Hf isotope composition of late Cenozoic basaltic rocks from northwestern Colorado, USA: New constraints on mantle enrichment processes

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ABSTRACT

Late Cenozoic basaltic lavas from northwestern Colorado and the northern Rio Grande rift have higher than expected $\epsilon_{\text{Hf}}$ values relative to the $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$ correlation of oceanic island basalts (OIB). In contrast, samples from the central and southern Rio Grande rift have lower than expected $\epsilon_{\text{Hf}}$ values, relative to the $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$ correlation of OIB. The variation in $\epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ values with geographic position is interpreted to be a result of sampling a predominantly asthenospheric source for lavas from the southern Rio Grande rift and adjacent Basin and Range, and a predominantly lithospheric source for lavas from northwestern Colorado.

The $\epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ values of the depleted asthenospheric mantle are likely to have formed from ancient depletion of spinel or garnet peridotite [1], which, respectively, produced anomalously low and high $^{176}\text{Hf}/^{177}\text{Hf}$ relative to the OIB array. Although a variety of enrichment processes for formation of the lithospheric mantle may be envisioned, silicate metasomatism caused by basaltic liquids crystallizing in the mantle best explains the Hf–Nd relationships in Colorado; the ancient metasomatizing liquids could not have been derived from melting garnet peridotite but instead must have been derived through melting spinel peridotite to produce the anomalously high $\epsilon_{\text{Hf}}$ values relative to $\epsilon_{\text{Nd}}$ values. The inference that Proterozoic lithosphere was stabilized in the spinel stability field contrasts strongly with the proposed lithospheric source regions of recent magmatism. Low Lu/Hf ratios of all of the samples from the Rio Grande rift and northwestern Colorado, compared to the calculated Lu/Hf ratio of the source based on Hf isotopic compositions, suggests that all of the lavas were derived from a garnet-bearing source. This implies that the subcontinental lithospheric mantle has stabilized garnet at the expense of spinel, perhaps through cooling of the lithosphere associated with formation of a stable craton and crustal thickening.

1. Introduction

The isotopic compositions of the subcontinental mantle are critical parameters for evaluating models of mantle evolution, which have been largely developed for the suboceanic mantle [e.g., 2,3]. In contrast to the suboceanic mantle, the subcontinental lithospheric mantle is likely to have remained isolated from the convecting mantle after initial crustal extraction [e.g., 4–6]. Studies of massif peridotites and mantle xenoliths from continental regions indicate that mantle beneath the continents may have a complex history, involving depletion events caused by initial crust extraction, and then later enrichment, probably from metasomatizing fluids [e.g., 7,8]. Several workers have noted that an efficient method of metasomatizing mantle is through silicate liquid metasomatism which veins the surrounding mantle [e.g., 9,10]. Evolution of such incompatible element enrichments for several billion years may be expressed as large differences in present-day isotopic compositions.

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The Hf isotope variations of the suboceanic mantle are relatively well constrained [e.g., 11,12], but we have essentially no knowledge of the Hf isotope variations in the subcontinental mantle. Although it is generally assumed that Hf isotope studies yield information which is similar to that obtained from Nd isotopes, the large fractionations that may occur for Lu/Hf make the Hf isotope system a powerful tool for deciphering the source region mineralogy of basalts, both today and in the geologic past. For example, Salters and Hart [13] compared Lu/Hf elemental ratios with Hf isotope compositions of oceanic lavas and noted that the initial site of melting of mid-ocean-ridge basalts (MORB) must be in equilibrium with garnet peridotite; MORB have long been thought to have been derived exclusively from spinel peridotite at shallow levels in the mantle. The large range in Hf isotope ratios in the MORB reservoir can be explained as mixing between two components, one that was ancient depleted spinel peridotite, and another that was ancient depleted garnet peridotite [1], or through variable proportions of garnet and clinopyroxene in complex two-stage melting models [12,13].

In this report we present $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratios measured from thirteen samples from northwestern Colorado and two samples from the central Rio Grande rift region. These data, as well as additional Hf isotope analyses on samples from the Rio Grande rift region reported previously [1], provide a detailed view of the interplay between enriched and depleted mantle reservoirs in an extensional continental tectonic setting, in addition to evaluation of models for ancient metasomatism in the Proterozoic lithospheric mantle. For example, lavas from the southern Rio Grande rift region were derived from a highly extended area, where seismically defined lithosphere is only 35 km thick [14]. Southern Rio Grande rift region lavas are interpreted to have been derived from a predominantly depleted asthenospheric component [14,15]. Lavas from northwest Colorado were derived from an area where late Cenozoic extension was minimal, and seismically defined lithosphere may be as thick as 100 km [16]. Previous workers have interpreted many northwestern Colorado lavas to have been derived from a lithospheric mantle component [17,18].

2. Geological setting

Miocene and younger magmatism in northwestern Colorado was predominantly basaltic in composition and can be temporally associated with early development of the Rio Grande rift. Extension in northwestern Colorado was minor, however, compared to that in the current Rio Grande rift depression, but a half-graben appears to have been in existence in the vicinity of Yampa and the Elkhead volcanic field (Fig. 1) from 26 to 7.5 Ma and was subsequently destroyed by Pliocene uplift and erosion [19]. Therefore, although the current physiographic expression of a
rift is poorly represented in northwestern Colorado, magmatism and extension are broadly contemporaneous with development of the Rio Grande rift and mafic rocks from northwestern Colorado can be considered as an extension of Rio Grande rift magmatism [20].

Three periods of magmatic activity are recognized in northwestern Colorado. The earliest and most voluminous volcanic activity took place from 24 to 20 Ma and erupted ~350 km$^3$ of magmas [19]. This phase is associated with volcanism at Yarmony and the Flat Tops volcanic field. A second and less voluminous phase (~190 km$^3$) of volcanism took place from 13.4 to 7.5 Ma; magmatism during this phase occurred at the Flat Tops volcanic field, Yampa, and the Elkhead volcanic field. The last stage of magmatism (<2 m.y. B.P.) was the least voluminous (0.3 km$^3$) (volumes from [20]).

Samples for this study were chosen to represent the range of rock types and compositions that were erupted in northwestern Colorado, and include samples from the Elkhead volcanic field, the Flat Tops volcanic field, Yarmony mountain, Yampa, and Quaternary basalts (Fig. 1). The volcanic rocks from these areas have been well characterized petrographically and chemically by previous workers [e.g., 20,21]. We believe that most of the samples analyzed for this study have not been significantly modified by crustal contamination; crust-free samples were chosen based on identifying samples from within related suites that have high MgO and Ni contents and low incompatible element contents. Such samples would presumably be the least fractionated, and hence the least contaminated. One sample, US-83 from the Flat Tops volcanic field, has been shown to have assimilated ~10% upper crust [21], and the decrease from its estimated mantle value is 4 $\epsilon_{\text{Hf}}$ units, approximately twice as great as the decrease in $\epsilon_{\text{Nd}}$ units. For comparison, samples that have assimilated 10–20% lower crust from the San Luis Hills in southern Colorado have similar decreases in $\epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ values compared to their estimated mantle value [1].

3. Analytical methods

We briefly review our chemical separation methods, which are different from those employed in other laboratories [e.g., 12,22]. Details can be found in Beard [23] and will be the subject of a forthcoming report [K. Barovich et al., in prep.]. Dissolution and leaching procedures are similar to those of Salters and Hart [12], although we employed high-temperature/pressure dissolution bombs to achieve consistent yields.

Hf, Zr and Ti were separated from the rest of the rock matrix using an anion exchange method modified from the same first-stage columns of [12]. The majority of Ti was removed from Hf and Zr using a second anion exchange column and $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}_2$. Final purification of Hf from Zr and any remaining Ti was done using a third anion exchange column and $\text{H}_2\text{SO}_4$ [24]. This chemical procedure provides a 90% Hf yield and is essentially free of any Zr or Ti, which is generally not obtained by other chemical separation methods. It is particularly important to separate all Ti from Hf, which can be difficult in high-Ti alkali and continental basalts.

Hf isotope ratios were determined using a six-collector VG 54 Sector mass spectrometer and three-jump dynamic mode data collection. Hf isotope ratios were normalized to $^{179}\text{Hf}/^{177}\text{Hf}$ ratio of 0.7325 for mass fractionation, and the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio is a combination of two determinations. Two loading methods were primarily used, one following the method of Corfu and Nobel [25], which uses a single Re filament with an Ir-C slurry, and the other following the method of Patchett and Tatsumoto [22], which uses a triple Re filament with $\text{H}_3\text{PO}_4$. Some experiments were done using double Re filaments. After extensive experimentation we decided that the triple Re filament loading method provides better ionization in our mass spectrometer than the single Re filament method (see [23] for details).

Using the single filament method, the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of JMC-475 (3 $\mu$g Hf) was measured as 0.282169 ± 12 ($2SE$, $n = 27$) in 1990 and 0.282147 ± 22 ($2SE$, $n = 13$) in 1992. Using the triple filament method the measured $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of JMC-475 (4 $\mu$g Hf) was 0.282167 ± 16 ($2SE$, $n = 7$) in 1992, which is within error of the 1990 and 1992 single-filament determinations. Mass fractionation corrections for thermal ionization are much lower using the triple filament method, where $^{176}\text{Hf}/^{177}\text{Hf} = 0.73357 ± 167$ ($2SE$, $n = 17$, pooled set of samples and stan-
dards), compared to the single-filament method, where $^{179}\text{Hf}/^{177}\text{Hf} = 0.73530 \pm 136 (2SE, n = 74$, pooled set of samples and standards). $^{177}\text{Hf}$ intensities were $\approx 1 \times 10^{-12} \text{A}$ for single-filament analysis ($\sim 30$–$70$ dynamic ratios determined on samples), and $\approx 2 \times 10^{-12} \text{A}$ for triple filament analysis ($\sim 50$–$100$ dynamic ratios determined on samples). We estimate that external reproducibility is $\pm 1.2 \epsilon_{\text{Hf}}$ units, based on duplicates of nine samples from Johnson and Beard [1] and four samples here (Table 1). Internal run statistics (2SE) are too pessimistic for most analyses, relative to the estimated external reproducibility. In part, this is a function of the rejection criteria used for estimating the internal statistics. At the onset of this project the external reproducibility for Hf on our mass spectrometer was unknown, and we used a criteria of rejecting up to 10% of the ratios that were 2SE from the mean, resulting in nearly every ratio being accepted and a high estimate of the in-run statistical error. By the end of this study we had a good estimate of our external reproducibility based on duplicate analyses of samples and standards, and changed our rejection criteria to 15% with a 1.5SE cutoff, resulting in closer agreement of the internal and external precision estimates.

4. Distribution coefficients

Our use of Hf isotope data to infer processes occurring in the spinel or garnet stability fields depends upon trace element modelling and it is therefore important to discuss the $D$ values and modeling approaches we have used. In predicting Hf isotope evolution paths, we believe the critical factor is the contrast in the ratio of the Sm/Nd and Lu/Hf $D$ values in different phases. To highlight these contrasts, we have considered only single-stage melting models with a single mineral assemblage, rather than the two-stage melting models that involve changes in mineralogy used by Salters and Hart [12,13]. The two most important phases are garnet and clinopyroxene because they control the bulk of the REE and Hf budget in the mantle. Orthopyroxene is also an important phase during melting because of the large melting proportion [e.g., 26], and it may be an important Hf-bearing phase in spinel peridotites [27]. With this in mind, we have elected to compile a preferred set of $D$ values (Table 2) by using the median $D$ value ratios for Sm/Nd, Sm/Hf, Lu/Hf and Lu/Sm for garnet and clinopyroxene as reported from several different studies [13,28–33]. To calculate partition coefficients for Nd, Sm, Lu and Hf we choose to use the median value for Sm, and then calculate the Nd, Hf and Lu partition coefficients using the median $D$ value ratios. We believe using partition coefficient ratios is the best approach because it may minimize the dependence of partition coefficients on bulk composition and pressure and temperature. For example, the experiments of Dunn [32] for Lu–Hf partitioning be-

<table>
<thead>
<tr>
<th></th>
<th>Nd</th>
<th>Sm</th>
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<th>Lu</th>
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<td>0.12</td>
<td>3.9</td>
<td>4.88 to 1.66</td>
<td>7.37</td>
<td>0.19</td>
<td>38.6</td>
<td>164 to 23.9</td>
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<td>Clinopyroxene</td>
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<td>0.37</td>
<td>1.93</td>
<td>1.42 to 2.25</td>
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<td>0.0194</td>
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Errors for $^{176}\text{Hf}/^{177}\text{Hf}$ ratios are 2SE from in-run statistics. Based on duplicate analyses of thirteen samples (this study and Johnson and Beard [1], separate dissolution and mass spectrometry) $\epsilon_{\text{Hf}}$ values are precise to 1.2 $\epsilon$ units. 'Reference' lists the source of $\epsilon_{\text{Nd}}$ values and major and trace element chemistry. Lu, Hf, Sm, Nd, Rb, Sr and Ni concentrations in ppm. SiO₂ and MgO in weight percent. Replicate analyses have been averaged for plotting and the purposes of discussion. Forty-seven analyses of JMC-475 at the University of Wisconsin between 1990 and 1992 produced an average $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of $0.282163 \pm 10 (2SE)$, which is equivalent to $^{176}\text{Hf}/^{177}\text{Hf}$ for CUR of 0.282827. This is equivalent to present-day chondrite (CHUR) $^{176}\text{Hf}/^{177}\text{Hf} = 0.282862$ and JMC-475 $^{176}\text{Hf}/^{177}\text{Hf} = 0.282198$ [66,67], where JMC-475 has $\epsilon_{\text{Hf}} = -23.47$. 

### Table 1

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<tr>
<th></th>
<th>Nd</th>
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<th>Sm/Nd</th>
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<th>Lu</th>
<th>Hf</th>
<th>Lu/Hf</th>
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![Image 1](https://via.placeholder.com/150)
### Table 2

Mineral–melt partition coefficients used in trace element modeling

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<th>Sample</th>
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<th>$\epsilon_{Nd}$</th>
<th>Lu</th>
<th>Hf</th>
<th>Sm</th>
<th>Nd</th>
<th>Rb</th>
<th>Sr</th>
<th>SiO$_2$</th>
<th>MgO</th>
<th>Ni</th>
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</table>

Ranges for Lu/Hf and Sm/Nd $D$ value ratios are from [13,28–33]. The choice of $D$ values is discussed in the text. The Lu $D$ value for garnet and clinopyroxene is the average from the median Lu/Hf and Lu/Sm $D$ value ratios.

tween clinopyroxene and basaltic liquid has a spread of ~ 30% for $D_{Hf}$ in clinopyroxene (temperature varied by 40°C and pressure by 5 kbar for these experiments), but the Lu/Hf $D$ value ratio only has a spread of ~ 11%.

There are few REE and Hf partition coefficients for orthopyroxene, olivine and spinel, so an analogous approach is not possible for these phases. Therefore, for orthopyroxene we have used the median values of Irving and Frey [29] for REE partitioning in orthopyroxene, and have constrained the Hf partition coefficient by setting the Hf clinopyroxene/orthopyroxene partition value equal to 0.2 and then using our $D_{Hf}$ for clinopyroxene to calculate the $D_{Hf}$ in orthopyroxene. The value of Hf partitioning between orthopyroxene and clinopyroxene is based on the recent studies of Kelemen and Dunn [34] and Rampone et al. [27] which measured Zr partitioning between orthopyroxene and clinopyroxene. Partition coefficients for olivine and spinel are more difficult to choose because the very low
trace element concentrations in these phases make megacrust–matrix studies problematic unless the mineral separates are 100% pure. Therefore, for olivine we have used the REE values reported by McKay [35], because they are the lowest values measured, and have set Hf between Sm and Nd. For spinel we have used the REE spinel/clinopyroxene values reported by Stosch [36] and then calculated D values using our clinopyroxene/liquid partition coefficients and have set Hf between Sm and Nd. For olivine and spinel, D values are relatively unimportant because their values are so low.

In general, regardless of the D values that are used, the trends for the spinel- and garnet-peridotite models presented below will be the same. This is because Lu/Hf fractionation in garnet is always much larger than in clinopyroxene.

5. Hf Isotope variations in the subcontinental mantle

$\epsilon_{Hf}$ and $\epsilon_{Nd}$ values of samples from the Rio Grande rift region and northwestern Colorado are positively correlated and span a range from $+9.5$ to $-10.4$ and $+8.7$ to $-12.6$ respectively (Table 1). This range is nearly as great as that for oceanic samples (Fig. 2). To facilitate comparison to oceanic basalt we will use the $\Delta\epsilon_{Hf}$ parameter as defined by Johnson and Beard [1], which is a measure of the difference between the measured $\epsilon_{Hf}$ value and the $\epsilon_{Hf}$ value that would be predicted based on a regression of oceanic island basalt (OIB) data. Oceanic island basalt have an average $\Delta\epsilon_{Hf}$ of 0, by definition, and an equal distribution of positive and negative $\Delta\epsilon_{Hf}$ values; 90% of all OIB analyses fall within $\pm 3.1$ $\Delta\epsilon_{Hf}$ values [1]. This is true for OIB as a whole, as well as individual island groups. In contrast, many samples from the Rio Grande rift region and northwestern Colorado have higher $\epsilon_{Hf}$ values that are skewed to either positive or negative $\epsilon_{Hf}$ values. For example, samples from the southern and the central Rio Grande rift region have negative $\Delta\epsilon_{Hf}$ values, and samples from the northern Rio Grande rift, the Elkhead volcanic field, and Quaternary basalt are skewed to positive $\Delta\epsilon_{Hf}$ values. Furthermore, $\Delta\epsilon_{Hf}$ values vs. $\epsilon_{Nd}$ values overall are negatively correlated for the entire sample suite from the Rio Grande rift region and northwestern Colorado (Fig. 3).

$\Delta\epsilon_{Hf}$ and $\epsilon_{Nd}$ values are related to geographic position: basalt that have the highest $\epsilon_{Hf}$ and $\epsilon_{Nd}$ values and most negative $\Delta\epsilon_{Hf}$ values are from the southern Rio Grande rift region, and basalt that have the lowest $\epsilon_{Hf}$ and $\epsilon_{Nd}$ values and most positive $\Delta\epsilon_{Hf}$ values are from northwestern Colorado. The broadly negative correlation between $\Delta\epsilon_{Hf}$ and $\epsilon_{Nd}$ for the entire suite is also found within magmatic centers at the Geronimo volcanic field, the Mogollon–Datil volcanic field, the Rayton Clayton volcanic field, the San Luis Hills [see 1] and the Elkhead volcanic field (data from this report). This is in marked contrast to Hf–Nd isotope variations in the OIB suites (Fig. 3).

Lavas from the southern and central section of the rift have high $\epsilon_{Nd}$ values and are characterized by negative $\Delta\epsilon_{Hf}$ values [1; this study]. Samples from the southern rift region, both within the rift and in the adjacent Basin and Range (Geronimo volcanic field), have the highest $\epsilon_{Nd}$ and most negative $\Delta\epsilon_{Hf}$ values, similar to low
Fig. 3. $\Delta \epsilon_{\text{Hf}}$ vs. $\epsilon_{\text{Nd}}$ for Rio Grande rift region and northwestern Colorado mafic volcanic rocks. $\Delta \epsilon_{\text{Hf}}$ is the difference of the measured $\epsilon_{\text{Hf}}$ value relative to the $\epsilon_{\text{Hf}}$ value that would be predicted based on the regression of OIB data, where $\Delta \epsilon_{\text{Hf}} = \epsilon_{\text{Hf}} - (1.36 \epsilon_{\text{Nd}} + 1.63)$. Discussion of the regression line for OIB is in [1]. Data sources for oceanic lavas and the Leucite Hills are as in Fig. 2; note the OIB field is for 90% of all measured OIBs; OIB is evenly spread between positive and negative $\Delta \epsilon_{\text{Hf}}$ values, by definition. Sample US-83 from the Flat Tops volcanic field has been interpreted to have assimilated $\sim 10\%$ upper crust [21].

$\Delta \epsilon_{\text{Hf}}$ MORB. In contrast, northern rift samples have $\epsilon_{\text{Hf}}$ values that range from +7.4 to -3.1 and $\epsilon_{\text{Nd}}$ values that range from +2.8 to -3.9, overlapping with the $\epsilon_{\text{Nd}}$ values of samples from the central rift. $\Delta \epsilon_{\text{Hf}}$ values (+3.9 to -0.5) are characteristically positive to slightly negative, as opposed to lavas from the central rift, which are negative (-1.4 to -5) [1].

Samples from northwestern Colorado, the primary subject of this report, have $\epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ values that range from +0.2 to -10.4 and -0.1 to -12.6, respectively, overlapping in part with samples from the northern rift, but extending the range to much lower $\epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ values. The most non-radiogenic Hf and Nd isotope ratios are from the Elkhead volcanic field, located in northeasternmost Colorado; these almost extend to the extreme Nd and Hf isotope compositions of lavas from the Leucite Hills that erupted through Archean crust, 180 km to the north [12]. Samples from the Elkhead volcanic field and Quaternary basalts have positive $\Delta \epsilon_{\text{Hf}}$ values (+6.2 to +2.4), whereas samples from Yampa, Yarmony and the Flat Tops volcanic field have $\Delta \epsilon_{\text{Hf}}$ values near zero (+1.0 to -2.3).

6. Lu–Hf and Hf isotope variations: Constraints on source region mineralogy

As has been pointed out by other workers, garnet can strongly effect the Lu/Hf fractionation of the source region and melts during magma generation [e.g., 13,37]. Combined Hf isotope and Lu/Hf concentration analysis provides unique constraints on source mineralogies that are present during basalt generation which are not possible to infer using the Sm/Nd system. For example, Salters and Hart [13] observed that the low Lu/Hf ratios of MORB were inconsistent with the high Lu/Hf ratios expected for the source, based on high measured $^{176}\text{Hf}/^{177}\text{Hf}$ ratios. They termed this the 'Hf paradox', and argued that initial melting of the MORB source region occurred in the garnet stability field, at a depth of >80 km, followed by continued melting in the spinel stability field.

Our results from the Rio Grande rift region provide strong evidence for production of nearly all late Cenozoic basaltic lavas by partial melting primarily in the garnet stability field (Fig. 4A). Melting in the spinel stability field alone cannot produce the low Lu/Hf ratios of the magmas, relative to those expected for the source based on Hf isotope compositions. That garnet peridotite is the source for basalts from the Geronimo volcanic field and lavas from Yampa is in agreement with the work of other investigators [e.g., 38,39]. Note that MORBs overlap the garnet and spinel fields, but are displaced to significantly higher measured Lu/Hf ratios (Fig. 4A), consistent with the genetic model of Salters and Hart [13]. Comparison with Sm/Nd–Nd isotope variations (Fig. 5A) highlights the exceptional discrimination ability of the Lu/Hf system to distinguish melting in the garnet and spinel lherzolite fields. The Sm/Nd system cannot effectively distinguish between melting garnet peridotite and spinel peridotite (Fig. 5A).

Calculation of the $[\text{Lu}/\text{Hf}]_\text{o}$ of the source based on the measured $\epsilon_{\text{Hf}}$ value of a rock is dependent on the assumption of the age of the mantle reservoir and its isotopic composition. The time of initial crust formation in Colorado, and
Fig. 4. (A) Chondrite-normalized Lu/Hf ([Lu/Hf]₀) ratio measured for lava relative to the calculated [Lu/Hf]₀ of the source based on the measured ε₁₈Hf value of the lava; details of calculating the [Lu/Hf]₀ of the source are in text. Melting fields calculated from non-modal batch melting of 1% (left side) to 20% (right side) garnet peridotite (solid lines and dashed ornament), and melting of 1% (left side) to 20% (right side) spinel peridotite (dashed lines and stippled ornament). Melting and modal proportions are as in [26] and D values are from Table 2. Vertical arrows show the effect of calculating the source [Lu/Hf]₀ using chondritic mantle at 1.8 Ga instead of depleted mantle at 1.8 Ga. The MORB field is from [12,59-60] with [Lu/Hf]₀ of the source calculated using a chondritic source at 1.8 Ga. Lavas with low [Lu/Hf]₀ ratios cannot be produced by melting in the spinel stability field; all samples, but 5LT-119 from Yarmony and RG-335 from the Taos Plateau volcanic field, require variable amounts of melting of garnet peridotite. Chondrite normalization factors are Sm = 0.1941 ppm, Nd = 0.5966 ppm, Lu = 0.0377 and Hf = 0.157. These values produce CHUR 147Sm/144Nd and 176Lu/177Hf ratios, and are used for all of the trace element modeling. Symbols as in Fig. 2. (B) Histogram of measured Lu/Hf ratios normalized to chondrite of Early Proterozoic mafic rocks from Colorado and New Mexico (data sources as in Fig. 4B). The x-axis scale is the same as in (A).

Fig. 5. (A) Chondrite-normalized Sm/Nd ([Sm/Nd]₀) ratio measured for lava relative to the calculated [Sm/Nd]₀ of the source based on the measured εNd value of the lava; details of calculating the [Sm/Nd]₀ of the source is in text. Melting fields (solid line = garnet peridotite field and dashed line = spinel peridotite field) and details of calculating them are the same as in Fig. 4. Distinguishing between melting in the garnet stability or spinel stability field is difficult using the Sm/Nd and Nd isotope variations alone. The MORB field is as in Fig. 4A, with the [Sm/Nd]₀ of the source calculated using a chondritic source at 1.8 Ga. Symbols as in Fig. 2. (B) Histogram of measured Sm/Nd ratios normalized to chondrite of Early Proterozoic mafic rocks from Colorado and New Mexico (data sources as in Fig. 4B). The x-axis scale is the same as in (A).

presumably the time of subcontinental lithospheric mantle stabilization, is reasonably well constrained to be 1.8 Ga [e.g., 40]. Colorado Front Range mantle at the time of crust formation was depleted relative to chondrite, with average ε₁₈Hf and εNd values of +7.6 and +5 respectively [40–42]. Therefore, we have used these compositions for calculating the [Lu/Hf]₀ of the source for the studied basalts. If the mantle was assumed to be chondritic instead of depleted at 1.8 Ga, the calculated value of the [Lu/Hf]₀ of the source would be 25–50% higher (vertical ar-
rows in Fig. 4A), which would pull the samples more deeply into the garnet field.

Below we develop an evolutionary model that contrasts the mineralogy of the ancient and modern lithospheric mantle. Early Proterozoic mafic volcanogenic rocks from Colorado and New Mexico typically have higher Lu/Hf ratios than the Rio Grande rift region samples, perhaps reflecting derivation from shallow primitive arc or back-arc sources that had no residual garnet (Fig. 4B). The [Ce/Yb]\textsubscript{n} ratios for these Proterozoic lavas are lower (0.42–19.8) than for the Rio Grande rift region samples (2.3–35.5) and the Yb\textsubscript{n} contents for the Proterozoic rocks are higher (2.6–31.3) than those of samples from the Rio Grande rift region (6–14) [43–50]. These observations are also consistent with derivation of the Early Proterozoic mafic volcanic rocks from a source which did not contain residual garnet.

Finally, we address the effects of fractional crystallization and recent mantle metasomatism on the trends illustrated in Fig. 4 and 5. Fractional crystallization only slightly decreases the [Lu/Hf]\textsubscript{n} of basalt. Assuming typical fractionating phases, olivine–clinopyroxene or olivine–orthopyroxene, 40% crystallization will decrease the Lu/Hf ratio by only ~ 5%, which is insignificant. Even for the Elkhead volcanic field minettes, which have clinopyroxene, olivine, biotite and minor apatite phenocrysts, 40% crystallization will only decrease the Lu/Hf ratio by 15%.

The effects of recent metasomatism, however, are more difficult to address. Several workers have suggested that mantle metasomatism related to Mesozoic/Cenozoic subduction has affected the mantle along the Colorado Front Range [20,51]. If this metasomatism is controlled solely by slab dewatering, elements with large ionic radii will be preferentially enriched relative to elements with smaller ionic radii [52]. Because the ionic radius of Hf is less than that of Lu, we would expect that the net affect of recent metasomatism will be to increase the [Lu/Hf]\textsubscript{n} of the mantle, and melts derived from it; because the Lu/Hf ratios of the Cenozoic lavas are already very low, the possibility of recent metasomatism is highly unlikely to lead to spurious interpretation of the melting mineralogy in magma generation. We conclude that despite small uncertainties regarding crystallization and recent metasomatism it is extremely unlikely that the Cenozoic lavas were generated to any significant degree from spinel peridotite.

7. Origin of enrichment in the subcontinental lithospheric mantle

The isotopic composition of the asthenospheric oceanic mantle is relatively well constrained and one of the most intriguing observations is that most oceanic island basalts (OIB) from the northern hemisphere, compared with OIB from the southern hemisphere, were derived from source regions that are depleted relative to chondrite [3]. To the extent that asthenospheric mantle below the continents and the oceans is the same, it is difficult to interpret the enriched isotopic compositions of northwestern Colorado lavas as melts of asthenospheric mantle, unless one wishes to call upon a unique asthenospheric source not sampled by northern hemisphere OIB or MORB. Therefore, the uncontaminated lavas from northwestern Colorado are believed to have inherited their unique isotopic compositions from ancient subcontinental lithospheric mantle [e.g., 20].

We have chosen to illustrate enrichment processes in the lithospheric mantle through simple two-component mixing of silicate liquids and depleted mantle, followed by isotopic evolution over several billion years. One component is depleted mantle which has Lu/Hf and Sm/Nd ratios that are constrained by the Hf and Nd isotope studies conducted by Patchett et al. [41], DePaolo [40] and Nelson and DePaolo [42]; these studies indicate that Proterozoic mantle along the Colorado Front Range was depleted relative to chondrite, with average ε\textsubscript{Hf} and ε\textsubscript{Nd} values (at 1.8 Ga) of ~ +7.6 and +5 respectively. This implies [Lu/Hf]\textsubscript{n} and [Sm/Nd]\textsubscript{n} ratios (normalized to chondrite) of 1.18 and 1.11 respectively for 1.8 b.y., assuming initially chondritic compositions at 3.6 Ga. The enriched metasomatizing component was modeled as silicate liquids that were derived from melting this depleted mantle. Melts were derived from garnet or spinel peridotite using non-modal batch melting, and the modes and melting proportions of Ottonello et al. [26]. The curves in Fig. 6 show the mixing relationship between two depleted mantle compositions (Colorado Front
Fig. 6. (A) $\Delta \varepsilon_{\text{Hf}} - \varepsilon_{\text{Nd}}$ diagram showing possible evolution of the subcontinental lithospheric mantle following ancient silicate melt metasomatism. The curves are mixing lines between depleted mantle (DM) and liquids derived from 1% partial melting of the same DM. Circles (○) indicate liquids derived from melting a DM with spinel peridotite mineralogy, and squares (■) indicate liquids derived from melting a DM with garnet peridotite mineralogy. These symbols also indicate the mixing percent of silicate liquid and DM (1%, 5%, 10%, 20%, 30%, 50% and 100%). The same mixing percentages are shown for each curve. The silicate liquids were assumed to have formed 1.8 b.y. ago and curves show present-day $\Delta \varepsilon_{\text{Hf}}$ and $\varepsilon_{\text{Nd}}$ values of the metasomatized mantle mixture (i.e., vein material mixed with DM 1.8 b.y. ago). The fields for oceanic lavas and the Leucite Hills are the same as in Fig. 3. The dashed fields are lavas from the Rio Grande rift region, as in Fig. 3; the solid fields are northwestern Colorado samples from this study (EVF = Elkhead volcanic field; Ym = Yarmony; Yp = Yampa; Q = Quaternary lavas). The Colorado Front Range (CFR) DM is modeled as having Lu and Sm contents at 2× chondrite; Nd and Hf contents were adjusted such that the mantle had $\varepsilon_{\text{Hf}}$ and $\varepsilon_{\text{Nd}}$ values of +7.6 and +5, respectively, at 1.8 Ga [40-42], and chondritic compositions at 3.6 Ga. The Hf isotopic composition of CFR DM is poorly constrained and is based on five analyses which have $\varepsilon_{\text{Hf}} = +10.9$ to $+2.4$ [41]. A value of +7.6 is used to force the mantle to have a present-day $\Delta \varepsilon_{\text{Hf}}$ value of 0. The spinel peridotite DM is modeled in a way similar to that for the CFR DM, but the Nd and Hf contents were adjusted so that it had present-day $\varepsilon_{\text{Hf}}$ and $\varepsilon_{\text{Nd}}$ values of +9.4 and +12.2 respectively ($\Delta \varepsilon_{\text{Hf}} = -8.8$), and chondritic compositions at 3.6 Ga. The present-day $\varepsilon_{\text{Hf}}$ and $\varepsilon_{\text{Nd}}$ values of the model spinel peridotite DM reflect the lowest $\Delta \varepsilon_{\text{Hf}}$ MORB, and are values that would not have been produced if chondritic mantle with spinel peridotite mineralogy was depleted several billion years ago [1].

Range depleted mantle and model spinel peridotite depleted mantle) and silicate liquids derived from 1% melting of depleted mantle with either a garnet peridotite mineralogy or a spinel peridotite mineralogy 1.8 b.y. ago, followed by evolving these mixtures to the present day.

This simple mixing model indicates that positive present-day $\Delta \varepsilon_{\text{Hf}}$ and negative $\varepsilon_{\text{Nd}}$ values are characteristic of mantle that has been metasomatized by silicate liquids derived from spinel peridotite (Fig. 6), assuming metasomatism of Proterozoic mantle that had isotopic compositions similar to those measured for the Colorado Front Range Proterozoic lavas. If metasomatism involving a model spinel depleted mantle occurred (Fig. 6), the positive $\Delta \varepsilon_{\text{Hf}}$ values of the Cenozoic lavas cannot be produced. Regardless of the assumptions of the isotopic compositions of the depleted Proterozoic mantle component (i.e., Colorado Front Range mantle or model spinel mantle) that is assumed, production of present-day low $\varepsilon_{\text{Nd}}$ and positive $\Delta \varepsilon_{\text{Hf}}$ values is only possible using ancient metasomating melts that were derived from spinel peridotite; this restricts the origin of metasomatic melts to the uppermost mantle. Such melts may be represented by Early Proterozoic mafic volcanic rocks, whose high Lu/Hf ratios (above) indicate that a major component of Proterozoic magmatism was derived from spinel peridotite. In no case can mixing with silicate liquids derived from garnet peridotite produce the positive $\Delta \varepsilon_{\text{Hf}}$ values of the Elkhead volcanic field and Quaternary basalts (Fig. 6).

Another possible way to produce enriched mantle is recycling subducted oceanic crust and associated sediment into the mantle. Mature sediment, especially pelagic sediment, has a high Lu/Hf ratio relative to its Sm/Nd ratio [53]. Input of this high Lu/Hf sediment into the mantle would produce trends of positive $\Delta \varepsilon_{\text{Hf}}$ values and negative $\varepsilon_{\text{Nd}}$ values. Immature sediment, such as arc-derived detritus, however, does not have high Lu/Hf ratios relative to its Sm/Nd ratio, probably because the sediment is too juvenile to have had a significant amount of zircon removed from it during processing through the sedimentary cycle [53]. The Early Proterozoic of Colorado and New Mexico was a time of very rapid crustal growth, and this newly formed crust is juvenile with depleted mantle model ages and crystallization ages being nearly identical [e.g., 40]. Some of the most mature sediments from the Early Proterozoic of Colorado are pelitic paragneisses of
the Idaho Springs Formation [54], and although these sediments have large negative Eu anomalies, they have low Lu/Hf ratios relative to their Sm/Nd ratio [41,54]. Therefore, to the extent that sediment such as the Idaho Springs Formation was subducted during Early Proterozoic crust formation, we do not favor sediment addition to the mantle as a viable mechanism for producing lithospheric mantle in this region that has positive $\Delta^{176}_{\text{Hf}}$ values and negative $\epsilon_{\text{Nd}}$ values.

8. Discussion

To a first approximation the negative correlation of $\Delta^{176}_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$, with $\Delta^{176}_{\text{Hf}}$ increasing and $\epsilon_{\text{Nd}}$ decreasing from the southern Rio Grande rift region to northwestern Colorado, can be interpreted as mixing between two components, one depleted and the other enriched. The depleted component is best represented by lavas from the southern Rio Grande rift (Mogollon–Datil volcanic field) and adjacent Basin and Range (Geronimo volcanic field). The enriched component is best represented by lavas from northwestern Colorado, in particular samples from the Elkhead volcanic field. Considering that the lithosphere is thinnest in the southern Rio Grande rift, the southern Rio Grande rift region basalts are interpreted as being derived from a predominantly asthenospheric component, as suggested by Perry et al. [15]. In Colorado the lithosphere is thicker and the basaltic rocks are derived from an enriched source, and thus we interpret these lavas as being derived from a predominantly lithospheric source. The origin of the asthenospheric source for lavas from the southern Rio Grande rift has been interpreted as a result of ancient (> 1 Ga) depletions of spinel peridotite, based on the positive $\epsilon_{\text{Nd}}$ and significantly negative $\Delta^{176}_{\text{Hf}}$ values [1].

The origin of the positive $\Delta^{176}_{\text{Hf}}$ values (at negative $\epsilon_{\text{Nd}}$) is interpreted as the result of mixing depleted mantle with melts that were derived from melting spinel peridotite and then ‘ageing’ the mixture for several billion years. Veining the mantle with melts that are similar in composition to Early Proterozoic mafic volcanic rocks from Colorado and New Mexico and ageing this veined metasomatized mantle for 1.8 Ga can produce the $\epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ values measured today. Although the percent of metasomatizing component required to produce the lowest $\epsilon_{\text{Nd}}$ values is high (> 50%), we envision that the veins in a veined lithospheric mantle would be preferentially melted and contribute the major amounts of Nd and Hf to generated magmas. Note that mixing liquids derived from garnet peridotite with depleted mantle will not produce large positive $\Delta^{176}_{\text{Hf}}$ values at negative $\epsilon_{\text{Nd}}$ values, and in fact produces an array that is orthogonal to the negative $\Delta^{176}_{\text{Hf}}$–$\epsilon_{\text{Nd}}$ correlation.

The samples from the Elkhead volcanic field are probably the best representatives of subcontinental lithospheric mantle. These samples have the most extreme isotopic compositions, similar in isotopic composition to rocks analyzed by Salters and Hart [12] from the Leucite Hills which erupted through Archean crust. The most enriched Elkhead minette sample is the sample closest to the Wyoming shear zone, which separates Archean crust from Proterozoic crust. Recent geophysical studies have suggested that Archean lithosphere may dip to the south beneath Colorado [55]. Hence the Elkhead samples may be derived, in part, from Archean lithosphere.

9. Conclusions

We favor metasomatism by silicate liquids that were derived from melting spinel peridotite in the uppermost mantle as the most likely explanation for positive $\Delta^{176}_{\text{Hf}}$ and negative $\epsilon_{\text{Nd}}$ values in the lithospheric mantle of Colorado, because mixing between such liquids and depleted mantle most closely matches the anti-correlation of $\Delta^{176}_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ that is observed. Further evidence that supports silicate metasomatism by liquids derived from melting spinel peridotite lies in the inferred source regions for Early Proterozoic mafic rocks from Colorado and New Mexico. These magmas are interpreted to have been derived from melting spinel peridotite based on their low Ce/Yb ratios and high Lu/Hf ratios and Yb contents. We envision that the developing Early Proterozoic lithospheric mantle became veined by residual melts that were produced by melting spinel peridotite, perhaps the unerupted equivalents of Early Proterozoic lava sequences in the region; today, these veins would have negative $\epsilon_{\text{Nd}}$ and
An important implication of this model is a change from spinel peridotite to garnet peridotite in the lithospheric mantle, as marked by the contrast between high Lu/Hf Proterozoic lavas and low Lu/Hf Cenozoic lavas. We envision the change from spinel to garnet peridotite to occur in the lithospheric mantle through crustal thickening and cooling over time, thereby stabilizing garnet at the expense of spinel (Fig. 7). In this model, the Early Proterozoic metasomatism occurred in the developing lithospheric mantle between the depths of ~20 and 80 km (Fig. 7). As the crust and lithosphere became thicker, this ~60 km thick section of mantle became depressed into the garnet-stability field (Fig. 7).

Lu/Hf abundances and Hf isotope compositions of all of the samples from the Cenozoic Rio Grande region constrain the mineralogy of the source region for the rift region basalts to have been garnet peridotite. This implies that at least initial melting had to occur at >80 km [e.g., 56]. Derivation of the basalts from a garnet peridotite source appears to be contrary to recent models that propose derivation of rift lavas thorough shallow melting of upwelling asthenosphere [e.g., 15], unless upwelling was so rapid that garnet did not re-equilibrate to spinel. Our data suggest that although some rift basalts may have been derived from the asthenospheric mantle, melting did not begin at a shallow level, similar to recent models for generation of MORBs [13].

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**References**

Hf ISOTOPE COMPOSITION OF BASALTIC ROCKS AND MANTLE ENRICHMENT PROCESSES

33 S.R. Hart and T. Dunn, Experimental cpx/melt partition-
