Marine Carbonates in the Mantle Source of Oceanic Basalts: Pb Isotopic Constraints

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For almost fifty years, geochemists have been interpreting the clues from Pb isotopic ratios concerning mantle composition and evolution separately. The Pb isotopes of ocean island basalts (OIB) indicate that their mantle source is heterogeneous, most likely due to the presence of end-components derived from recycled crust and sediment. Some OIB have unusually high 206Pb/204Pb coming from one of the end-components with a long time-integrated high 238U/204Pb or μ (HIMU). Most OIB and many mid-ocean ridge basalts (MORB) also have high 206Pb/204Pb, indicating a HIMU-like source. Moreover, measured 232Th/238U (κ) for most MORB are lower than those deduced from their 208Pb/204Pb and 206Pb/204Pb. Such high μ and low κ features of oceanic basalts are inconsistent with the known geochemical behavior of U, Pb and Th and temporal evolution of the mantle; these have been respectively termed the 1st and 2nd Pb paradox. Here we show that subducted marine carbonates can be a source for HIMU and a solution to the Pb paradoxes. The results are consistent with the predictions of the marine carbonate recycling hypothesis that posit the Pb isotopes of oceanic basalts indicate a common origin and/or magma generation process.

Together with Sr isotopes, the Pb isotopes of OIB showed, for the first time, that the mantle is heterogeneous, most likely due to the presence of enriched mantle 1 (EM1), enriched mantle 2 (EM2) and HIMU end-components from recycled crust and sediment. High μ OIB from Saint Helena, Mangaia and Tubuai islands have unusually high 206Pb/204Pb (>20.0) and low 87Sr/86Sr (<0.7028), and the bulk of OIB and many MORB also have high 206Pb/204Pb although higher 87Sr/86Sr (>0.7028). That is, almost all oceanic basalts have high 206Pb/204Pb that plot to the right of Geochron, a line in the 206Pb/204Pb versus 207Pb/204Pb diagram containing the current Pb isotopes of terrestrial materials, assuming the Earth remained a closed system (Fig. 1A). Both 206Pb and 207Pb increase due to the respective decay of radioactive 238U and 235U and, hence, the mantle source of oceanic basalts must have a long time-integrated (~b.y.) U/Pb > BSE refs2–4. Such a high U/Pb is unexpected because U is more incompatible than Pb and, thus, the ratio should be low at least in the depleted MORB mantle (DMM) source that has experienced repeated melt extraction. This has been termed the main or 1st Pb paradox, and its proposed solutions include transfer of Pb into the core, preferential retention of Pb relative to U in the continent or residual mantle sulfide, hydrothermal transfer of Pb from mantle to continent, U recycling into the mantle since Early Proterozoic, and crustal contamination of an early-formed (ca. 4.5 Ga) mantle reservoir. Notably, a majority of these solutions call for a decrease in Pb to increase U/Pb refs2,5. Moreover, the distinctiveness between the sources of HIMU end-component, which has characteristically low 87Sr/86Sr, and HIMU-like characteristics of many oceanic basalts, which have variable and higher 87Sr/86Sr, has become blurred. A majority of the proposed solutions do not consider that the HIMU end-component is distinct because it must also have a long time-integrated, low Rb/Sr, as the decay of radioactive 87Rb increases 86Sr.

Measured κ (2.5 average) for most MORB are lower than those deduced from their 208Pb/204Pb and 206Pb/204Pb, which are fairly homogeneous and only slightly lower than bulk silicate Earth (BSE; κ ca. 4.0) refs5,14. The increase in Pb results from the decay of radioactive 232Th. The measured low κ of MORB indicates that the Th/U decrease from the original BSE κ in DMM may have occurred as recently as ca. 600 Ma ref.15. However, the Th-enriched continental crust derived from DMM is much older than this and, thus, the Th/U evolution of the mantle is a dilemma. This has been termed the 2nd Pb paradox, and its proposed solutions include a mantle
BSE κ that decreased concurrently with continental extraction\textsuperscript{15,16}, an upper mantle BSE κ that abruptly changed to 2.5 at 600 Ma\textsuperscript{13} and mantle recycling of U due to the Earth’s oxidizing condition since Early Proterozoic\textsuperscript{2,11,14,17}.

Quite recently, we hypothesized that some Archaean marine carbonates provide the radiogenic 206Pb/204Pb, unradiogenic 87Sr/86Sr, low K₂O, and high CaO of HIMU, as well as the overall positive correlation between CaO and 206Pb/204Pb in OIB ref.\textsuperscript{18}. Our hypothesis is consistent with the Archaean-formed Δ33S anomaly in HIMU OIB ref.\textsuperscript{19} and the similar trace element contents of carbonatitic melt inclusions in diamonds and HIMU lavas\textsuperscript{20}. We also proposed that the unusually radiogenic Pb isotopes of OIB (Fig. 1A) and 1st and 2nd Pb paradoxes are parts of a system of equations, and the higher concentration of U relative to Pb and Th in marine carbonates offers a self-consistent solution to these equations\textsuperscript{21}. Such a holistic interpretation of Pb isotopes, however, assumes some Archaean marine carbonates formed in equilibrium with seawater containing U, but little to no Pb and Th, as well as high Sr but little to no Rb ref.\textsuperscript{18}. This assumption is inconsistent with the anoxic Archaean ocean that should have prevented U mobilization in seawater and its eventual subduction into the mantle\textsuperscript{2,11,14,17}.

To verify if some Archaean marine carbonates have high U/Pb and U/Th, we analyzed the Pb and Sr isotopes of the carbonate fractions of the few stromatolitic limestones that have the low 87Sr/86Sr of coeval seawater\textsuperscript{22,23}. Notably, these carbonates preserve the composition of Archaean oceans, have long time-integrated low Rb/Sr and are generally unaltered, as alteration would have raised their 87Sr/86Sr refs\textsuperscript{22,23}. Accordingly, the Pb isotopes of these unaltered samples should also be able to constrain their long time-integrated U, Th and Pb concentrations and ratios. We adopted this approach because the current U, Th, Pb, Rb, and Sr concentrations of many Archaean limestone outcrops have been modified by contamination and alteration\textsuperscript{22–26}. We also analyzed their bulk Pb and Sr isotopes for comparison. Four samples (184, 185, 1977/7, and 1977/43) are from the 2.8 Ga Mosher Carbonate Formation in the Canadian Shield\textsuperscript{27} and one sample (187) is from the 3.0 to 2.6 Ga Bulawayan Supergroup in the Zimbabwe Craton\textsuperscript{28}. The location and full description of the samples can be found in ref.\textsuperscript{23}.

**Results**

The bulk limestone Pb isotopes are highly variable, but their carbonate fractions have systematically higher 206Pb/204Pb and 207Pb/204Pb (Table 1; Figs 1 and 2). On the other hand, the carbonate fractions of samples 184, 185 and 1977/7 have systematically lower 87Sr/86Sr than their respective bulk values whereas those of samples 187 and 1977/43 are similar. The 87Sr/86Sr of the carbonate fractions of samples 187, 1977/7 and 1977/43 and their previously reported values\textsuperscript{23} are the same within error despite the difference in the leaching procedure used, and are also similar to the recent estimate of Archaean seawater 87Sr/86Sr ref.\textsuperscript{28}.

The 206Pb/204Pb and 207Pb/204Pb of bulk and carbonate fractions of our samples plot with or at the extension of the wide 206Pb/204Pb-207Pb/204Pb array of the carbonate fractions of Manjeri limestones\textsuperscript{24} that also occur in the Zimbabwe Craton and of Nsuze limestones\textsuperscript{26} and Transvaal dolomites\textsuperscript{30} in the Kaapvaal Craton (Fig. 1A). Notably, oceanic basalts plot within this array. The array, in turn, plots below the arrays of the carbonate fractions of Cheshire limestones\textsuperscript{29} as well as of surface (plotted) and very radiogenic drill core (not shown) samples.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** 206Pb/204Pb versus A. 207Pb/204Pb and B. 208Pb/204Pb for Archaean limestones. Bulk stromatolitic limestones (solid symbols) are connected by tie lines to their respective carbonate fractions (open symbols). Analytical errors are smaller than the symbols used. Shown for reference are the carbonate fractions of other Archaean limestones (see text for sources of data), oceanic basalts (gray field), FOZO (dash area inside gray field), and HIMU end-component (dark gray field). The 2.82 Ga isochron in A. is the regression line for the extremely radiogenic (206Pb/204Pb = 30.2 to 104.4; 207Pb/204Pb = 19.4 to 34.1; 208Pb/204Pb = 42.514 to 74.402) Mushandike stromatolites\textsuperscript{24} (not shown).
from Mushandike stromatolites24, all in the Zimbabwe Craton. In detail, the 206Pb/204Pb and 207Pb/204Pb of three Mosher limestones (184, 185, 1977/43), together with some of the Transvaal dolomites, are more radiogenic than OIB. Finally, the 208Pb/204Pb for given 206Pb/204Pb of bulk limestones, their carbonate fractions and those of many Archaean limestones are highly variable, but for many samples they are lower than those of oceanic basalts (Fig. 1B). Significantly, some Cretaceous serpentinites and 1.9 Ga altered oceanic crust have unusually low 208Pb/204Pb, clearly indicating the extremely low Th content and, hence, Th/U of oxygenated seawater 18,31.

The systematically high 206Pb/204Pb plus 207Pb/204Pb and low 208Pb/204Pb of the carbonate fractions we analyzed clearly indicate that some Archaean limestones have long time-integrated high $\mu$ and low $\kappa$. A possibility is that such limestones precipitated locally in Archaean ‘oxygen oases’ in shallow-platforms27,32. Indeed, the very radiogenic Pb isotopes of the aforementioned Archaean Mushandike limestones were most probably generated in a shallow restricted basin with variable, but limited communication with the open ocean24. Alternatively, they may have been formed during localized concentrations or ‘whiffs’ of oxygen in the Archaean 33, as proposed for the Nsuze metasediments 34. Whichever the case, marine carbonates that precipitated in equilibrium with oxygenated seawater theoretically can have extremely high $\mu$ and low $\kappa$ ref.35. Accordingly, the radiogenic Pb isotopes of some Archaean carbonates and interlayered metasediments are most probably due to in-growth of uranogenic 206Pb and 207Pb in their carbonate fraction, rather than from contamination by a high $\mu$ Archaean crust24–26,36.

**Discussion**

Although there is consensus that the HIMU, EM1 and EM2 end-components are recycled surface material, there is little agreement on the origin of individual end-components. A currently popular idea is that HIMU is from altered MORB whereas EM1 and EM2 are from pelagic and terrigenous sediments, respectively2,3. Irrespective of sources, however, the end-components almost always mix with a ‘common’ or focus zone (FOZO) component2,3,37. The marine carbonate recycling hypothesis not only offers an alternative origin for the HIMU signature, but also explanations for some common threads in the geochemistry of oceanic basalts, particularly their unusually

| Sample       | 206Pb/204Pb | 207Pb/204Pb | 208Pb/204Pb | 87Sr/86Sr  | 87Sr/86Sr* |
|--------------|-------------|-------------|-------------|-----------|-----------|
| 184*         | 24.864      | 16.107      | 39.335      | 0.710224  |
| 184*         | 27.208      | 16.206      | 39.551      | 0.702060  | 0.70217   |
| 185*         | 23.670      | 16.061      | 40.012      | 0.710354  |
| 185*         | 24.404      | 16.094      | 40.354      | 0.701980  | 0.70209   |
| 187*         | 16.437      | 15.253      | 34.113      | 0.701541  |
| 187*         | 18.202      | 15.441      | 33.762      | 0.701510  | 0.70162   |
| 1977/7*      | 18.689      | 15.592      | 36.173      | 0.702607  |
| 1977/7*      | 19.157      | 15.714      | 35.978      | 0.702220  | 0.70233   |
| 1977/43*     | 24.034      | 16.704      | 39.664      | 0.701920  |
| 1977/43*     | 26.002      | 17.098      | 39.804      | 0.701760  | 0.70187   |

Table 1. Lead and Sr isotopic ratios of Archaean limestones with the low $87\text{Sr}/86\text{Sr}$ of coeval seawater.

*Carbonate fraction data from refs22,23, normalized to NBS987 $87\text{Sr}/86\text{Sr} = 0.710254$. Analytical errors are ±0.000018 for $87\text{Sr}/86\text{Sr}$, ±0.002 for 206Pb/204Pb, ±0.003 for 207Pb/204Pb and ±0.010 for 208Pb/204Pb; 2σ precisions for individual Sr and Pb measurements are better than these.
high, $\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$ and $\frac{^{207}\text{Pb}}{^{204}\text{Pb}}$ (Fig. 1A) and the almost ubiquitous link between OIB end-components and the HIMU-like FOZO $^{2,3,18,37}$. Our new analyses for a few select Archaean limestones lend some credence to the hypothesis.

Sample 1977/43 and its carbonate fraction as well as those of samples 184 and 185 plot at the extension of HIMU OIB in the $\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$ and $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ diagram (Fig. 2). Although such limestones appear scarce, it is noteworthy that the measured Pb and Sr isotopes of many Archaean limestone outcrops may be secondary, as these are mainly effects of later metamorphism and/or alteration$^{22–26}$. That our Archaean carbonate fractions still show their original $\mu$, $\kappa$ and Rb/Sr features is most likely due to a combination of favorable preservation and the sluggishness of element diffusion in solid rocks$^{38,39}$. Significantly, if a subducted Archaean oceanic slab containing carbonates and/or carbonated metasediments would partially melt in the deep mantle, carbonate-rich melt would most likely form first since calcareous metasediment has the lowest melting temperature of all lithologies in the subducting lithosphere$^{40,41}$. Moreover, high modes of melting would occur once melting initiates, as limestone is mainly comprised of a single calcite phase$^{42}$. The carbonate-rich melt could then infiltrate and/or metasomatize the lithospheric mantle portion of the slab, as carbonate has higher diffusion rate than basaltic melt$^{43,44}$. Subsequent melting of carbonate-metasomatized ancient upper mantle could produce OIB melts$^{18,21,41}$.

To illustrate the origin of the $\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$ and $\frac{^{207}\text{Pb}}{^{204}\text{Pb}}$ of HIMU OIB, we first calculated the evolution of the carbonate fraction of sample 185 from the 2.8 Ga Bulk silicate Earth$^{7}$ to present (dash lines), and our model for the origin of HIMU OIB (solid lines). The model was constructed by metasomatizing (mixing) 99% of a slightly younger, 2.4 Ga evolving upper mantle ($\frac{^{206}\text{Pb}}{^{204}\text{Pb}} = 13.728$, $\frac{^{207}\text{Pb}}{^{204}\text{Pb}} = 14.614$, $\frac{^{208}\text{Pb}}{^{204}\text{Pb}} = 33.210$, 0.051 ppm Pb) ref. $^{7}$ with 1% of a hypothetical Archaean limestone ($\frac{^{206}\text{Pb}}{^{204}\text{Pb}} = 24.404$, $\frac{^{207}\text{Pb}}{^{204}\text{Pb}} = 16.200$, $\frac{^{208}\text{Pb}}{^{204}\text{Pb}} = 43.00$; open square – M) containing the Pb of the most enriched, 8% partial melt from carbonated pelite (67.2 ppm; see ref. $^{41}$ for details of experimental data, and modeling). The latter Pb concentration was used because of the dearth of experimental data for partial melting of limestone at high pressures. Each upper mantle and total silicate Earth symbol represents 0.4 Ga interval whereas each tick mark along the model mixing line represents 0.2 increment of melt contribution. See text for additional discussion.

*Figure 3.* $\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$ versus A. $\frac{^{207}\text{Pb}}{^{204}\text{Pb}}$ and B. $\frac{^{208}\text{Pb}}{^{204}\text{Pb}}$ diagrams showing the evolution of the carbonate fraction of sample 185 from the 2.8 Ga Bulk silicate Earth$^{7}$ to present (dash lines), and our model for the origin of HIMU OIB (solid lines). The model was constructed by metasomatizing (mixing) 99% of a slightly younger, 2.4 Ga evolving upper mantle ($\frac{^{206}\text{Pb}}{^{204}\text{Pb}} = 13.728$, $\frac{^{207}\text{Pb}}{^{204}\text{Pb}} = 14.614$, $\frac{^{208}\text{Pb}}{^{204}\text{Pb}} = 33.210$, 0.051 ppm Pb) ref. $^{7}$ with 1% of a hypothetical Archaean limestone ($\frac{^{206}\text{Pb}}{^{204}\text{Pb}} = 24.404$, $\frac{^{207}\text{Pb}}{^{204}\text{Pb}} = 16.200$, $\frac{^{208}\text{Pb}}{^{204}\text{Pb}} = 43.00$; open square – M) containing the Pb of the most enriched, 8% partial melt from carbonated pelite (67.2 ppm; see ref. $^{41}$ for details of experimental data, and modeling). The latter Pb concentration was used because of the dearth of experimental data for partial melting of limestone at high pressures. Each upper mantle and total silicate Earth symbol represents 0.4 Ga interval whereas each tick mark along the model mixing line represents 0.2 increment of melt contribution. See text for additional discussion.
is primarily an extension of the upper mantle. This notion is consistent with geochemical data indicating a uniform Th/U ratio for the ancient upper mantle and modern DMM refs 21,45,46.

Our model also implies that mixing between an even smaller amount of Archaean (or perhaps younger) limestone and ancient upper mantle can produce the variable and radiogenic Pb and Sr isotopic ratios of the FOZO component refs 18,21. On the other hand, the HIMU-like 206Pb/204Pb and radiogenic 87Sr/86Sr of the bulk of OIB can be produced through mixing between ancient mantle and carbonated crust plus sediment (e.g., containing ankerite refs 19). In this case, mixing between ancient mantle (FOZO) and carbonated, variably altered MORB plus mafic (EM1) ref 47 to silicic (EM2) ref 48 metasediment are most likely involved (see also ref 19). Finally, mixing between carbonatitic melts from the present-day down-going slab that intersects the solidus for carbonated MORB at ca. 300 to 700 km ref 49 and DMM can produce the radiogenic Pb and Sr isotopes of modern enriched-MORB. Thus, recycling of marine carbonates can also solve the 1st Pb paradox ref 31.

We additionally propose that the Th deficiency in many ancient carbonates produced the limited variation of the κ values of OIB that hover around the BSE κ, as these are primarily extensions of the evolving upper mantle (Fig. 3B). The homogeneous DMM κ value deduced from MORB 206Pb/204Pb and 208Pb/204Pb is also an upper mantle signature refs 21,45,46. However, the fairly recently decoupled low Th/U of MORB (i.e., 2nd paradox) ref 13 comes from the aforementioned carbonatic melts from the down-going slab refs 18,49 that are mainly from Proterozoic to Phanerozoic limestone, as melts from carbonated sediment has high Th/U ref 18. The occurrence of carbonatic melts containing U in DMM is consistent with the isotopically distinct, high 238U/235U of MORB ref 21. The ‘exotic’ 238U/235U is formed in the oceanic crust at the bottom of the modern oxic ocean and subducted into the mantle, but must have been recycled back relatively quickly to the surface ref 17.

In summary, our results indicate the existence of Archaean carbonates with the appropriate Pb and Sr isotopes to generate the HIMU source, per the marine carbonate recycling hypothesis. Through qualitative modeling, we illustrate via mixing between recycled upper mantle and partial melts from 1) select ancient marine carbonates the compositional signature of HIMU OIB, and 2) ancient carbonated crust and sediment the solutions to both 1st and 2nd Pb paradoxes. Notably, a recent study also concludes that the high U/Pb and U/Th of ancient seawater as the source of the Pb isotopic signature of the HIMU end-component ref 61. Instead of Archaean carbonatic melt, however, the study proposes metasomatism of the source with U-enriched, supercritical liquid derived from Proterozoic (1.9 Ga) seawater. Incidentally, Proterozoic seawater would also impart a higher 87Sr/86Sr (>0.704)22,23 to the HIMU source. The study also locates the HIMU source domains roughly in the mid-mantle, where they can be fortuitously entrained by upwelling mantle plumes ref 31. We acknowledge that the hypothesis is inconsistent with some existing data and prevailing interpretations. Foremost among these are that carbonates should break and dissolve completely during subduction ref 45,61, there are very few Archaean carbonate outcrops that posses the putative HIMU composition, and carbonate melts ref 41 and carbonatites ref 23,25 are generally depleted in Zr, Hf and Ti but these are not possessed by HIMU OIB ref 62. However, there are also data indicating the occurrence of carbonate-sourced diamonds deep in the mantle ref 45,62 and that carbonates can be preserved to great mantle depths ref 63. Moreover, HIMU OIB is only a small fraction of OIB ref 21. Caution must also be taken when equating the current outcrops as true representations of the actual amount of subducted Archaean carbonates. Finally, our model indicates that the HIMU plume source contains only a minute amount of carbonatitic melt, and higher degrees of partial melting of a silicate-dominated source should increase the Zr, Hf and Ti contents of the resultant silicatic melt ref 22,25. Thus, more data are needed to test our hypothesis.

Methods
The limestone samples were broken into cm-sized fragments, washed with distilled water, dried, and pulverized in an agate mortar and pestle. About 50 mg of the limestone powders were completely dissolved using a mixed, ultra-pure HF:HNO3 solution in Teflon beakers and then analyzed for bulk limestone Pb and Sr isotopic composition following the established sample purification and thermal ionization mass spectrometry procedure at the Scripps Institution of Oceanography ref 38. To analyze the Pb and Sr isotopic composition of carbonate fractions, ca. 100 mg of powders were leached with 3 ml 1 M ultra-pure acetic acid in Teflon beakers, ultrasonicated for 15 minutes and left to react at room temperature for ca. 24 h. Then the mixtures were centrifuged and supernates were carefully separated and dried down. Afterwards, ca. 0.5 ml ultra-pure, concentrated HNO3 was added to the supernates to oxidize any organics. The samples were dried down again prior to Pb and Sr purification and isotopic analysis following the same above procedure. Note that the separation procedure for carbonate fraction used in this study differs from that employed in refs 22,23 in the use of mild acetic acid rather than hydrochloric acid.

Strontium and Pb isotopic ratios were analyzed using a 9-collector, Micromass Sector 54 thermal ionization mass spectrometer. Total procedural blanks are 35 pg for Sr and 60 pg for Pb. Strontium isotopic ratios were fractionation-corrected to 86Sr/88Sr = 0.1194 and are reported relative to 86Sr/88Sr = 0.710254 ± 0.000018 (n = 22) for NBS 987. Lead isotopic ratios were analyzed using the double-spike method to correct for mass fractionation during analysis; separate measurements of spiked and unspiked samples were made on different aliquots from the same dissolution. The SBL-74 207Pb/206Pb double-spike from the University of Southampton was used, producing the following results for NBS981: 206Pb/204Pb = 19.9282 ± 0.0023, 207Pb/204Pb = 15.4870 ± 0.0031 and 208Pb/204Pb = 36.6952 ± 0.0097 (n = 7). These values and those of the samples were adjusted to 206Pb/204Pb = 19.9356, 207Pb/204Pb = 15.4891 ± 0.0031 and 208Pb/204Pb = 37.7006 ref 49. 2σ precisions for individual Sr and Pb measurements are better than the analytical errors for NBS987 and NBS981.

Data Availability
All data generated or analyzed during this study are included in this published article.
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Author Contributions
P.R.C. devised the research project, analyzed the samples, ran the numerical models, and led the manuscript writing. C.M. and S.P. assisted in the processing and analysis of the samples and J.V. provided the samples; S.P., C.M. and J.V. assisted in writing the manuscript.

Additional Information
Competing Interests: The authors declare no competing interests.

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