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Geochemistry and models of mantle circulation

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Geochemical data help to constrain the sizes of identifiable reservoirs within the framework of models of layered or whole-mantle circulation, and they identify the sources of the circulating heterogeneities as mainly crustal and/or lithospheric, but they do not decisively distinguish between different types of circulation.

The mass balance between crust, depleted mantle and undepleted mantle based on $^{143}Nd/^{144}Nd$, Nb/U and Ce/Pb, and the concentrations of very highly incompatible elements Ba, Rb, Th, U, and K, shows that *ca.* 25–70% (by mass) of depleted mantle balances the trace element and isotopic abundances of the continental crust. This mass balance reflects the actual proportions of mantle reservoirs only if there are no additional unidentified reservoirs.

Evidence on the nature and ages of different source reservoirs comes from the geochemical fingerprints of basalts extruded at mid-ocean ridges and oceanic islands. Consideration of Nd and He isotopes *alone* indicates that ocean island basalts (OIBs) may be derived from a relatively undepleted portion of the mantle. This has in the past provided a geochemical rationale for a two-layer model consisting of an upper depleted and a lower undepleted ('primitive') mantle layer. However, Pb-isotopic ratios, and Nb/U and Ce/Pb concentration ratios demonstrate that most or all OIB source reservoirs are definitely *not* primitive. Models consistent with this evidence postulate recycling of oceanic crust and lithosphere or subcontinental lithosphere. Recycling is a natural consequence of mantle convection. This cannot be said for some other models such as those requiring large-scale vertical metasomatism beneath OIB source regions.

Unlike other trace elements, Nb, Ta, and Pb discriminate sharply between continental and oceanic crust-forming processes. Because of this, the primitive mantle value of Nb/U = 30 (Ce/Pb = 9) has been fractionated into a continental crustal Nb/U = 12 (Ce/Pb = 4) and a residual-mantle (MORB (mid-ocean ridge basalt) plus OIB source) Nb/U = 47 (Ce/Pb = 25). These residual mantle values are uniform within about 20% and are not fractionated during formation of oceanic crust. By using these concentrations ratios as tracers, it can be shown that the possible contribution of recycled continental crust to OIB sources is limited to a few percent. Therefore, recycling must be dominated by oceanic crust and lithosphere, or by subcontinental lithosphere. Oceanic crust normally bears a thin layer of pelagic sediment at the time of subduction, and this is consistent with OIB sources that are dominated by subducted oceanic crust with variable but always small additions of continental material.

Primordial ^{3}He, ^{36}Ar, and excess ^{129}Xe, in oceanic basalts demonstrate that the mantle has been neither completely outgassed nor homogenized, but they do not constrain the degree of mixing or the size of reservoirs. Also, helium does not correlate well with other isotopic data and may have migrated into the basalt source from other regions. The high $^{3}He/^{4}He$ ratios found in some OIBs suggest that, even though the basalts are not derived from primordial mantle, their sources may be located close to a reservoir rich in primordial gases. This leads to models in which the OIB sources are in a boundary layer within the mantle. The primordial helium migrates into this layer from below. The interpretation of the rare-gas data is still quite controversial.

It is often argued that the upper mantle is a well-homogenized reservoir, but the data indicate heterogeneities on scales ranging from 10^0 to 10^6 m. The $^{206}Pb/^{204}Pb$ ratios in the oceanic mantle range from 17 to 21, which is similar to the range in most continental rocks. The degree of mixing cannot be directly inferred from these data unless the size and composition of the heterogeneities and the time of their introduction into the system are known. The relative uniformity of Nb/U and Ce/Pb ratios in the otherwise heterogeneous MORB and OIB sources indicates that this reservoir was indeed homogenized after the separation of the continental crust, and that the observed isotopic and chemical heterogeneities were introduced subsequently.

Overall, the results are consistent with, but do not prove, a layered mantle where the upper layer contains both MORB and OIB sources, and the lower, primitive mantle is not sampled by present-day volcanism. Alternative models such as those involving a chemically graded mantle have not been sufficiently explored.

INTRODUCTION

Studying mantle geochemistry is somewhat like examining the surface of a marble cake and trying to deduce its internal structure from the observed distribution of brown and yellow. Mantle tomography offers the hope for 'seeing' the internal structure and thereby interpreting the marble cake. But because we are working with tracers that do not affect the physical properties of the rock in any measurable and direct way, this effort will have to depend on interpreting *correlations* of velocity structure and geochemical tracers.

The more traditional, although usually not explicitly stated, approach is to interpret the geochemical surface map using what is known about plate kinematics and, to a lesser extent, convection dynamics. For example, plumes are more likely to be formed from low-density boundary layers than from an internally heated medium. The plumes are stationary or at least mechanically decoupled from the plate movements and their sources are therefore believed to be located deeper in the mantle. In contrast, ridge migration is strongly coupled to the geometry and movement of the plates and is 'passive' in this sense. Therefore, the ridges sample predominantly the uppermost mantle, not a rising deep-mantle current. Without such additional constraints or inferences, geochemistry alone has very little to say about mantle structure.

GEOCHEMICAL TRACERS OF MANTLE RESERVOIRS

The conventional use of geochemical tracers to characterize source regions of basaltic melts in the mantle rests on the assumption that the isotopic composition of a partial melt in the mantle is representative of the entire volume of mantle rock from which the melt has been extracted. This assumption has been questioned repeatedly during the past 15 years. Hofmann & Hart (1978) argued on the basis of measured and estimated diffusion coefficients in solid and liquid silicates that partially molten mantle rocks should come to local equilibrium between solid and melt in geologically very short times of the order of less than 10^4 years. They argued further that if this were not so, then much of the work done in experimental petrology on the melting relations of mantle rocks would be meaningless. Most workers subsequently accepted the conclusion that individual mineral grains are extremely unlikely to survive in a state of disequilibrium with partial melts except in situations where melts are formed and extracted very rapidly. These conclusions have been reaffirmed by Hart & Zindler (1988) in the light of more recent experimental data. Examples of exceptions might be found in partially molten xenoliths or perhaps in the wall rock of a rapidly rising hotter diapir. Ordinary convective motions in the mantle should always be slow enough to ensure attainment of local equilibrium, especially so because the pressure and temperature changes accompanying these motions force the material to recrystallize as it undergoes phase changes.

Mesoscale heterogeneities

It is appropriate to ask the question how far in space does local equilibrium extend. What happens on the decimetre to kilometre scale where diffusional transport becomes negligibly small, even in partially molten systems and over geologically long periods of time? When mantle peridotites are examined in outcrop, it becomes immediately clear that these rocks can be quite heterogenous on this scale (Reisberg & Zindler 1986). Whether the heterogeneities are veins (Hanson 1977), trace-element enriched lumps (Sleep 1984), dikes or (almost) infinitely drawn out former oceanic crust (Allègre & Turcotte 1986), if the 'enriched' portions can be melted preferentially and this melt be extracted without chemical and isotopic equilibration with the more 'depleted', refractory portions, then the isotopic composition of the melt will be biased in favour of the enriched portions of the source. This theme has been discussed in numerous variants (Hanson 1977; Sleep 1984; Hart & Zindler 1986; Zindler *et al.* 1984; Allègre & Turcotte 1986; Fitton & Dunlop 1985). The consequence common to all these variants is that the isotopic composition of the melt will depend on the overall degree of melting, because this determines how much of the more-refractory portion of the source rock is sampled by the melt. For the sake of convenience, I will call the scale ranging from decimetre to kilometre the *mesoscale*.

Whether or not the partially molten mantle attains equilibrium on the mesoscale depends on whether or not the melt permeates all the refractory portions of the source region. If it does, diffusion in the melt alone will tend to equilibrate the melt over a distance of a metre in a few thousand years. Migration and mixing of the melt will greatly enhance the overall equilibration, and it is likely that this sort of equilibrium will effectively extend to the kilometre scale. If the melt does *not* permeate all of the rock, isotopic and chemical equilibration is quite unlikely on the mesoscale, because the solids that are not in direct contact with an intergranular melt (or fluid) are unlikely to equilibrate with it. Experiments by Waff & Buhlau (1979) have shown that a partial melt does not wet the intergranular surfaces, but it does penetrate peridotite through a fully interconnecting network porosity along grain corners. If this is also true in the mantle, then mesoscale equilibrium should easily be attained.

Another approach to this problem is to study melts and residues in natural settings where the degree of melting changes with time or location. If mesoscale disequilibrium prevails, then those regions that have undergone the lowest degree of melting should have produced melts with the isotopic characteristics of the highest incompatible-element enrichment, because these melts would preferentially sample the most fertile and most trace-element enriched portions of the source. Several cases have been documented where the opposite is true. Hawaiian lavas consistently change to lower $^{87}Sr/^{86}Sr$ and higher $^{143}Nd/^{144}Nd$ ratios as the degree of melting decreases toward the end of the life of each volcano (Chen & Frey 1985; Feigenson 1984; Lanphere *et al.* 1980; Hofmann *et al.* 1987). Along the mid-Atlantic ridge, the most enriched melts are found in regions where the residual periodites indicate that the largest melt fraction has been extracted. Small sea mounts sometimes show very heterogeneous compositions

(Zindler *et al.* 1984), which may well be caused by mesoscale disequilibrium, but most show the same depleted isotopic and chemical character as nearby ordinary ridge segments (Batiza & Vanko 1984). Thus, although mesoscale disequilibrium cannot be dismissed out of hand, the weight of the evidence points to a rather minor role at best, and there are good reasons to think that the regional variations displayed by oceanic basalts do indeed reflect regional, rather than mesoscale heterogeneities in the mantle. The applicability of geochemical tracers to problems of large-scale mantle structure and circulation depends on the correctness of this inference.

GEOCHEMICAL TRACERS

(*a*) *Isotopes*

Isotopic compositions of heavy, refractory elements are the most reliable tracers of the source compositions of mantle derived basalts. This is so because any mass-dependent isotopic fractionation during melting is negligible. Even if such fractionation did occur in Nature, it would be automatically corrected during mass spectrometric analysis. Non-mass-dependent fractionation, as suggested by O'Hara & Mathews (1981), has never been observed in the multi-isotopic elements Sr and Nd where, purely for reasons of analytical quality control, two or more non-radiogenic isotopic ratios are routinely monitored for non-mass-dependent effects in many laboratories. These are trivial matters to isotope geochemists, but they must be mentioned periodically because they are still raised frequently in lectures and discussions.

The chief disadvantage of isotope ratios is that they are applicable to only a small number of elements that contain radiogenic daughter isotopes of long-lived parent nuclides. Three of the most commonly used isotopic tracers, Sr, Nd, and Hf, are strongly correlated in most mantle derived rocks (Richard *et al.* 1976; DePaolo & Wasserburg 1976; O'Nions *et al.* 1977; Patchett & Tatsumoto 1980) and do not yield much independent information. The resulting so-called mantle array has been variously interpreted as mixtures of primitive and depleted sources, mixtures of continental or oceanic crust and depleted mantle, and mixtures of metasomatically enriched and depleted mantle. Because of this, they are very useful for the purpose of constraining mass balances of mantle reservoirs and mapping the isotopic heterogeneities at the surface, but not for identifying the nature of the source materials. Deviations from the purely linear correlation in several ocean island basalts (OIBS) (White & Hofmann 1982) demonstrate that more than two source reservoirs must be present, but this alone does not constrain the origin of these reservoirs. It seems unlikely that additional data on Sr, Nd, and Hf isotopes will change this. The continental crust has been extracted from the mantle and is enriched in the so-called incompatible elements. If other enrichment processes have operated in the mantle, they may have created parent–daughter fractionations that are indistinguishable from the differentiation of primitive mantle into continental crust and depleted residue.

The isotopic ratios of Pb and He are well correlated with those of Sr in some regions but not in others, and their interpretation is still being disputed by the specialists. Reviews of the combined isotopic data in OIB and mid-ocean ridge basalts (MORBS) have led to the tentative identification of as many as five distinct source reservoirs (White 1985; Zindler & Hart 1986), but it is far from clear just how separate these sources are and how they may have been produced. Some of the issues involved will be discussed further below.

(*b*) *Trace elements*

Trace element abundance ratios are suitable tracers under certain circumstances, where they can be used as 'quasi-isotopic' ratios. They considerably expand the geochemical arsenal available to fingerprint and identify sources, and some of these ratios permit much more specific source assignments than is possible on the basis of isotopic ratios alone. However, there is always the risk of trace-element fractionation between the basalt sampled at the surface and its source in the mantle. This fractionation is minimized when the melt fraction is much greater than the bulk partition coefficients of the elements involved. This is illustrated in figure 1, which is a plot of the equation

$$\frac{c_1}{c_2} = \frac{c_1^0}{c_2^0}\cdot\frac{F+D_2(1-F)}{F+D_1(1-F)}, \tag{1}$$

where c and c^0 are the concentrations in the melt and in the source, respectively, F is the melt fraction and D is the bulk partition coefficient defined as $D = c(\text{solid})/c(\text{melt})$. The subscripts refer to elements 1 and 2. For example, the widely used Zr/Nb or La/Sm ratios may well be perfectly good tracers in MORBS because the melt fractions are comparatively large, but not in some OIBS, where melt fractions are smaller and the same elements may be fractionated.

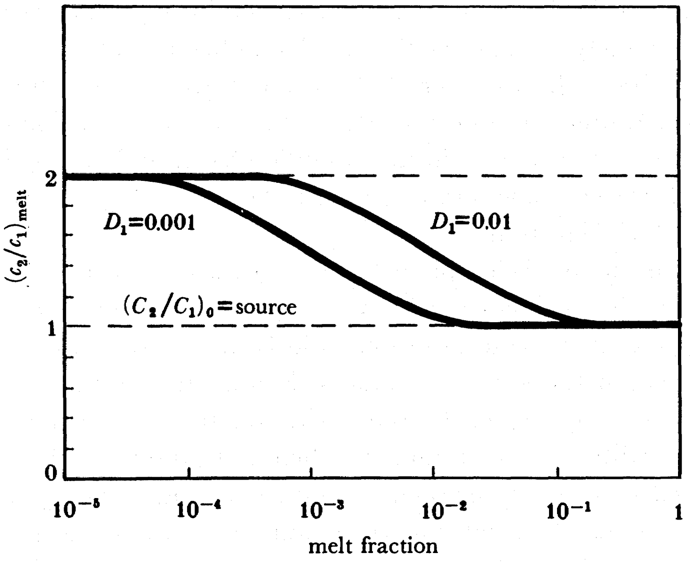

FIGURE 1. Concentration ratios of two trace elements in a melt as a function of melt fraction (equation (1)). The two curves are for bulk partition coefficients between solid and melt, $D_1 = 0.001$ and $D_1 = 0.01$. The ratio of bulk partition coefficients is in both cases $D_2/D_1 = 2$. For highly incompatible elements, ($D < 0.001$), and melt fractions, $F > 0.01$, the concentration ratio in melt approaches the source ratio. This is the basis for using trace-element concentration ratios to characterize source compositions.

U and Th are among the most incompatible elements in mantle rocks, that is, their bulk partition coefficients between solid and melt are very small, much smaller than melt fractions believed to be realistic for MORBS. Yet, the thorium isotope ^{230}Th in many MORBS is not in radioactive equilibrium with its parent nuclide ^{238}U (Allègre & Condomines 1982). Such a disequilibrium in a radioactive decay chain is possible only if there has been a chemical fractionation (or separation) between parent and daughter within the geologically very short time span of several half lives of ^{230}Th ($t_{\frac{1}{2}} = 7.5\times10^4$ years). The most likely, although unexpected and somewhat alarming, explanation of this phenomenon is that Th is fractionated from U between the MORB and its source (Allègre & Condomines 1982), and this raises serious doubts about the 'quasi-isotopic' status of other abundance ratios of highly incompatible elements. U and Th have partition coefficients in the major mantle minerals olivine, orthopyroxene, clinopyroxene, garnet, and spinel of $D < 10^{-2}$ (Watson *et al.* 1987), and the bulk partition coefficients of mantle mineral assemblages consisting of these phases (but dominated by olivine and orthopyroxene) should have bulk partition coefficients of $D < 10^{-3}$. Figure 1 shows that such elements should not be fractionated in MORBs, which have melt fractions far exceeding the critical value of $F = 0.01$ (see Klein & Langmuir 1987; Hofmann 1988). Galer & O'Nions (1986) explained this unexpected fractionation as follows: in the unmelted mantle, the highly incompatible elements are concentrated in trace minerals, which have comparatively large partition coefficients for these elements. During mantle upwelling beneath the ocean ridges, partial melting at the base of the melting regions begins necessarily at very small melt fractions, so that the trace-mineral phases are not immediately consumed by the melt. They can therefore fractionate these elements, and if the melt fraction is able to migrate upward slightly faster than the solid phases, the fractionated melt enters the higher regions where melt fractions become naturally larger. The trace-element-rich melt derived from below now mixes with the locally produced melt and imposes its inherited trace element composition on the bulk melt. The general significance of this type of element fractionation is still rather uncertain, largely because of the small number of MORB samples in which the phenomenon has been observed. Moreover, the observed degree of Th–U fractionation is much smaller than the observed differences of trace element ratios such as La/Sm, which have been used extensively to trace MORB sources in the Atlantic Ocean and elsewhere (Schilling *et al.* 1983). Therefore, such tracer studies are not likely to be invalidated by the evidence derived from $^{230}\mathrm{Th}/^{232}\mathrm{Th} - ^{238}\mathrm{U}/^{232}\mathrm{Th}$ studies.

One way to ascertain the quasi-isotopic behaviour of trace-element ratios is to choose two trace elements that have identical bulk partition coefficients. Hofmann *et al.* (1986) have shown that this condition is met if the concentration ratio is independent of melt fraction over a sufficiently large range of melt fractions. In practical terms, this means when a trace element ratio is identical in relatively depleted MORBs with relatively large melt fractions *and* in relatively enriched OIBs with small melt fractions, then that ratio must also be the same in the sources of all these basalts. Over a dozen such ratios have been identified (Jochum & Hofmann 1989). Most of these are identical not only in oceanic basalts but also in most rocks of the continental crust. They are therefore not useful as tracers of terrestrial fractionation processes but merely confirm the meteorite model for the composition of the Earth. However, two of these ratios, Nb/U and Ce/Pb, are higher by a factor of four in the mantle sampled by MORBs and OIBs than in the continental crust. These ratios are unique tracers that can distinguish between mantle enrichments which have produced OIB sources and sources derived from the continental crust.

MASS BALANCE

Some of the earliest studies of ocean-floor basalts revealed that they have unusual chemical and isotopic compositions. Beginning with Tatsumoto *et al.* (1965) who showed that MORBs have very low $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios, and K, Rb, U and Th concentrations, these rocks were subsequently found to be also relatively depleted in Cs, Ba, Nb, Ta, and the light rare-earth elements. It also became clear that, qualitatively, their chemistry is complementary to that of the continental crust. Those elements that are most strongly enriched in the continental crust are also the most incompatible in the mantle, that is, they are partitioned most strongly into any available silicate melt in contact with the common minerals of the upper mantle, olivine, pyroxene, garnet and spinel. From an *a priori* knowledge of the bulk earth composition (derived from chondritic meteorites with some important modifications particularly to volatile elements), Taylor & McLennan (1985, pp. 266, 267) estimated that about 30% of the total terrestrial inventory of these 'incompatible' elements are now in the continental crust.

The relation of the continental crust to the source reservoir of ocean floor basalts was quantified when isotopic data for neodymium became available. The ^{143}Nd/^{144}Nd ratio of the bulk earth is identical to that of chondritic meteorites. Moreover, this ratio is relatively uniform in most continental rocks and also in MORBS; consequently, a rather well constrained mass balance can be calculated using the simple assumption that primitive mantle material has been differentiated into ('enriched') continental crust and complementary ('depleted') mantle (DePaolo 1980; Jacobsen & Wasserburg 1979; O'Nions *et al.* 1979; Allègre *et al.* 1983.) The simplest expression of this has been formulated in the following three equations (Davies 1981):

$$m_p + m_d + m_c = 1, \tag{2}$$

$$m_d\, C_d\, \epsilon_d + m_c\, C_c\, \epsilon_c = 0, \tag{3}$$

$$m_p\, C_p + m_d\, C_d + m_c\, C_c = C_p, \tag{4}$$

where m are the mass fractions of the three reservoirs p (primitive mantle), d (depleted mantle), and c (continental crust), C are the respective neodymium concentrations, and ϵ are the relative deviations of the ^{143}Nd/^{144}Nd ratios from the chrondritic (primitive mantle) value, which is defined by $\epsilon_p \equiv 0$. The ϵ values, the mass of the continental crust, and the Nd concentrations of the primitive mantle and the continental crust are measured or assumed, so that the equations can be solved for m_p, m_d, and C_d. These calculations yielded the important result that the depleted fraction of the mantle $m_d \approx 0.25$–0.5. Davies (1981) and Allègre *et al.* (1983) estimated that the errors in the input parameters are large enough so that m_d might be as high as 0.8. Recent re-evaluations of the neodymium concentrations of the bulk silicate earth (Sun 1982; Hart & Zindler 1986; Wänke 1981) and of the continental crust (Taylor & McLennan 1985) tend to reaffirm the more stringent limit of $m_d \leqslant 0.5$. It is noteworthy that this estimate agrees well with values derived from the enrichment of the highly incompatible elements (Rb, Ba, U, Th, etc.) in the continental crust, if it is assumed that these elements have been stripped nearly quantitatively from the depleted portion of the mantle.

A very important limitation of this mass balance is the assumption that the continental crust is the only enriched reservoir. This is known to be incorrect, because the OIBS are also derived from enriched reservoirs of unknown mass, and these were necessarily neglected in the above mass balance. Indeed, some authors have inferred that the OIB sources constitute a large fraction of the mantle (Weaver 1985). If this were so, than there might not be any remaining primitive reservoir, the entire mantle would be differentiated (either depleted or enriched) and this might eliminate the more-popular two-layer mantle models.

Hofmann *et al.* (1986) found that the concentration ratios Nb/U and Ce/Pb could be used for independent mass balances, which explicitly include the OIB source reservoirs. The advantage of these ratios over all the isotopic tracers is that they do *not* discriminate between MORB and

OIB sources. Instead, they discriminate between the *combined* MORB plus OIB source, the continental crust, and the primitive mantle. Figure 2 shows the resulting mass fraction of the combined MORB plus OIB source reservoir, characterized by Nb/U = 47 and Ce/Pb = 25, as a function of the concentrations of U and Pb in the continental crust. Also shown are two estimates of crustal concentrations of U and Pb by Taylor & McLennan (1985, 'T.M.') and Zindler & Hart (1986, 'Z.H.'). The mass fractions of residual mantle range from 0.35 to 0.72 and are thus somewhat higher than those obtained by Nd isotopes, but they are still significantly smaller than 1.0. Consequently, the OIB portion of the residual mantle *may* be quantitatively significant, but it is still too small for the combined MORB plus OIB sources to occupy the entire mantle.

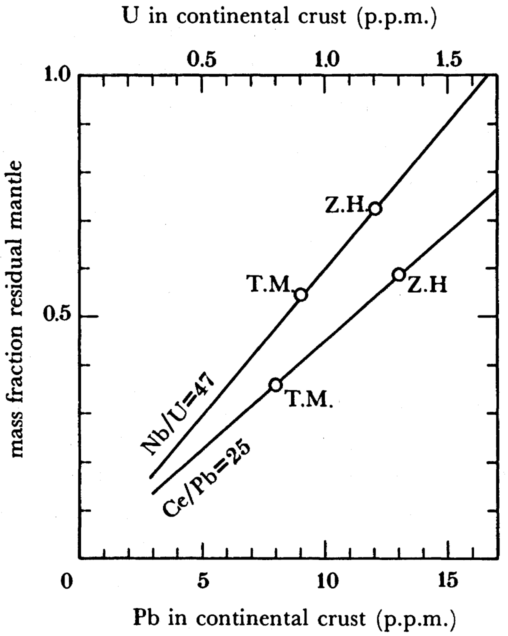

FIGURE 2. Mass fraction of residual mantle (MORB plus OIB source) as a function of U and Pb concentration in the continental crust. The mass balance is calculated using Nb/U = 47 and Ce/Pb = 25 for the residual mantle, Nb/U = 12 and Ce/Pb = 4 for the continental crust, and Nb/U = 30 and Ce/Pb = 9 for the primitive mantle (Hofmann *et al.* 1986). The points labelled T.M. and Z.H. represent concentration estimates of U and Pb in the continental crust by Taylor & McLennan (1985) and Zindler & Hart (1986).

The major remaining uncertainty about the mass balance of crust–mantle reservoirs is that we know relatively little about the composition of the subcontinental lithosphere. Some authors believe that it is also enriched in incompatible elements (see McKenzie & O'Nions 1983; Hawkesworth *et al.* 1984; O'Reilly & Griffin 1988). If its trace-element characteristics are similar to those of the continental crust, even in diluted form, then the effective mass of the continental 'crust', and therefore also the mass fraction of the depleted mantle have been underestimated in all the published mass balances. Partly because of this, the geochemistry of the subcontinental lithosphere is an important object of current investigation.

In summary, it can be concluded that only 30–70% of residual mantle will balance the chemistry of the continental crust. The remainder of the mantle may still have its primitive composition, unless another enriched reservoir exists that would require more of the mantle to be differentiated. Not enough is known about the subcontinental lithosphere to decide whether it might constitute such a reservoir.

ORIGIN OF OIB SOURCES AND MORB SOURCE HETEROGENEITIES

(*a*) *Primitive mantle*

Schilling (1973), Hart *et al.* (1973), and Sun & Hanson (1975) recognized the relatively undepleted nature of many OIB sources and, following the ideas of Morgan (1971), suggested that the ocean islands are created by plumes that originate in the deep, undepleted mantle and rise through the depleted upper mantle. The geochemical evidence for this rested mostly on Sr isotopes and rare-earth chemistry of OIBs. These ideas received strong support, first from Nd and later from Hf isotopic data, because these data were well correlated with Sr isotopes and the primitive-mantle value of Nd and Hf isotopic compositions is well constrained by meteorite data. In contrast, the $^{87}Sr/^{86}Sr$ ratio of the primitive mantle cannot be inferred from meteorites, because the Earth has a much lower Rb/Sr (and therefore also $^{87}Sr/^{86}Sr$) ratio than meteorites (Gast 1960). The $^{143}Nd/^{144}Nd$ ratios of OIBs determined by Richard *et al.* (1976), DePaolo & Wasserburg (1976) and O'Nions *et al.* (1977) spanned the range between the depleted MORB values and that of the primitive mantle. Wasserburg & DePaolo (1979) interpreted this using essentially the same plume model formulated earlier by Schilling, Hart, and Sun & Hanson.

Armstrong (1981) disagreed with the above model, pointing out that the isotopic data for Nd and Sr could also be explained by recycled continental crust. This idea was not easily disproved. However, Pb isotopes of both old and young continent-derived sediments tend to be higher in (relative) ^{207}Pb abundance than most (although not all) OIBs (see White *et al.* 1985; Sun 1980). On the other hand, Pb isotopes are even less consistent with OIBs being derived from a primitive reservoir. This may be seen in figure 3, which shows the Pb-isotopic data of continental rocks compiled by Zartman & Doe (1981), compared with data for MORBs from Ito *et al.* (1987) and OIB data from the compilation of Zindler & Hart (1986). It is obvious that continental Pb isotopes follow a separate and significantly steeper trend than oceanic Pb isotopes, and most OIBs are too low in ^{207}Pb to be derived from continental material. Moreover,

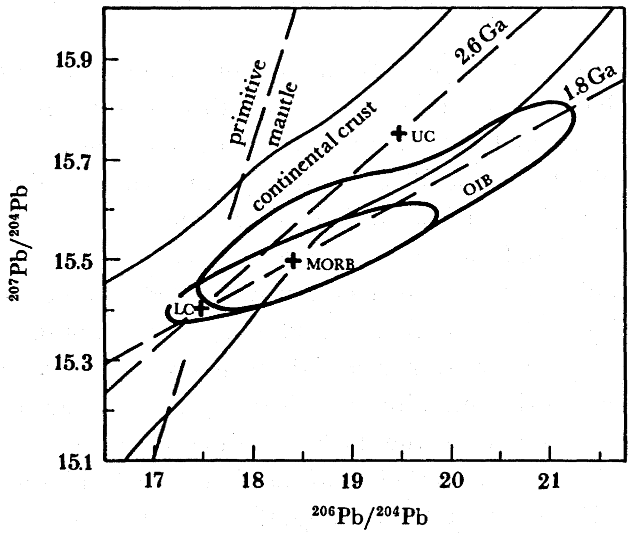

FIGURE 3. Pb-isotopic compositions and model ages of the major crustal reservoirs. The estimated average compositions of the upper (UC) and lower (LC) continental crust according to Zartman & Doe (1981) and MORB according to the new compilation by Ito *et al.* (1987) are shown by crosses. The OIB data are from the compilation of Zindler & Hart (1986). The bulk composition of any closed U–Pb system formed 4.57 Ga ago must lie on the line labelled primitive mantle.

with very few exceptions, the oceanic Pb isotopes are also far too radiogenic to be derived from an undifferentiated U–Pb reservoir, which is defined by the line conventionally called the *geochron*. The only way that these results could be reconciled with a 'primitive' mantle source for OIBS has been to postulate that this deep-mantle reservoir has lost lead to the core several hundred million years *after* the accretion of the Earth (a process termed 'core pumping' by Allègre *et al.* 1982). Core pumping was finally laid to rest by Newsom *et al.* (1986) who showed that OIBS have the same ratios of Pb and Mo to light rare-earth elements as MORBS. If Pb had moved to the core from OIB sources but not from MORB sources, then the strongly siderophile element Mo should have been removed even more efficiently, and the concentration ratios of both elements with the distinctly non-siderophile rare-earth elements should be lower in OIBS than in MORBS. Contrary to these expectations, Pb/Ce and Mo/Pr ratios were found to be identical in MORBS and in OIBS, and therefore removal of lead to the core cannot account for the differences in U/Pb ratios between MORB and OIB sources.

The dilemmas presented by the Pb isotopes were reinforced by Nd-isotopic compositions of some OIBS that do not lie on possible mixing lines between primitive and depleted mantle. Nd-isotope data from Kerguelen and Tristan da Cunha require sources that are enriched in light rare-earth elements relative to a primitive-mantle source.

(*b*) *Recycling*

The increasing difficulties to reconcile the simple models with the geochemical data prompted Hofmann & White (1980, 1982), Chase (1981) and Ringwood (1982) to suggest a recycling model that differs from that of Armstrong in that it emphasizes oceanic crust and lithosphere rather than the continental crust. The oceanic crust is cumulatively by far the largest volume of enriched material. At current production rates, it takes only about 300 Ma to make a volume of oceanic crust equivalent to that of the entire continental crust. If even a small portion of this oceanic crust is stored in the mantle without being completely rehomogenized with ordinary mantle, and if the preferred place of storage is in a thermal boundary layer within the mantle or at its base, this enriched material will make a suitable source for most OIBS.

Figure 3 shows that OIBS and MORBS generally follow similar isotopic trends. U/Pb ratios are generally higher in OIBS than in the MORB source, and this increase may ultimately (after 1–2 Ga, on average) be responsible for the fact that most OIBS have more radiogenic lead than most MORBS. Similarly, the Nb/U and Ce/Pb concentration ratios discussed below indicate that OIBS and MORBS are ultimately derived from the same reservoir.

Because the oceanic crust is only about 6 km thick, it has generally been believed that rehomogenization is inevitable, in spite of the fact that subducted oceanic crust is converted to eclogite and is therefore denser than ordinary peridotite mantle. Consequently the idea of accumulation and storage of oceanic crust has been dismissed by most geophysicists. However, the analysis of Christensen (this symposium) indicates that such accumulation may be mechanically feasible after all. Moreover, the thickness of the oceanic crust is not uniform but reaches as much as 20 km in some places such as Iceland, and such thickened pieces of dense subducted oceanic crust might accumulate preferentially.

Yet another recycling model was offered by McKenzie & O'Nions (1983), who proposed recycling of the subcontinental lithosphere. The critical assumption for this model is that this lithosphere has an appropriately (trace-element) enriched composition. There is indeed evidence for enrichment found in many mantle xenoliths, but there is also at least some evidence that the type of enrichment predominating in the continental lithosphere shows the deficiency in Ti, Nb and Ta, which is characteristic of the continental crust itself (Hawkesworth *et al.* 1987). If this type of enrichment characterized the entire subcontinental lithosphere, it would not be a suitable source of OIBs for the same reasons given above for the continental crust. Still, not enough is known about the subcontinental lithosphere to make a definitive judgement.

(*c*) *Metasomatism*

Other authors proposed that OIB sources are created by ancient or recent metasomatism in the mantle (Menzies & Murthy 1980; Wass & Rogers 1980; Bailey 1982; Vollmer 1983). There are reasons to believe that metasomatic transport in the mantle is restricted to the mesoscale (as defined above) or less. Extensive, large-scale metasomatism would almost certainly create large-scale zoning and extreme chemical heterogeneities through chromatographic mechanisms (Hofmann 1986), whereas real oceanic basalts are characterized by variable enrichment or depletion but otherwise highly coherent trace-element ratios. In particular, some elements of rather different chemical affinities form nearly uniform ratios in all oceanic basalts. Examples of these are Ba/Rb, Zr/Sm, Sr/Ce, P/Nd, K/U, Nb/U and Ce/Pb (Hofmann & White 1983; Hofmann *et al.* 1986; Jochum *et al.* 1983, 1988). It is very difficult to believe that these element pairs would not be separated during any large-scale metasomatic transport. On the other hand, metasomatism certainly does occur in the mantle, and its effects have been studied extensively in mantle xenoliths. If this occurs locally or on the mesoscale, such as in a subduction environment, it may ultimately affect the composition of significant parts of the subcontinental lithosphere. Partial melting may then ‘take advantage’ of the general enrichment, but average out the chemical heterogeneities created by the metasomatic process.

ADDITIONAL GEOCHEMICAL EVIDENCE

(*a*) *Noble-gas isotopes*

The discovery of large quantities of primordial ^{3}He in oceanic basalts (Lupton & Craig 1975) demonstrated that the Earth has never been completely outgassed, even if its silicate mantle formed an early, extensive magma ocean. The ^{3}He is not recycled from the atmosphere into the mantle, because He entering the atmosphere from the mantle escapes rapidly into space. Although ^{3}He is also produced in the solid Earth spallogenically and by neutron reactions, the current consensus is that the bulk of the ^{3}He emanating from the mantle is primordial. The ^{3}He/^{4}He ratios in MORBS are 10, in OIBs up to 30 times higher than in the current atmosphere. This has revived the ideas that OIBs may be derived from a primitive mantle reservoir after all (Kurz *et al.* 1982; Staudacher *et al.* 1986). In particular, these data appeared to provide powerful arguments against all recycling models. Subsequently, it was recognized that He isotopes correlate with ^{87}Sr/^{86}Sr in some regions but not in others. This led Kurz *et al.* (1982) to suggest that some OIBs originate from a primitive-mantle reservoir, whereas others come from recycled crust, and this view is still popular at present. Recently, high ^{3}He/^{4}He ratios have also been found in crustal xenoliths (Porcelli *et al.* 1986), and this indicated that helium may migrate through the mantle. Thus, the significance of ^{3}He with regard to any of the current models is uncertain at best. The same can be said for Ar, Ne and

Xe isotopes. For example, some mantle samples contain excess ^{129}Xe, which must have been inherited from the first 10^8 years of Earth history, but the significance of this is not yet well understood.

(*b*) *Nb and Pb*

These elements have the unusual property that they distinguish sharply between processes forming continental crust and those forming oceanic crust. By searching for other incompatible elements that would best correlate with these two elements, it was found that Nb/U ratios are the same in MORBs and in OIBs, and the same is true for Pb/Ce ratios (Hofmann *et al.* 1986; Newsom *et al.* 1986). Such uniform ratios may be regarded as 'quasi-isotopic' as explained earlier, that is they are identical in the basalt and its source. This in itself is not surprising, because about a dozen such element pairs are known (Jochum *et al.* 1988). What is surprising is the fact that these two concentration ratios are *not* the same as the corresponding ratios of the primitive mantle, as is observed for other uniform ratios such as Zr/Hf, Nb/Ta, Y/Ho and others. The value of $\mathrm{Nb/U} = 47 \pm 10$ in oceanic basalts (exclusive of subduction related volcanics) is significantly higher than the primitive mantle value of $\mathrm{Nb/U} = 30$ and the value of the continental crust of $\mathrm{Nb/U} \approx 12$. Many island arc volcanics have even lower values. Very similar relations hold for Ce/Pb ratios. The significance of this to the crust–mantle mass balance has already been discussed. Of equal importance is the constraint these data provide for the origin of the OIB sources. It means that the OIB sources have undergone the same differentiation process as the MORB sources, so that *both* are now complementary to the continental crust. On the basis of this constraint, a primitive mantle source can be ruled out even in those cases, such as certain Hawaiian basalts (such as the Koolau volcanics) that are distinguished by high ^{3}He and apparently nearly primitive Sr, Nd, and Pb isotopic compositions. Similarly, a source dominated by recycled continental crust can also be ruled out, because such material would cause the Nb/U and Ce/Pb to be lower, not higher than primitive. This does not mean that the OIB sources must be totally devoid of primitive or continental components, it only means that such components must be minor ones at most. Weaver *et al.* (1987) have shown that the islands of Gough and Tristan da Cunha have somewhat lower Nb/Th and Nb/La ratios than other islands and proposed that their sources are mainly subducted oceanic crust contaminated with a few percent of recycled pelagic sediment. Such a sedimentary component is expected to be introduced into the mantle during subduction, and the only surprise is that its geochemical signature is not more commonly found in OIBs.

RESIDENCE TIME OF LEAD IN THE MORB SOURCE

Galer & O'Nions (1985) have recently calculated the age of the depletion of Th relative to U in the MORB source mantle from the relative abundances of ^{208}Pb and ^{206}Pb in MORB, assuming a simplified, single-event mantle evolution. If the ratio of their respective parent nuclides, ^{232}Th/^{238}U changed from an original (primitive mantle) value of 3.9 to 2.5 at the time of the depletion event, then this event took place as recently as 600 ± 200 Ga ago, in the present-day MORB source. This result is contrary to expectations derived from relations of ^{207}Pb/^{204}Pb against ^{206}Pb/^{204}Pb (figure 3), which indicate a differentiation age of 1.8 Ga for MORB plus OIB, or from the mean age of the continental crust, which is about 2.6 Ga by using crustal Pb isotopes (figure 3), or at least 1.5 Ga by using the crust–mantle evolution models of Jacobson & Wasserburg (1979). To reconcile these observations, Galer & O'Nions formulated a new model of mantle differentiation, in which the upper (MORB source) mantle is in a steady state and therefore contains no information on specific differentiation events. Fresh, primitive mantle material is added to this steady-state reservoir by entrainment from the lower mantle, and this is balanced by losses to the continental crust. The steady-state concentration of each element is determined only by its bulk partitioning between the upper mantle and the continental crust.

This model is still quite new, and several aspects remain to be evaluated. For example, Allègre *et al.* (1986) have estimated a terrestrial Th/U of 4.2 rather than 3.9. If correct, the higher ratio would increase the calculated differentiation time from 600 Ma to about 1200 Ma, and this would be in reasonable agreement with mean differentiation ages calculated from other isotopic systems. Another open question concerns the evidence for rapid mixing in the upper mantle, which is required if a steady state is to be attained.

STATE OF MIXING IN THE MANTLE

It is often argued that the upper mantle is a well-homogenized reservoir, and this assertion is supported by theoretical arguments as well as by numerical experiments (see, for example, Hoffman & McKenzie 1985). However, this is not immediately obvious from the geochemical data themselves. Taken at face value, the isotopic and trace-element data for all oceanic basalts indicate a highly heterogenous, poorly mixed mantle. For example, $^{206}Pb/^{204}Pb$ ratios range from 17 to 21, and this range is larger than the difference between Zartman & Doe's (1981) best estimates of the upper and lower crustal averages in continental rocks (figure 3). The apparent state of homogeneity improves only moderately if the sampling is restricted to the so-called N-type MORB, that is, if all OIBS and suspected 'plume-type' MORBS are removed from the sample considered. The N-type MORB samples analysed and reviewed by Ito *et al.* (1987) have a range of $^{206}Pb/^{204}Pb = 17$ to 19.4. Similarly, these same samples have Ba concentrations between 1.5 p.p.m. and 32 p.p.m. (by mass) (Jochum & Hofmann 1989). This range exceeds considerably that expected from differences in the degree of melting and fractional crystallization and most likely reflects differences in source composition. Finally, extreme isotopic compositions have been observed such as $^{40}Ar/^{36}Ar = 25000$ (Staudacher *et al.* 1986) in some depleted MORBS. Entrainment and rapid homogenization of even small amounts of mantle material with a primitive or atmospheric ratio of $^{40}Ar/^{36}Ar \approx 300$ would not allow such high ratios to survive, unless all the entrained Ar were vented immediately to the atmosphere. Thus, the idea of a well-mixed reservoir cannot be deduced directly from the data; rather it must be reconciled with the data by assuming that the observed heterogeneities are not stored within the mixing bowl but are introduced from the outside and only a short time before they reappear in the various oceanic basalts.

CONCLUSIONS

The heterogeneities that can be detected and identified by geochemical means are not directly detectable by seismic techniques. Future progress in connecting the two types of evidence will therefore depend on establishing correlations between seismic velocity structure and geochemistry.

The salient conclusions from geochemical evidence are as follows.

(1) Less than 70%, perhaps as little as 25%, of the mantle mass is sufficient to balance the chemical composition of the continental crust, but the remaining primitive (or less depleted) mantle reservoir does not appear to be sampled directly by plumes or by MORBS.

(2) OIB sources are most easily explained by some type of recycling. However, typical continental crust or continent-derived sediments are either absent or only a minor component of OIB sources. This reduces the choice of recycling candidates to delaminated subcontinental lithosphere and/or subducted oceanic crust and lithosphere.

(3) Metasomatism may have modified the composition of the OIB sources but is judged to be a local phenomenon, which is probably important mainly during subduction and the concomitant devolatilization of the subducted crust. In this way, it may have affected the composition of the subcontinental lithosphere.

(4) The bulk of the continental crust was separated from the mantle before the residual mantle was differentiated into MORB and OIB sources, but the residence times of heterogeneities in this residual mantle remain uncertain.

(5) The popular notion that the MORB source is a well-mixed reservoir can be reconciled with geochemical data only if one assumes that all the heterogeneities are stored outside that reservoir. The geochemical peculiarities common to both MORBS and OIBS (Pb-isotope trends, Nb/U and Ce/Pb ratos) favour the interpretation that both the depleted and the enriched parts of the mantle belong to a common mantle reservoir, which was once homogenized but has since become quite heterogeneous through secondary differentiation processes.

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