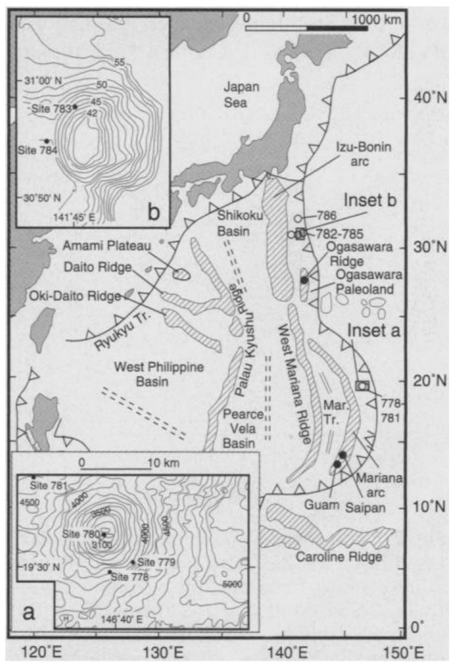

Fig. 1. Simplified tectonic map of the western Pacific illustrating the position of Conical Seamount (inset a) and Torishima Forearc Seamount (inset b). The positions of the ODP drilling sites are shown in the insets.

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age information from SCLM peridotite suites (*3*). However, because the Leg 125 peridotites are from disparate locations and one sample from each seamount has a more radiogenic osmium isotope composition, such a technique will be unreliable for these peridotites. Instead, the unradiogenic Os isotopic composition of these samples unequivocally indicates that they record an extremely old melting event. These samples might be expected to be related with magmagenesis during the initiation of subduction (40 to 48 Ma) or to represent accreted Pacific Plate material, which would suggest a maximum extraction age from the depleted upper mantle of 180 Ma.

A simple model to explain the data is that a single early melting event stripped out essentially all the Re and that the peridotites then became isolated from the convecting upper mantle. For this model, the minimum melt extraction age is 820 to 1230 Ma (Table 1) for the five unradiogenic samples, with the oldest ages for the Izu-Bonin peridotites (*16*). The two more radiogenic samples have extraction ages of 30 to 60 Ma, which is compatible with them being formed within the subduction zone or as part of the Pacific Plate. This would require mantle with widely differing ages to be interleaved within the forearc mantle section. Another more likely possibility is that the peridotites record a melting event but from a DMM source. Using an average $^{187}Os/^{188}Os$ ratio of 0.1246 for abyssal peridotites still yields an age of 500 to 900 Ma for these peridotites (*17*).

What are such fragments of old depleted mantle doing in a modern arc system? Because they are highly depleted, the Leg 125 peridotites are less dense than the fertile upper mantle (*18*). This density contrast will lead to stabilization of this mantle and make it difficult to subduct. Whether such depleted mantle is a feature of arcs is debatable. If so, subduction zones may be graveyards for ancient oceanic lithosphere. The inferred early age of this mantle is considerably older than melt depletion events that took place in the back-arc, less than 48 Ma (*8*). However, if melts migrating to the surface interacted with such an unradiogenic mantle, they would acquire its Os isotopic composition. A distinct unradiogenic Os isotope signature in arc lavas would be good evidence for the prevalence of such mantle in arc systems.

A second interpretation of the data is that these peridotites were involved in melting in a subduction zone around 40 to 48 Ma, which is compatible with other geochemical studies of these peridotites (*9, 10*). This in turn indicates that the mantle from which they were derived was already substantially more unradiogenic than DMM at the time of this melting event. One can calculate the degree of melting involved in the generation of such mantle relative to DMM at any point in the past (*19*). For example, for the most unradiogenic sample (0.1193) at 2500 Ma, which represents an average extraction age of DMM (*20*), the source would have to have partially melted 10 to 14% relative to a chondritic mantle with a present-day $^{187}Os/^{188}Os$ of 0.12757. If this melting occurred just after the accretion of Earth (4550 Ma), then it would represent 3 to 5% melting of a primitive mantle. Either way, these values are considerably greater than had been suggested for the amount of melting that was involved to produce the DMM source [0.5 to 2% (*20*)].

If a $^{187}Os/^{188}Os$ ratio of 0.1246 is a good estimate of the DMM source and it was extracted at 2500 Ma, then this represents ~5% partial melting of primitive mantle. This would yield a εNd value for DMM of >30, which is considerably greater than that recorded by MORB basalts (*20*). This calculated discrepancy between Os and Nd isotopes in DMM is robust and holds for whatever age of extraction of DMM from the primitive mantle is preferred. The spread in the range of analyzed $^{187}Os/^{188}Os$ ratios of both the Leg 125 and abyssal peridotites demands that there were episodic melting events in these segments of mantle. Therefore, DMM developed in an episodic fashion with partial melting events followed by convective homogenization (*21*). The more extreme degrees of partial melting recorded by Os isotopes may reflect the inability of Os isotopes to be homogenized in the depleted upper mantle. The compatible nature of Os during partial melting means that Os has had a long residence time in the depleted upper mantle, and that it was not affected by mass transfer of material from the lower mantle in a similar manner to that of the incompatible isotope tracers such as in the U-Th-Pb system (*22*). The decoupling of Os isotopes from incompatible lithophile isotope tracers highlights how Os isotopic studies of modern-day oceanic peridotites will reveal key information about the timing of extraction of crustal material from the DMM reservoir.

A final possibility for the origin for these peridotites is that they are pieces of delaminated SCLM. Recent Os isotopic data for peridotites beneath the Kerguelen Plateau also yield Proterozoic model ages (*14*). However, in the case of the Kerguelen Plateau, there is evidence that SCLM was transported beneath the plateau after the splitting of Gondwana. There is no obvious evidence for such material to underlie the IBM subduction system, although at the time of initiation of the IBM subduction zone system, its boundaries were considerably closer to the Eurasian continental margin. The SCLM model still requires that subduction zones are graveyards for ancient mantle material. The attraction of the SCLM model is that the ancient mantle would be stored in the continental lithosphere in a known reservoir of ancient mantle. Its weakness is in the implied presumption that all ancient oceanic mantle was derived from the SCLM in the absence of additional supportive evidence. Our main reservation for a

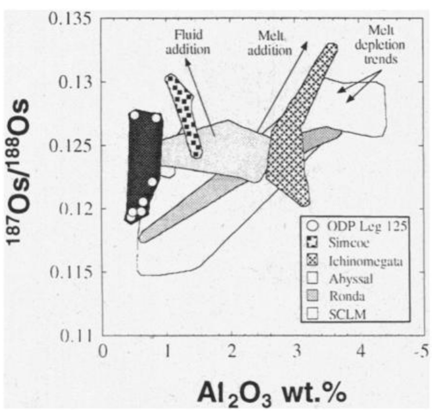

Fig. 2. Os isotopic–Al_2O_3 relations for the ODP Leg 125 peridotites. Also plotted are data for SCLM samples from the Ronda, Pyrenees, Australia, United States, and Germany (*3, 4, 24*) and melt depletion trends for Ronda and the other peridotite suites. Abyssal peridotite data are from (*5*) with Al_2O_3 data from (*25*). Subduction zone peridotite data from Simcoe, Washington, and from Ichinomegata, Japan, are from (*6*); also plotted are vectors for addition of radiogenic Os from the subducting slab.

Table 1. Al_2O_3 and Os concentrations and Os isotopic data for the ODP Leg 125 peridotites. All samples are spinel harzburgites except as noted, and none contain >10 ppt Re (*11*). Errors in $^{187}Os/^{188}Os$ in terms of least units cited.

Hole	Core	Interval	Al_2O_3 (*15*) (weight %)	$^{187}Os/^{188}Os$	Os (ppt)	γOs (*23*)	T_{RD} (*16*) (Ma)
				Conical seamount			
779A	8R-1	49–55	0.64	0.120541 ± 92	649	−5.51	1050
779A	14R-2	40–48	0.85	0.127144 ± 39	1594	−0.33	60
779A	19R-2	108–113*	0.79	0.122089 ± 75	2597	−4.30	820
				Torishima forearc seamount			
783A	18R-1	64–71†	0.52	0.127374 ± 76	3996	−0.15	30
783A	18R-1	64–71‡	–	0.127185 ± 43	2518	−0.30	60
784A	42R-1	40–48	0.62	0.119758 ± 151	122	−6.12	1170
784A	45R-1	101–106	0.46	0.119333 ± 47	2566	−6.46	1230
784A	45R-2	33–38	0.48	0.119748 ± 100	1793	−6.12	1170

*Dunite. †Amphibole-bearing spinel harzburgite. ‡Replicate.

SCLM origin of these peridotites is the close spatial proximity of mantle with such widely varying extraction ages, when every other geochemical aspect of the peridotites suggests they are petrogenetically related (*9, 10*).

These Os isotope data indicate that unusually old depleted mantle is stranded within subduction zones. Our preferred interpretation is that the peridotites analyzed are from the oceanic mantle, which suggests that portions of the upper mantle are less radiogenic in Os isotopes than previously recognized.

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11. The surfaces of the rock samples were cleaned to remove any obvious alteration material. The samples were then milled in an agate Tema until a very fine powder was produced. Powder (2 g) was spiked and digested with aqua regia in a Carius tube. Os and Re were separated using a solvent extraction scheme and were purified using a microdistillation method and small anion columns, respectively. Os concentrations, $^{187}Os/^{188}Os$ ratios, and Re concentrations were measured as negative ions on a Finnigan 261 mass spectrometer. Analytical methods are presented in detail elsewhere [A. S. Cohen and F. G. Waters, *Anal. Chim. Acta* **332**, 269 (1996)]. Precision of the $^{187}Os/^{188}Os$ ratios, based on counting statistics, ranges from 0.03 to 0.13% (2σ). Standards run during the course of this work are reproduced at a precision of 0.2%. A full procedural replicate analysis of one sample agreed within 0.15%. Unfortunately, there was a considerable difference in the Os concentration between the replicates, suggesting some heterogeneity in distribution of Os in the sample. However, the fact that the replicates have identical $^{187}Os/^{188}Os$ ratios supports the notion that there is negligible Re in the peridotites. Procedural blanks for Os during the course of this work varied from 16 pg to less than 2 pg. Blank corrections ranged from 0.02 to 1.5%. Re concentrations were negligible (<10 ppt) and were swamped by the Re blank.
12. REE data from (*10*); the amphibole-bearing harzburgite has a smooth REE pattern increasing from La to Lu. By contrast, all the other samples have U-shaped patterns with variable light REE enrichment.
13. Seawater alteration and sea-floor weathering processes both add radiogenic Os to peridotites (*5*). Drilled peridotites that have not weathered on the sea floor are generally not affected by Os addition (*5*). Roy-Barman and Allègre leached an ODP-drilled peridotite with oxalic acid and found no difference in the $^{187}Os/^{188}Os$ ratio of the unleached and leached sample. The peridotites in this study are serpentinized but are all from deep sections of the drill core. No manganoan coating was observed on the peridotites. Moreover, it has been suggested that serpentinization of these peridotites is not by seawater alteration at a ridge crest, but by fluids from the underlying subducting plate [M. J. Mottl, *Proc. ODP Sci. Res.* **125**, 373 (1992)].
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15. Al_2O_3 data from (*10*).
16. In the model age calculation, the peridotite is assumed to contain no Re, and therefore the $^{187}Os/^{188}Os$ ratio of the peridotite has not changed because the Re was extracted during an ancient melting event. The age is calculated from the time in the past that the measured $^{187}Os/^{188}Os$ ratio intersects a chondritic Re-Os evolution curve with a present-day $^{187}Os/^{188}Os$ ratio of 0.12757 and a $^{187}Re/^{188}Os$ ratio of 0.3972 [R. J. Walker, R. W. Carlson, S. B. Shirey, F. R. Boyd, *Geochim. Cosmochim. Acta* **53**, 1583 (1989)]. Recent work suggests that the putative primitive upper mantle has an $^{187}Os/^{188}Os$ ratio of 0.1290 and a $^{187}Re/^{188}Os$ ratio of 0.423 [T. Meisel, R. J. Walker, J. W. Morgan, *Nature* **383**, 517 (1996)]. Using these parameters gives slightly older (100 Ma) model ages but does not affect our conclusions.
17. T_{RD} model ages from DMM are calculated in a similar fashion to (*16*) except that the $^{187}Os/^{188}Os$ ratio of modern-day DMM is taken to be 0.1246 (*5*) and that it is extracted from a chondritic mantle at 2500 Ma. This calculation depends on the age of extraction of the DMM reservoir from the primitive mantle, but T_{RD} from DMM always gives a younger model age than does T_{RD} from the chondritic mantle.
18. The refectory nature of the Leg 125 peridotites (highly forsteritic olivine, low Al_2O_3 contents) means that its density is still slightly lower than that of ambient fertile mantle, even when the peridotites have cooled substantially. Therefore, it is relatively buoyant and will become stabilized (see W. L. Griffin, S. Y. O'Reilly, C. G. Ryan, O. Gaul, D. A. Ionov, *AGU Spec. Monogr.*, in press).
19. Modeling of the amount of melt extraction is as follows: For each peridotite, an initial Re content is assigned using its Os content and the assumption that it has a chondritic Re/Os ratio of 0.8. The simplest approach is to assume that Os has a bulk partition value of 1, so the Os concentration does not change during melting. Using more realistic Os partition values does not markedly change the conclusion of the calculations. The Re concentration and therefore the $^{187}Re/^{188}Os$ ratio is changed such that the sample would evolve from the chondritic mantle curve (*15*) to its measured $^{187}Os/^{188}Os$ ratio for any given extraction date. The amount of melting is then calculated using the observation that Re and Al_2O_3 correlate linearly during partial melting and that Re is completely extracted after ~25% partial melting. Although modeling assumptions change the absolute values calculated, each calculation is internally consistent and the relative difference in partial melting between samples is also consistent.
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23. γOs is a percentage difference between the measured $^{187}Os/^{188}Os$ ratio and the $^{187}Os/^{188}Os$ ratio of present-day mantle. In this case we use a present-day $^{187}Os/^{188}Os$ ratio of 0.12757 (*16*). Negative γOs values indicate subchondritic Os isotope rations; positive values indicate suprachondritic ratios.
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Semiconductor Nanocrystals as Fluorescent Biological Labels

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Semiconductor nanocrystals were prepared for use as fluorescent probes in biological staining and diagnostics. Compared with conventional fluorophores, the nanocrystals have a narrow, tunable, symmetric emission spectrum and are photochemically stable. The advantages of the broad, continuous excitation spectrum were demonstrated in a dual-emission, single-excitation labeling experiment on mouse fibroblasts. These nanocrystal probes are thus complementary and in some cases may be superior to existing fluorophores.

Fluorescence is a widely used tool in biology. The drive to measure more biological indicators simultaneously imposes new demands on the fluorescent probes used in these experiments. For example, an eight-color, three-laser system has been used to measure a total of 10 parameters on cellular antigens with flow cytometry (*1*), and in cytogenetics, combinatorial labeling has been used to generate 24 falsely colored probes for spectral karyotyping (*2*). Conventional dye molecules impose stringent requirements on the optical systems used to make these measurements; their narrow excitation spectrum makes simultaneous excitation difficult in most cases, and their broad emission spectrum with a long tail at red wavelengths (Fig. 1A) introduces spectral cross talk between different detection channels, making quantita-

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