1 **Trace element partitioning and Lu-Hf isotope systematics in spinel peridotites**
2 **from the Rio Grande Rift and Colorado Plateau: Towards improved age**
3 **assessment of clinopyroxene Lu/Hf-¹⁷⁶Hf/¹⁷⁷Hf in SCLM peridotite**

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7

8 **Abstract**

9 Our study of Colorado Plateau and Rio Grande rift spinel peridotite xenoliths
10 determined bulk Lu-Hf budgets and cpx, opx, and whole rock $^{176}\text{Hf}/^{177}\text{Hf}$ to evaluate
11 the potential age significance of Lu/Hf-Hf isotope correlations in sub-continental
12 lithospheric mantle (SCLM) derived xenoliths. The samples have fertilities (spinel
13 Cr# range from 0.1 to 0.5), and equilibration temperatures (950-1050 °C) that
14 overlap with those of spinel peridotites commonly used in Lu-Hf dating studies. The
15 Lu/Hf of clinopyroxene (cpx) and its associated whole rock (WR) are similar in
16 fertile samples, but cpx has a lower Lu/Hf than that of the WR in refractory samples.
17 Orthopyroxene (opx) has systematically higher Lu/Hf than cpx, but in many
18 samples, the opx and cpx have identical $^{176}\text{Hf}/^{177}\text{Hf}$, suggesting that the Hf isotope
19 composition of these minerals is supported by the Lu/Hf of the WR rather than that
20 of the individual minerals. Many opx fractions and whole rocks have less radiogenic
21 $^{176}\text{Hf}/^{177}\text{Hf}$ than their corresponding cpx (but similar to that of the host magma),
22 reflecting contamination. Because the $^{176}\text{Hf}/^{177}\text{Hf}$ of cpx is supported by the WR
23 Lu/Hf, it is necessary to use the latter rather than the cpx Lu/Hf for isochron dating.
24 However, because the actual WR Lu/Hf values are susceptible to secondary
25 overprinting, we recommend using model WR Lu/Hf values (determined from
26 mineral Lu and Hf concentrations and modal abundances) to construct external cpx
27 isochrons. Model WR and measured cpx $^{176}\text{Hf}/^{177}\text{Hf}$ are correlated ($r^2 = 0.98$) in a
28 suite of eastern Colorado Plateau xenoliths and yield an apparent age of 1.2 Ga
29 (versus 1.5 Ga when – incorrectly – using cpx Lu/Hf). Despite the good correlation
30 between Lu/Hf and $^{176}\text{Hf}/^{177}\text{Hf}$, we do not find correlations between indicators of
31 melt depletion and Lu/Hf or $^{176}\text{Hf}/^{177}\text{Hf}$. This suggests that Lu/Hf – $^{176}\text{Hf}/^{177}\text{Hf}$

correlations are not the result of melt depletion. Instead, we propose that Lu/Hf – $^{176}\text{Hf}/^{177}\text{Hf}$ correlations are the result of mixing between depleted and enriched components (e.g. metasomatism of depleted lithospheric mantle). We emphasize that additional data should be utilized (e.g. whole rock Lu-Hf budget, degree of metasomatism, opx $^{176}\text{Hf}/^{177}\text{Hf}$) when interpreting apparent Lu-Hf isochrons for age significance.

1. Introduction

The Lu-Hf system is a powerful tool for constraining the timing of ancient melt depletion events associated with the formation of continental lithospheric mantle (Bianchini et al., 2014; Carlson et al., 2004; Choi and Mukasa, 2012; Choi et al., 2008; Choi et al., 2010; Chu et al., 2009; Lazarov et al., 2012; Liu et al., 2012; Schmidberger et al., 2002; Shaw et al., 2007; Wittig et al., 2006). Because lutetium is more compatible than Hf during mantle partial melting (Hart and Dunn, 1993; Hauri et al., 1994), Lu/Hf in residual peridotites will increase as the degree of melt extraction increases. In suites of SCLM xenoliths that underwent variable degrees of melt extraction during the same melting event, this results in correlations between Lu/Hf and $^{176}\text{Hf}/^{177}\text{Hf}$ that can be used to determine the age of melt depletion. The Lu-Hf system is considered to be particularly useful because it is generally thought to be more resistant to metasomatic overprinting than the Rb-Sr or Sm-Nd systems (Ionov et al., 2005; Salters and Zindler, 1995; Schmidberger et al., 2002; Wittig et al., 2006; Yu et al., 2009).

Because Lu and Hf are present in high concentrations in cpx relative to other spinel peridotite phases, “isochrons” are often constructed from suites of genetically-related peridotites using $^{176}\text{Lu}/^{177}\text{Hf}_{\text{cpx}}$ and $^{176}\text{Hf}/^{177}\text{Hf}_{\text{cpx}}$ rather than bulk peridotite values, which can be susceptible to contamination from host melts (Choi and Mukasa, 2012). For the remainder of the manuscript we will use the term “external cpx isochron” to refer to practice of using $^{176}\text{Lu}/^{177}\text{Hf}_{\text{cpx}}$ and $^{176}\text{Hf}/^{177}\text{Hf}_{\text{cpx}}$ from multiple samples to construct an “isochron” for dating purposes. This is similar in principle to traditional “whole rock isochrons.” The use of external cpx isochrons assumes that during and after melt extraction either: 1) the cpx $^{176}\text{Hf}/^{177}\text{Hf}$ evolved as a function of the cpx Lu/Hf (i.e. cpx is closed to Hf isotopic exchange with other minerals from the sample), or 2), minerals were open to Hf exchange so that $^{176}\text{Hf}/^{177}\text{Hf}$ is supported by whole rock Lu/Hf, but the Lu/Hf of WR is effectively identical to cpx Lu/Hf owing to high concentrations of Lu and Hf in cpx relative to other phases present. Additionally, it is assumed that the whole rocks had the same Hf isotope composition initially, and the Lu-Hf system has remained closed on the whole rock scale since the initial melt extraction event (i.e. no metasomatic overprinting has occurred). If any of these assumptions are incorrect, then Lu/Hf – $^{176}\text{Hf}/^{177}\text{Hf}$ correlations may not accurately record the age of the melt depletion event.

Several studies of SCLM-derived peridotites have discussed the validity of these various assumptions and their impact on apparent model ages. Carignan et al. (1996) observed cpx fractions that are not in lead isotopic equilibrium with associated olivine fractions owing to variable effects of metasomatism on different

mineral phases. Liu et al. (2012) discuss the impact of thermal history and maintaining isotopic equilibrium on age interpretation and outline the potential for deriving erroneously old ages from external cpx isochrons. Numerous studies (e.g. Bianchini et al., 2007; Ionov et al., 2006; Wittig et al., 2010; Wu et al., 2006; Yu et al., 2009) outline the myriad effects of metasomatism on Nd and Hf isotope composition and demonstrate the susceptibility of those systems to secondary overprinting. In this study we provide a rigorous evaluation of these ideas and observations and their application towards interpreting the apparent Lu-Hf ages of spinel peridotites.

We measured whole rock, orthopyroxene, and clinopyroxene trace element abundances and Hf and Nd isotope compositions of two suites of well-equilibrated spinel peridotite xenoliths to evaluate the factors that affect the Lu-Hf systematics in spinel peridotites. In doing so, it is possible to establish the trace element budget of the samples, infer whole rock Lu/Hf and compare them to cpx Lu/Hf. Comparison between cpx and opx Hf and Nd isotope compositions can establish whether samples' isotopic compositions are supported by mineral or whole rock parent-daughter ratios. Lastly, Hf isotope compositions can be compared with indicators of both melt depletion and metasomatism to elucidate the causes and age significance of Lu/Hf – $^{176}\text{Hf}/^{177}\text{Hf}$ correlations that are commonly observed in suites of spinel peridotite xenoliths.

2. Samples and Analytical Methods

We examined a suite of spinel peridotites (lherzolite to harzburgite) from Cerro Chato (CC) and Elephant Butte (EB), which are on the Eastern margin of the Colorado Plateau and the Central Rio Grande rift, respectively. Samples are described in detail in Byerly and Lassiter (2012; 2014). Xenolith sampling locations, equilibration temperatures, and petrographic textures are presented in the appendix (Table A1). The samples from Cerro Chato are derived from Proterozoic lithospheric mantle that has been variably melt depleted (spinel Cr# ranges from 0.15 to 0.45) and metasomatised (cpx (La/Sm)_N ranges from 0.7 to 11). Two groups of xenoliths are present at Elephant Butte. One group samples Proterozoic lithosphere and is broadly similar to the Cerro Chato xenoliths, except they are generally more refractory (spinel Cr# ranges from 0.14 to 0.50). The other group from Elephant Butte samples asthenospheric mantle that has been recently accreted to the base of the Proterozoic lithosphere (Byerly and Lassiter, 2012). These xenoliths are fertile (average bulk Al₂O₃ ~ 4 wt. %, spinel Cr# ranges from 0.08 to 0.13) and are LREE-depleted. We observed olivine, opx, cpx, and spinel (± interstitial glass) in the xenoliths. Sulfides are also present, but are only identifiable via electron probe analysis. The asthenosphere- and lithosphere-derived samples have overlapping two-pyroxene (T_{BKN}, Brey and Köhler, 1990) equilibration temperatures that range from 943 to 1065 °C and 848 to 1104 °C, respectively.

Trace element concentrations in cpx and opx were measured by LA-ICP-MS on an Agilent 7500ce quadrupole, following the methods of Byerly and Lassiter (2012). Spot sizes of 150 µm were used for LA-ICP-MS analyses of cpx and opx. We used NIST-612 and BCR-2G as primary and secondary standards, respectively.

Analyses of all elements for BCR-2G were accurate to within 10% of the accepted values and Ti, La, Ce, Nd, Sm, and Yb were accurate to within 5%. Repeated analyses of BCR-2g were reproducible to within ~10% (1 s.d.). Multiple (5-10) grains of each mineral were analyzed per sample. Chemical separation of Nd from REE was achieved with HDEHP resin following the methods of Byerly and Lassiter (2012). Chemical separation of Lu and Hf followed the methods of Connelly et al. (2006). Neodymium was measured using double rhenium filaments on a Thermo Triton TIMS. The AMES neodymium standard was run frequently between samples and produced an average $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.512070 ± 0.000010 (2 s.d. - external). The BHVO-2 standard was also analyzed throughout the study and produced an average $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.512970 ± 0.000010 (2 s.d. - external) which is consistent with the literature value of 0.512980 ± 0.000012 (Jochum et al., 2005). Lutetium and Hf were measured via MC-ICP-MS on a Micromass (GV) Isoprobe, as outlined in Byerly and Lassiter (2014). A ~30 ppb solution of the Hf-isotope standard JMC475 was measured 5-10 times per day during the study. The within-day external reproducibility of the JMC475 standard was typically about one epsilon unit. Samples are reported relative to the accepted JMC475 value of $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160$. A solution of BHVO-2 was run as a secondary standard throughout the study and had an average $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.283096 ± 0.000020 (2 s.d.) which is consistent with the literature value of 0.283104 (Jochum et al., 2005). Blanks were <30 pg for Nd, <40 pg for Hf, and <5 pg for Lu. Whole-rock powders were analyzed for major and trace elements at the GeoAnalytical lab at Washington State University.

3. Results

Major element analyses, $^{187}\text{Os}/^{188}\text{Os}$ analyses, and some cpx trace element and $^{143}\text{Nd}/^{144}\text{Nd}$ analyses were previously reported in Byerly and Lassiter (2012). Results of clinopyroxene and orthopyroxene trace element analyses are presented in Tables 1 and 2. Orthopyroxene and clinopyroxene trace element compositions are generally well correlated (Figures 1a, b). The asthenosphere-derived samples are LREE depleted ($(\text{La}/\text{Sm})_{\text{N}}$ ranges from 0.04 to 0.42). The lithosphere-derived samples are LREE enriched. Excluding one sample whose $(\text{La}/\text{Sm})_{\text{N}}$ is 0.7, the lithosphere-derived samples have $(\text{La}/\text{Sm})_{\text{N}}$ that range from 1.4 to 10. Clinopyroxene fractions from both suites of xenoliths display negative high field strength element (HFSE) anomalies relative to REE (e.g. $\text{Hf}/\text{Hf}^* < 1$, where $\text{Hf}^* = \sqrt{\text{Nd}_N \cdot \text{Sm}_N}$). Orthopyroxene fractions display a complementary enrichment in HFSE (e.g. $\text{Hf}/\text{Hf}^* > 1$) relative to REE.

Clinopyroxene, opx, and whole-rock Hf and Nd isotopic analyses are presented in Tables 3 and 4. Systematics of the Nd and Hf isotope compositions of the asthenosphere-derived samples from Elephant Butte are discussed in Byerly and Lassiter (2014). The asthenosphere-derived samples have cpx ϵ_{Nd} values that range from +8 to +27. The lithosphere-derived samples have a narrower range of cpx Nd isotope compositions (ϵ_{Nd} from +4 to +10). Orthopyroxene fractions and bulk xenoliths have Nd isotope compositions that are identical to or less radiogenic than the cpx Nd isotope compositions. The ϵ_{Hf} values of cpx from the asthenosphere-derived Elephant Butte samples range from +12 to +40 and are positively correlated with ϵ_{Nd} values. Lithosphere-derived samples from Elephant Butte have cpx ϵ_{Hf}

values ranging from +17 to +78, which do not correlate with ϵ_{Nd} . Clinopyroxene fractions from Cerro Chato have ϵ_{Hf} values that range from +18 to +304. Whole rock and opx $^{176}\text{Hf}/^{177}\text{Hf}$ are similar to or less radiogenic than the $^{176}\text{Hf}/^{177}\text{Hf}_{\text{cpx}}$ from the same sample.

4. Discussion

4.1 Trace element partitioning between clinopyroxene and orthopyroxene

There are many models that define the effects of pressure, temperature, and composition on trace element partitioning between coexisting phases. A common practice is to employ lattice strain models fitted to experimental data to estimate pyroxene-melt partition coefficients (Sun and Liang, 2012; Wood and Blundy, 1997; Yao et al., 2012). These models use the Brice (1975) equation for lattice strain energy to estimate partition coefficients as a function of temperature and ionic radius, a function of crystal composition (e.g. Wood and Blundy, 2003, for review). Witt-Eickschen and O'Neill (2005) used data from chemically well-equilibrated natural samples to construct a model for the effects of temperature and composition on cpx-opx-olivine-spinel partitioning. Yao et al. (2012) showed their opx-melt model combined with the cpx-melt model of Sun and Liang (2012) to be in good agreement with the Witt-Eickschen and O'Neill model.

We used the measured clinopyroxene and orthopyroxene trace element compositions in the CC and EB xenoliths to estimate cpx/opx partition coefficients. The predominance of 120° triple junctions suggests that most of the xenoliths from this study are in textural equilibrium. Rare earth elements and HFSE are generally

well correlated between cpx and opx (Figure 1) which is consistent with cpx-opx equilibrium. We also confirmed our assumption of cpx-opx equilibria using the methods of Agranier and Lee (2007) and Lee et al. (2007). Examples of this are presented in the appendix (Figure A1). Average calculated $D_{\text{cpx/opx}}$ values for the asthenosphere-derived and lithosphere-derived samples are shown in Figure 2. The lithosphere-derived samples, which have more refractory compositions than the asthenosphere-derived samples, have lower average $D_{\text{cpx/opx}}$ for REE and HFSE. Figures 3a and 3b illustrate that for both suites of samples, the $D_{\text{cpx/opx}}$ values that we estimate are consistent with those predicted by the formulation of Witt-Eickschen and O'Neil (2005). That study primarily focused on moderately refractory xenoliths whose spinel Cr# range from 0.13 to 0.47. The Elephant Butte and Cerro Chato samples overlap with and extend the range to more fertile compositions (spinel Cr# ranges from 0.08 to 0.50).

Partitioning between cpx and opx (i.e. $D_{\text{cpx/opx}}$) is controlled by both temperature and composition. However, the relative impact of each of these variables differs from element to element. For example, lattice strain models (e.g. Wood and Blundy, 1997; Yao et al., 2012) and the Witt-Eickschen and O'Neill (2005) model predict that variations in temperature impart larger effects on $D_{\text{cpx/opx}}$ for LREE than for HREE. For example, the Witt-Eickschen and O'Neill model predicts a 50% variation for $D_{\text{Nd}}^{\text{cpx/opx}}$, but only a 15% variation in $D_{\text{Lu}}^{\text{cpx/opx}}$ for a 100 °C temperature variation (from 950 to 1050 °C) at a fixed composition. In contrast, for the HREE, Zr, and Hf, variations in composition at constant temperature result in large variations in $D_{\text{cpx/opx}}$ ($\sim 50\%$ for in $D_{\text{Lu}}^{\text{cpx/opx}}$) but smaller variations in $D_{\text{cpx/opx}}$

214 for LREE ($\sim 30\%$ for $D_{\text{Nd}}^{\text{cpx/opx}}$). The large effect of composition on HREE, Zr, and Hf
215 distribution coefficients for the limited range in temperature covered by the EB and
216 CC samples is manifested as a strong negative correlation between $D^{\text{cpx/opx}}$ and cpx
217 MgO content (Figures 4a,b) and other indices of peridotite fertility (e.g. spinel Cr#).
218 One result of this compositional effect is that cpx-opx partition coefficients for
219 HREE, Zr, and Hf will decrease with increased melt removal (cpx MgO content
220 generally increases and cpx Na content decreases with melt extraction).

221 **4.2 Incompatible trace element budget in spinel peridotites**

222 The incompatible trace element budget of the EB and CC samples can be
223 constrained by comparing the trace element composition of the bulk xenoliths with
224 those of their constituent minerals relative to their modal abundances. Mineral
225 modes were estimated using a least squares regression of olivine, orthopyroxene,
226 clinopyroxene and spinel major element compositions to bulk xenolith
227 compositions. These are shown in Table 5. In some xenoliths from Elephant Butte,
228 there is a small amount ($<1\%$) of interstitial glass present. The interstitial glass is
229 not included in the modal analysis. Other than the interstitial glass and trace sulfides
230 that are present in the samples, we did not identify any phases via optical or
231 microbeam analysis other than olivine, orthopyroxene, clinopyroxene, and spinel.
232 Clinopyroxene and orthopyroxene trace element abundances were measured by LA-
233 ICP-MS whereas olivine trace element compositions were estimated using the
234 $D^{\text{cpx/olivine}}$ model of Witt-Eickschen and O'Neill (2005). Although $D^{\text{cpx/olivine}}$ values are
235 typically high ($D_{\text{Lu}}^{\text{cpx/olivine}}$ ranges from 30 to 50, $D_{\text{Ho}}^{\text{cpx/olivine}}$ ranges from 300 to
236 450), olivine/cpx ratios are sufficiently high that olivine hosts several percent of the

total HREE. Spinel is not likely to contribute significant amounts of REE, Zr, or Hf owing to its low modal abundance (1-3% in the EB and CC xenoliths) coupled with the extremely low concentrations (typically <10 ppb) of these elements in spinel (Bedini et al., 1997; Eggins et al., 1998; Harvey et al., 2012). From this point forward we refer to the sum of the cpx, opx, and olivine trace element compositions weighted to their modal abundances as the “model whole rock” composition.

Figure 5 shows clinopyroxene, orthopyroxene, bulk-xenolith, and model whole-rock compositions for two different samples. In the asthenosphere-derived samples (e.g. 07EB4.01, Figure 5a) the measured bulk composition is commonly within error of the model whole rock for the MREE-HREE. However, for the LREE, HFSE (Zr, Hf), and LILE (Sr) the model whole-rock concentration is less than the bulk-xenolith concentration. In the lithosphere-derived samples (e.g. CC07-2-01, Figure 5b) the model whole rock composition typically accounts for only 60-75% of the measured REE and only 20-40% of measured Zr and Hf. These large deficits in REE and HFSE require an additional unidentified phase (or phases) to host a significant quantity of these elements in the bulk xenolith. High field strength element deficits are greater than deficits in similarly compatible REE and LREE deficits are larger than M-HREE deficits. This indicates that the residual component is LREE enriched but also enriched in HFSE relative to REE.

Deficits between model whole rock trace element compositions and bulk-xenolith trace element compositions are commonly observed in peridotite xenoliths and generally attributed to a catch-all “grain-boundary component” (Bedini and Bodinier, 1999; Condie et al., 2004; Garrido et al., 2000; Harvey et al., 2012; Kalfoun

et al., 2002). The fact that the residual component in the lithosphere-derived samples is enriched in HFSE relative to REE is problematic because typical metasomatic melts or fluids are either depleted in HFSE relative to REE, or show “normal” HFSE/REE (e.g. not HFSE enriched). Apatite (O'Reilly and Griffin, 2000) and amphibole (Eggins et al., 1998) are LREE-enriched and are often observed as secondary phases in peridotite xenoliths. The large deficits in Hf and Zr relative to the REE cannot, however, be explained by the presence of apatite or amphibole alone. Instead, a phase that is strongly enriched in HFSE relative to REE must be present. Bodinier et al. (1996) observed reaction layers on spinel consisting of phlogopite and Ti-oxides that host a large (>50%) proportion of the bulk xenolith's HFSE despite the extremely low modal abundance of these phases. Kalfoun et al. (2002) found rutile and Ti-oxides in off-craton xenoliths from SE Siberia with very high concentrations of Zr and Hf (> 10,000 ppm and >200 ppm, respectively). Rutile that is found in spinel peridotites, however, typically occurs in fine grained aggregates associated with feldspar and secondary olivine (Ionov et al., 1999), which we do not observe in the EB and CC xenoliths.

Samples that have been metasomatised ($[La/Sm]_N > 1$) generally have greater deficits in the modeled vs. observed HFSE compared to unmetasomatised samples ($[La/Sm]_N < 1$), consistent with a primarily metasomatic origin for the HFSE deficits (Figure 6). The measured whole rock trace element patterns are generally smooth and lack the pronounced depletions in HFSE relative to REE that are present in the model whole rock trace element patterns. This suggests that the observed deficits in HFSE are not related to the addition of an exotic component. Instead, the

enrichments in HFSE relative to REE in the grain boundary component could be the result of the introduction of a relatively “normal” metasomatic component at the grain boundary followed by diffusion of REE and HFSE at different rates into the mineral grains. Several studies suggest that HFSE diffusion rates are at least an order of magnitude lower than REE diffusion rates (Cherniak et al., 1997a; Cherniak et al., 1997b; Van Orman et al., 2001). A recent study by Cherniak and Liang (2012), however, suggests that Ti diffuses in Cr-diopside at a rate similar to HREE, but at least one to two orders of magnitude slower than divalent major elements such as Fe, Mg, and Ca. Zirconium and Hf likely diffuse at a slower rate than Ti because they have larger ionic radii than Ti. If an enriched metasomatic component is introduced to the grain boundary and allowed sufficient time to diffuse, the more slowly diffusing elements (e.g. Zr and Hf) will be preferentially enriched closer to the grain boundary relative to the more quickly diffusing REE.

Compositional maps of samples with large HFSE deficits in the model trace element compositions show high concentrations of Ti along grain boundaries, consistent with the presence of a HFSE-rich grain boundary component (Appendix, Figure A2, upper panel). This Ti-rich grain boundary is not present in samples that show good agreement between modeled and measured HFSE compositions (Appendix, Figure A2, lower panel). The sample CC07-2-01, which shows high concentrations of Ti along its grain boundaries, also displays a gradient of high Ti concentrations in cpx near grain boundaries with decreasing Ti concentrations moving towards the core (Figure 7). Using the length of the diffusion profile and an estimate of Ti diffusivity it is possible to estimate the time since the introduction of

the HFSE-rich grain boundary component (i.e. the timing of metasomatism). Using the relationship $t = x^2/D$, with a diffusion distance of $\sim 125 \mu\text{m}$, and diffusivity of $3.82 \times 10^{-22} \text{ m}^2/\text{s}$ ($\log D_0 = -10.53 \pm 1.55$) we estimate a diffusion time of ~ 1 million years. The diffusivity of Ti was estimated at 1080°C (the equilibration temperature of the sample) following Cherniak and Liang (2012). Despite the large uncertainty in available diffusion data (Cherniak and Liang, 2012), our estimates for diffusive timescales range from 0.04 to 45 Ma, or very recent given the 1.6 to 1.8 Ga age of the lithosphere in this region.

4.3 Comparisons between cpx, opx, and bulk xenolith Nd and Hf isotope compositions

Clinopyroxene Lu/Hf are generally lower than opx (and therefore whole rock) Lu/Hf in spinel peridotites. If the Hf isotope compositions of a sample's constituent minerals are supported by their respective Lu/Hf, then opx and WR $^{176}\text{Hf}/^{177}\text{Hf}$ should be systematically more radiogenic than cpx due to their higher Lu/Hf. The same would be expected for $^{143}\text{Nd}/^{144}\text{Nd}$ in opx and WR because opx and WR Sm/Nd are higher than in cpx. By comparing cpx, opx, and WR Nd and Hf isotope ratios from a single sample, it is possible to determine whether its isotopic ratios are supported by mineral or whole rock Sm/Nd and Lu/Hf.

A comparison of Hf and Nd isotope ratios in the lithosphere- and asthenosphere-derived samples is shown in Figure 8. Orthopyroxene and WR Hf and Nd isotope ratios are consistently either equal to or less radiogenic than cpx Hf and Nd from the same sample. For all samples, $\epsilon_{\text{Nd,Hf}}$ values in cpx are greater than or

equal to $\epsilon_{Nd,Hf}$ values in opx which are greater than or equal to $\epsilon_{Nd,Hf}$ whole rock values. Despite the fact that opx and WR values commonly fall below the 1:1 line with cpx, there is a general positive correlation such that samples with more radiogenic cpx Nd and Hf also have more radiogenic Nd and Hf in opx and WR. These features suggest that the samples' Nd and Hf isotope ratios are supported by the whole rock Sm/Nd and Lu/Hf.

Radiogenic ingrowth (supported either by mineral or whole rock Lu/Hf) cannot produce opx and WR Hf less radiogenic than cpx Hf because opx and WR Lu/Hf is higher than for cpx. Orthopyroxene has Hf concentrations that are typically 10-20 times lower than in cpx. Therefore, opx is more susceptible to secondary overprinting than cpx. Two of the lithosphere-derived samples, which have trace element patterns indicative of metasomatic overprinting, have opx $^{176}Hf/^{177}Hf$ that are less radiogenic than cpx. Choi and Mukasa (2012) also observed opx with less radiogenic $^{176}Hf/^{177}Hf$ than cpx, which they attributed to late-stage metasomatism that primarily over-printed opx Hf isotope ratios. Asthenosphere-derived samples have similar cpx and opx ϵ_{Hf} and ϵ_{Nd} , consistent with the lack of metasomatism recorded in these samples.

Hafnium isotope ratios measured on bulk xenolith powders are generally less radiogenic than cpx and opx separates from the same sample (Figure 8), and trend towards the host basalts and other primitive lavas from the region (Beard and Johnson, 1993; McMillan et al., 2000) - proxies for metasomatising melts. The less-radiogenic Hf and Nd ratios observed in the whole rocks are likely the result of metasomatic grain boundary components.

The relative difference between cpx and opx or WR Nd isotope ratios is typically less than that for Hf isotope ratios. This is not expected because $D_{\text{Nd}}^{\text{cpx/opx}}$ values are much greater than $D_{\text{Hf}}^{\text{cpx/opx}}$ values (observed ranges for $D_{\text{Nd}}^{\text{cpx/opx}}$ and $D_{\text{Hf}}^{\text{cpx/opx}}$ are 90-260 and 7-22, respectively). Therefore it is expected that opx (and also WR) Nd isotope ratios would be more susceptible to overprinting than Hf isotope ratios owing to the lower concentrations relative to cpx of Nd in opx compared to Hf. Mineral separates were acid leached during sample preparation to remove external contamination. The procedure consists of a 15 minute leach at 60 °C in 2M HCl, followed by multiple rinses with 18.2 MΩ H₂O. Thus, it is possible that the opx and WR Nd isotope ratios closely resemble cpx Nd isotope ratios (i.e. pre-metasomatism composition) owing to the efficient removal of Nd in grain boundary components during the leaching process. Hafnium, which is less soluble than Nd in dilute HCl, is less likely to be leached during sample preparation than Nd. Therefore opx and WR Hf isotope compositions may display greater offsets from cpx relative to Nd isotope compositions due to the persistence of Hf in the grain boundary component after sample leaching.

The lithosphere-derived samples originate from mantle that is pervasively metasomatised as evidenced by LREE-enrichment observed in xenoliths from throughout the Rio Grande Rift/Colorado Plateau region (Alibert, 1994; Byerly and Lassiter, 2012; Kil and Wendlandt, 2007; Roden and Shimizu, 1993). Flat-slab subduction of the Farallon plate strongly influenced western North American tectonics during the Laramide orogeny (80-35 Ma; Humphreys et al., 2003). Fluids and melts associated with flat-slab subduction are a potential source of the SCLM

metasomatism. The lithosphere-derived xenoliths display LREE and LILE enriched metasomatic signatures that are typical of Colorado Plateau xenoliths (Byerly and Lassiter, 2012). The lithosphere-derived Cerro Chato samples generally have young (typically < 350 Ma) depleted-mantle-Nd model ages (Appendix, Table A2). The depleted mantle model ages represent a maximum estimate for the time of metasomatism, which could be more recent if Nd isotope ratios reflect mixing instead of radiogenic ingrowth. The young model ages suggest the metasomatic signatures that are observed in the lithosphere-derived cpx are related to young (<100 Ma) flat-slab Farallon subduction. The Ti diffusion profile that is observed in a lithosphere-derived Cerro Chato sample (Figure 7) requires very recent (<45 Ma) introduction of the metasomatic grain boundary component.

The LREE enrichment observed in lithosphere-derived clinopyroxene fractions may explain the clustering of WR, opx, and cpx Nd isotope compositions if these compositions instead reflect complete resetting by recent metasomatism. This is consistent with the observation that Nd isotope compositions of the Cerro Chato samples cluster around that of the host basalt (a proxy for the metasomatising agent). Additionally, lithosphere-derived cpx Nd and Hf isotope compositions are decoupled (Appendix, Figure A3). This has been observed before in SCLM-derived xenoliths (Armytage et al., 2015; Bedini et al., 2004; Choi and Mukasa, 2012; Yu et al., 2009) and has been ascribed to metasomatic overprinting of Nd isotope ratios that left Hf isotope ratios relatively undisturbed.

The observed cpx-opx-WR Hf and Nd isotope systematics of the EB and CC xenoliths suggest their isotopic ratios were supported by their whole rock Sm/Nd

and Lu/Hf, but were later variably reset by recent metasomatic overprinting. Clinopyroxene is less susceptible to metasomatic overprinting of Hf and Nd than opx (and WR) due to the higher relative concentrations of these elements in cpx. Therefore opx and WR isotope ratios are less reliable than cpx isotope ratios for studying the long-term history of a sample. Thus for the remainder of the discussion we focus only on cpx isotope ratios.

4.4 Significance of Lu/Hf – Hf isotope correlations

4.4.1 Use of clinopyroxene Lu/Hf versus whole rock Lu/Hf

The $^{176}\text{Hf}/^{177}\text{Hf}$ of clinopyroxene fractions are strongly correlated with cpx Lu/Hf and model WR Lu/Hf (Figure 9) in the Cerro Chato samples. Several studies observe $\text{Lu}/\text{Hf}_{\text{cpx}} - ^{176}\text{Hf}/^{177}\text{Hf}_{\text{cpx}}$ correlations in single suites of xenoliths and interpret these correlations to be the result of variable fractionation of Lu and Hf during ancient melt extraction from the mantle or formation of overlying crust (e.g., Choi and Mukasa, 2012; Choi et al., 2008; Choi et al., 2010; Liu et al., 2012). These interpretations are commonly supported by the apparent overlap between external cpx isochron ages with crust formation ages and/or osmium model ages. However, below we illustrate an alternative approach towards the interpreting the significance of Lu/Hf – $^{176}\text{Hf}/^{177}\text{Hf}$ correlations.

Because $^{176}\text{Hf}/^{177}\text{Hf}_{\text{cpx}}$ is supported by whole rock Lu/Hf, it is necessary to use whole rock Lu/Hf for interpreting the age significance of $\text{Lu}/\text{Hf}_{\text{cpx}} - ^{176}\text{Hf}/^{177}\text{Hf}_{\text{cpx}}$ correlations. In samples from Cerro Chato, the model whole rock Lu/Hf values correlate much better ($r^2 = 0.980$) with the $^{176}\text{Hf}/^{177}\text{Hf}$ of

clinopyroxene fractions than the measured whole rock Lu/Hf ($r^2 = 0.384$, Appendix Figure A4). This is likely due to recent metasomatic emplacement of grain boundary components, which are responsible for the observed mismatches between measured and model whole rock trace element compositions. Young (<300 Ma) Nd depleted mantle model ages coupled with short (<45 Ma) Ti diffusion times indicate that this metasomatism is recent. Because the measured whole rock Lu/Hf is influenced by recent input of metasomatic grain boundary components, it is not representative of the long-term Lu/Hf of the samples. Therefore the model whole rock Lu/Hf is preferred over that measured directly on the whole rock.

The Lu/Hf modeled from whole rocks is higher than that measured in the associated cpx. This difference tends to be large (40-60%) in very refractory samples (Figure 10). This is due the combined effect of the decrease in $D_{\text{cpx/opx}}$ as fertility decreases (Figure 4) paired with the overall decrease in cpx modal abundance and cpx/opx ratio with increased melt removal (Niu, 1997). Because whole rock Lu/Hf are higher than cpx Lu/Hf, any age determination using cpx Lu/Hf for samples whose Hf isotope ratios are supported by whole rock Lu/Hf will produce erroneously old ages.

A comparison between the Lu-Hf ages estimated using cpx Lu/Hf versus model whole rock Lu/Hf for the lithosphere-derived samples from Cerro Chato, which are derived from Proterozoic SCLM, is shown in Figure 9. The external cpx isochron yields an apparent age of ~1.5 Ga whereas the model whole rock Lu/Hf isochron yields an apparent age of ~1.2 Ga. Two comparisons between apparent Lu-Hf ages using cpx Lu/Hf versus model whole rock Lu/Hf using previously published

data from other localities are presented in the appendix (Figure A5). In both cases recalculating Lu-Hf ages using the model whole-rock Lu/Hf results in ages that are significantly younger than previously reported using cpx Lu/Hf. Bianchini et al. (2014) also noted this for samples from the East African rift whereby model ages calculated using cpx Lu/Hf were older than model ages calculated using model whole rock Lu/Hf (~1.9 Ga versus ~1.6 Ga, respectively).

4.4.2 Alternative interpretation of Lu/Hf – Hf isotope correlations

If Lu-Hf external cpx isochrons reflect the timing of melt extraction from the mantle, then Lu/Hf and Hf isotope compositions should correlate with indicators of melt depletion, such as whole-rock Al_2O_3 , spinel Cr#, or cpx Yb (Dick and Bullen, 1984; Hellebrand et al., 2001). This, however, is not observed for the lithosphere-derived xenoliths from Cerro Chato or for many other suites of xenoliths (Appendix, Figure A6). Thus, in many cases, correlations between Lu/Hf and Hf isotope compositions do not appear to be the direct result of variable Lu/Hf fractionation during mantle melting (and subsequent radiogenic Hf ingrowth).

If Lu/Hf – $^{176}\text{Hf}/^{177}\text{Hf}$ correlations are not produced by variable mantle melting and subsequent ingrowth, then other mantle processes must be introducing Hf isotope variations that correlate with Lu/Hf. The Cerro Chato samples have cpx fractions with $^{176}\text{Hf}/^{177}\text{Hf}$ that are strongly correlated with $1/[\text{Hf}]_{\text{Model WR}}$ (Figure 11a). This could result from radiogenic ingrowth whereby the samples with the lowest Hf concentrations inherit the greatest relative proportion of radiogenic Hf from the decay of Lu (i.e. have the most radiogenic $^{176}\text{Hf}/^{177}\text{Hf}$ today). However, the correlation could also reflect mixing between depleted and enriched components

(i.e. variable metasomatic overprinting of depleted mantle lithosphere). This is consistent with the fact that Cerro Chato cpx fractions have variably LREE/LILE-enriched trace element concentrations that are indicative of metasomatic overprinting. Additionally, the evidence suggests that bulk-xenolith and opx Hf isotope compositions, which are commonly shifted to less radiogenic values than cpx, are influenced by metasomatic processes. This is apparent in correlations between whole rock $^{176}\text{Hf}/^{177}\text{Hf}$ and $1/[\text{Hf}]_{\text{Measured WR}}$ (Figure 11b) as well as opx $^{176}\text{Hf}/^{177}\text{Hf}$ and $1/[\text{Hf}]_{\text{opx}}$ (Figure 11c). Thus, the observed correlation between Lu/Hf and $^{176}\text{Hf}/^{177}\text{Hf}$ in the Cerro Chato samples may be primarily influenced by variable metasomatic overprinting. The correlation between Lu/Hf and $^{176}\text{Hf}/^{177}\text{Hf}$ may therefore have no age significance.

Pervasive metasomatic overprinting of Hf isotope compositions in SCLM-derived spinel peridotites potentially explains the anomalously high initial ϵ_{Hf} values that are commonly observed in external cpx Lu-Hf isochrons. The initial ϵ_{Hf} values should represent the composition of the SCLM source, which is generally assumed to be depleted mantle, at the time of Lu-Hf fractionation. The Hf isotopic evolution of depleted mantle through time has been estimated by looking at the initial composition of juvenile rocks and zircon grains through time (e.g. Vervoort and Blichert-Toft, 1999). Alternatively one can take the estimated composition of average depleted mantle today ($\epsilon_{\text{Hf}} \sim +20$) and project it back through time to CHUR using an assumed differentiation age or Lu/Hf of depleted mantle. These models broadly agree; for example both estimate the depleted mantle at 2 Ga to have an ϵ_{Hf} value of +7 to +10. Several studies have observed Lu-Hf external cpx isochrons with

initial ϵ_{Hf} values that are higher than those expected for depleted mantle at the time of Lu-Hf fractionation (melt extraction), e.g., $+28 \pm 17$ at 1.8 Ga (Spitsbergen; Choi et al., 2010), $+19 \pm 5$ at 1.7 Ga (Yangyuan, North China Craton; Liu et al., 2012); $+15 \pm 4$ at 2.6 Ga (Hannuoba, North China Craton; Choi et al., 2008); $+20 \pm 15$ at 1.2 Ga (this study). However, if Lu/Hf – $^{176}\text{Hf}/^{177}\text{Hf}$ correlations are the result of recent mixing, then the “initial” Hf isotope composition (e.g. y-intercept on external cpx isochron) should approximate the enriched (e.g. metasomatic) component, not depleted mantle at the apparent time of Lu-Hf fractionation. If the enriched, high-Hf concentration component is instead modern depleted mantle or the host basalt, then the issue with high initial ϵ_{Hf} disappears. In Figure 11 the host basalt plots close to the “initial” Hf value, which suggests the host basalt could be an end member that mixed with depleted lithosphere resulting in a correlation between $^{176}\text{Hf}/^{177}\text{Hf}$ and Lu/Hf.

5. Conclusions

Clinopyroxene-opx partition coefficients inferred from correlated cpx and opx trace element concentrations in two suites of spinel peridotite xenoliths from the Colorado Plateau and Rio Grande Rift overlap with partition coefficients predicted from lattice strain and thermodynamic models (Witt-Eickschen and O'Neill, 2005; Yao et al., 2005) with $D_{\text{Lu}}^{\text{cpx/opx}}$ values ranging from 3.5 to 6.1 and $D_{\text{Hf}}^{\text{cpx/opx}}$ values ranging from 7.0 to 22. $D_{\text{Lu}}^{\text{cpx/opx}}$ and $D_{\text{Hf}}^{\text{cpx/opx}}$ values are correlated with indicators of melt extraction (e.g. cpx MgO content), such that $D^{\text{cpx/opx}}$ values for Lu and Hf decrease by up to a factor of 3 with increased melt extraction. $D^{\text{cpx/opx}}$

values for M-LREE show less correlation with composition than do HREE and Hf. Owing to the decrease in the cpx/opx ratio and $D^{cpx/opx}$ values with increased melt extraction, opx becomes an important host of many moderately incompatible trace elements (including Lu and Hf) in refractory peridotites.

Many RGR and CP peridotites have (recently emplaced) grain boundary components that, in some cases, host >50% of the total REE and HFSE budgets. Similar enriched grain-boundary components have been reported for many other SCLM-derived peridotite suites (Bedini and Bodinier, 1999; Condie et al., 2004; Garrido et al., 2000; Harvey et al., 2012; Kalfoun et al., 2002). In the EB and CC xenoliths, the relative amounts of REE and HFSE in the measured whole rock that are not accounted for by cpx, opx, olivine and spinel are correlated with the degree of metasomatism (e.g. cpx LREE-enrichment). Additionally, x-ray maps show high concentrations of Ti along cpx grain boundaries that decrease towards the core in samples with large HFSE deficits. Diffusion timescales estimated from these concentration gradients are relatively young (<45 Ma) indicating that introduction of the grain boundary component is recent.

Colorado Plateau and RGR xenoliths have orthopyroxene fractions with $^{176}\text{Hf}/^{177}\text{Hf}$ that are identical to or less radiogenic than coexisting cpx from the same samples, despite having higher Lu/Hf than cpx. Identical Hf isotope compositions in coexisting cpx and opx in several samples indicates that mineral Hf isotope compositions in the peridotite suites equilibrated and are supported by whole rock Lu/Hf. Some opx have lower $^{176}\text{Hf}/^{177}\text{Hf}$ than cpx as a result of secondary overprinting. Orthopyroxene fractions have lower Hf concentrations than cpx and

thus their Hf isotope compositions are more likely to be modified by metasomatism than cpx. Most suites of SCLM-derived spinel peridotites have mineral Hf isotope compositions that are supported by whole rock Lu/Hf. Therefore, Lu-Hf isochrons should be calculated using whole rock Lu/Hf instead of cpx Lu/Hf because a large portion of Lu and Hf is also hosted in opx. However, the presence of grain boundary components typically disturbs whole rock Lu/Hf. For example, in SCLM-derived Cerro Chato xenoliths (Colorado Plateau margin), clinopyroxene Hf isotope compositions do not correlate with measured whole rock Lu/Hf, but model whole rock Lu/Hf is strongly correlated with cpx $^{176}\text{Hf}/^{177}\text{Hf}$. Model Lu/Hf are calculated from mineral compositions and modes and thus “see through” recent overprinting from grain boundary components. Using (model) whole rock Lu/Hf instead of cpx Lu/Hf will yield significantly younger Lu-Hf ages (in the case of the SCLM-derived Colorado Plateau margin xenoliths, 300 Ma younger) because the Lu/Hf value of (model) whole rocks are higher than those of the associated cpx.

Because $D_{\text{Lu}}^{\text{cpx/opx}}$ is less than $D_{\text{Hf}}^{\text{cpx/opx}}$, isochrons using cpx Lu/Hf will always overestimate depletion ages. Furthermore, many suites of xenoliths display a lack of correlation between Lu/Hf or $^{176}\text{Hf}/^{177}\text{Hf}$ with indices of melt depletion, good correlation between Hf isotopes and $1/[\text{Hf}]$, and the correspondence of “initial” $^{176}\text{Hf}/^{177}\text{Hf}$ with host lava compositions. This suggests that many peridotite external cpx Lu-Hf “isochrons” may, in fact, result from recent mixing and/or metasomatism. Although an old component is needed to generate highly radiogenic Hf isotope compositions commonly observed in SCLM peridotites, care must be taken in assigning age significance to external cpx Lu-Hf “isochrons”.

559

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Figure Captions

Figure 1 a) Lu concentration in opx versus Lu concentration in cpx. Blue circles, asthenosphere-derived samples; Red squares, lithosphere-derived samples. b) Hf concentration in opx versus Hf concentration in cpx. The good correlation between opx and cpx trace element concentrations suggests the samples were in equilibrium.

Figure 2 Average $D_{\text{cpx/ox}}$ estimated from the trace element concentrations in cpx and opx for asthenosphere-derived samples (solid blue line, dashed where inferred) and lithosphere-derived samples (solid red line, dashed where inferred). Blue and red fields represent ranges of estimated $D_{\text{cpx/ox}}$ for asthenosphere and lithosphere-derived samples, respectively.

Figure 3 Comparison of measured $D_{\text{cpx/ox}}$ versus estimated $D_{\text{cpx/ox}}$ following the model of Witt-Eickschen and O'Neill (2005) for Lu (a) and Hf (b). Symbols same as in Figure 1.

Figure 4 Plot of $D_{\text{cpx/ox}}$ vs. Cpx MgO content (wt. %) for Lu (a) and Hf (b) Symbols as in Figure 1. Also shown are amphibole-free samples used in the calibration of Witt-Eickschen and O'Neill (2005) partition model (black diamonds).

Figure 5 Comparison between clinopyroxene (blue), orthopyroxene (red), whole rock (green), and model whole rock (dashed green – wider green field indicates error associated with calculating model whole rock) trace element abundances for two different xenoliths. a) Sample 07EB4.01, an asthenosphere-derived sample, shows good agreement between measured and modeled trace element compositions. b) Sample CC07-2-01, a lithosphere-derived sample, shows a poor match between measured and modeled trace element compositions, especially the HFSE and LREE.

Figure 6 Difference between bulk-xenolith Hf concentration and bulk-mineral Hf concentration versus $(\text{La}/\text{Sm})_{\text{N}}$ in Cpx. Samples with high $(\text{La}/\text{Sm})_{\text{N}}$ in Cpx (a proxy for the degree of metasomatism) tend to have large amounts of Hf (and other trace elements) that are present in the grain boundaries. This suggests a metasomatic origin for the grain boundary component.

Figure 7 a) Transect from opx to cpx showing the high concentrations of Ti along the grain boundary b) close-up of Ti diffusion profile in cpx extending from the grain boundary.

Figure 8 Comparison of cpx, opx, and bulk-xenolith Hf (a) and Nd (b) isotopes. Y-axis indicates either opx (filled symbol) or whole rock (open symbol) $^{176}\text{Hf}/^{177}\text{Hf}$. Red squares, lithosphere-derived opx (closed square) and bulk-xenolith (open square). Blue circles, asthenosphere-derived opx (closed circle) and bulk-xenolith (open circle). Green diamond shows Hf and Nd isotopic compositions of the host basalts. Mixing curves (black lines) illustrate the effect of metasomatic overprinting,

611 whereby opx or WR $^{176}\text{Hf}/^{177}\text{Hf}$ are more sensitive to metasomatism than cpx
 612 $^{176}\text{Hf}/^{177}\text{Hf}$.
 613
 614 Figure 9 Plot of $^{176}\text{Hf}/^{177}\text{Hf}$ versus $^{176}\text{Lu}/^{177}\text{Hf}$ using clinopyroxene Lu/Hf and model
 615 whole rock Lu/Hf from a suite of SCLM-derived xenoliths from the eastern Colorado
 616 Plateau.
 617
 618 Figure 10. Difference (in %) between model whole rock Lu/Hf and clinopyroxene
 619 Lu/Hf versus clinopyroxene modal abundance.
 620
 621 Figure 11. a) Clinopyroxene $^{176}\text{Hf}/^{177}\text{Hf}$ versus $1/[\text{Hf}]_{\text{model WR}}$. The trend could be
 622 explained by mixing of a depleted residual lithosphere component with an enriched
 623 metasomatic component. Open black square, Cerro Chato host basalt. b) Whole rock
 624 $^{176}\text{Hf}/^{177}\text{Hf}$ versus $1/[\text{Hf}]_{\text{Measured WR}}$ c) Orthopyroxene $^{176}\text{Hf}/^{177}\text{Hf}$ versus $1/[\text{Hf}]_{\text{Opx}}$

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9
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Figure 10

Figure 11

Table 1

Table 1 - Clinopyroxene Trace Element Compositions (in ppm)
^a Cpx trace element compositions previously reported in Byerly and Lassiter, 2012

	07EB1.01 ^a	(1 sd)	07EB1.05	(1 sd)	07EB2.03 ^a	(1 sd)	07EB4.01 ^a	(1 sd)	07EB4.05 ^a	(1 sd)	07EB4.21 ^a	(1 sd)	07EB1.06 ^a	(1 sd)	07EB1.11 ^a	(1 sd)
Ti	2460	100	3400	120	3450	140	4380	290	3500	140	2210	80	370	10	440	10
Sr	35	2	58	4	57	6	67	3	52	2	9	1	21	2	22	1
Y	15	1	18	1	20	1	19	1	15	0.4	14	1.0	3.3	0.1	4.1	0.1
Zr	17	1	27	1	29	1	32	2	22	1	6.8	0.4	3.4	0.2	4.4	0.2
La	0.15	0.01	1.06	0.04	0.59	0.35	0.78	0.05	0.49	0.09	0.06	0.04	1.08	0.05	1.18	0.03
Ce	1.06	0.04	3.21	0.12	2.60	0.19	3.30	0.12	2.66	0.11	0.28	0.03	2.19	0.12	2.14	0.08
Nd	2.24	0.10	3.61	0.11	3.54	0.28	4.65	0.20	3.71	0.12	1.35	0.04	1.05	0.03	1.17	0.05
Sm	1.20	0.06	1.57	0.07	1.63	0.07	1.94	0.14	1.54	0.04	0.92	0.04	0.33	0.02	0.37	0.02
Eu	0.52	0.01	0.67	0.03	0.67	0.03	0.80	0.04	0.65	0.03	0.43	0.02	0.12	0.01	0.14	0.01
Gd	1.81	0.07	2.30	0.09	2.52	0.15	2.69	0.14	2.15	0.11	1.65	0.09	0.42	0.02	0.51	0.02
Dy	2.69	0.15	3.13	0.12	3.48	0.17	3.60	0.26	2.81	0.06	2.49	0.07	0.57	0.02	0.69	0.02
Er	1.70	0.09	1.97	0.08	2.21	0.06	2.20	0.16	1.74	0.05	1.60	0.06	0.38	0.01	0.47	0.02
Yb	1.62	0.08	1.87	0.06	2.05	0.09	2.10	0.12	1.67	0.08	1.61	0.09	0.40	0.02	0.50	0.02
Lu	0.22	0.01	0.26	0.01	-	-	0.29	0.01	0.24	0.01	0.23	0.01	0.058	0.003	-	-
Hf	0.57	0.02	0.83	0.03	0.93	0.03	1.05	0.04	0.74	0.03	0.38	0.02	0.107	0.003	0.14	0.01

	CC07-1-06 ^a	(1 sd)	CC07-1-09 ^a	(1 sd)	CC07-1-14 ^a	(1 sd)	CC07-1-20 ^a	(1 sd)	CC07-1-29 ^a	(1 sd)	CC07-1-35 ^a	(1 sd)	CC07-1-41 ^a	(1 sd)	CC07-1-51 ^a	(1 sd)	CC07-2-01	(1 sd)	CC07-3-01	(1 sd)
Ti	850	100	460	70	720	220	370	20	660	30	400	90	600	40	570	140	3600	380	570	60
Sr	130	10	260	10	150	20	380	20	110	10	360	20	290	20	200	80	180	10	350	10
Y	6.2	0.6	12.0	1.3	6.5	0.4	4.7	0.2	7.5	0.3	8.3	1.5	10.0	0.4	7.5	1.0	12.0	0.5	7.4	0.3
Zr	23.0	5.5	8.1	1.3	9.0	1.2	1.1	0.1	3.2	0.9	29.0	0.6	22.0	8.3	12.0	1.0	33.0	2.3	13.0	0.9
La	3.91	0.38	3.31	0.33	2.60	0.15	5.14	0.69	2.23	0.19	9.12	0.50	5.94	1.10	3.98	0.35	3.42	0.21	8.33	0.52
Ce	12.3	0.5	10.7	0.8	8.70	0.92	9.0	1.5	4.70	0.33	21.3	1.5	19.8	1.80	9.99	1.40	12.3	0.6	18.8	0.9
Nd	6.52	0.70	6.20	0.58	4.39	0.32	2.04	0.31	2.78	0.26	8.90	0.86	10.60	0.85	5.20	0.36	10.80	0.44	6.69	0.27
Sm	1.31	0.14	1.33	0.14	0.79	0.04	0.30	0.04	0.96	0.09	1.35	0.23	1.92	0.17	1.03	0.10	2.86	0.16	0.98	0.06
Eu	0.45	0.05	0.46	0.06	0.28	0.02	0.13	0.01	0.31	0.02	0.42	0.05	0.57	0.07	0.34	0.29	0.95	0.06	0.30	0.02
Gd	1.09	0.10	1.35	0.17	0.78	0.06	0.41	0.02	1.24	0.12	0.91	0.24	1.58	0.14	0.88	0.16	2.64	0.12	0.84	0.04
Dy	1.14	0.09	1.94	0.27	1.12	0.12	0.78	0.04	1.51	0.07	1.09	0.21	1.71	0.09	1.17	0.11	2.50	0.13	1.13	0.06
Er	0.68	0.07	1.40	0.19	0.80	0.09	0.58	0.02	0.87	0.04	0.71	0.17	1.13	0.05	0.81	0.16	1.27	0.07	0.84	0.05
Yb	0.65	0.08	1.31	0.16	0.79	0.05	0.57	0.03	0.71	0.02	0.79	0.19	1.04	0.03	0.80	0.09	1.07	0.05	0.89	0.04
Lu	0.09	0.01	0.17	0.02	0.12	0.00	0.08	0.01	0.11	0.01	-	-	0.15	0.01	-	-	0.15	0.01	-	-
Hf	0.40	0.16	0.22	0.06	0.19	0.02	0.04	0.00	0.15	0.02	0.19	0.01	0.21	0.12	0.17	0.09	0.97	0.09	0.20	0.02

Table 2

Table 2 - Orthopyroxene Trace Element Compositions (in ppm)

	07EB1.01	(1 sd)	07EB1.05	(1 sd)	07EB2.03	(1 sd)	07EB4.01	(1 sd)	07EB4.05	(1 sd)	07EB4.21	(1 sd)	07EB1.06	(1 sd)	07EB1.11	(1 sd)		
Ti	636	24	884	35	757	78	991	93	731	65	503	22	153	9	161	6		
Sr	0.12	0.04	0.22	0.09	0.13	0.07	0.19	0.30	0.16	0.17	0.11	0.21	0.06	0.15	0.27	0.53		
Y	1.12	0.07	1.17	0.06	1.08	0.06	1.21	0.07	0.88	0.03	0.88	0.07	0.32	0.03	0.33	0.03		
Zr	1.18	0.09	1.95	0.08	1.45	0.08	1.78	0.13	1.09	0.07	0.39	0.12	0.42	0.15	0.40	0.18		
La	-	-	-	-	-	-	0.005	0.009	-	-	-	-	0.006	0.001	-	-		
Ce	0.005	0.003	0.017	0.008	0.008	0.008	0.020	0.019	0.010	0.002	-	-	0.012	0.004	0.007	0.003		
Nd	0.017	0.004	0.028	0.010	0.020	0.007	0.032	0.011	0.018	0.005	0.013	0.013	0.010	0.003	0.009	0.002		
Sm	0.016	0.005	0.023	0.007	0.017	0.006	0.022	0.004	0.015	0.004	0.011	0.004	0.006	0.001	0.003	0.002		
Eu	0.009	0.001	0.010	0.001	0.008	0.002	0.011	0.002	0.008	0.002	0.007	0.002	0.003	0.001	0.002	0.001		
Gd	0.049	0.007	0.056	0.010	0.044	0.008	0.053	0.007	0.037	0.003	0.035	0.009	0.013	0.002	0.013	0.002		
Dy	0.138	0.012	0.144	0.011	0.121	0.016	0.150	0.011	0.105	0.009	0.102	0.014	0.038	0.006	0.035	0.004		
Er	0.148	0.009	0.156	0.012	0.149	0.008	0.166	0.014	0.122	0.006	0.123	0.010	0.047	0.008	0.048	0.006		
Yb	0.242	0.014	0.259	0.019	0.249	0.017	0.287	0.015	0.212	0.017	0.209	0.012	0.083	0.006	0.089	0.006		
Lu	0.042	0.001	0.048	0.002	0.046	0.004	0.051	0.004	0.039	0.002	0.041	0.002	0.014	0.001	0.000	0.000		
Hf	0.037	0.003	0.054	0.007	0.042	0.005	0.057	0.007	0.037	0.004	0.019	0.003	0.010	0.002	0.010	0.001		
	CC07-1-06	(1 sd)	CC07-1-09	(1 sd)	CC07-1-14	(1 sd)	CC07-1-20	(1 sd)	CC07-1-29	(1 sd)	CC07-1-35	(1 sd)	CC07-1-41	(1 sd)	CC07-1-51	(1 sd)	CC07-2-01	(1 sd)
Ti	233	22	173	18	174	18	162	5	323	19	216	99	218	19	273	161	1330	96
Sr	0.69	0.39	0.27	0.18	0.82	0.49	1.29	0.22	0.12	0.08	0.96	0.06	0.31	0.17	0.62	0.20	1.19	0.73
Y	0.55	0.11	0.94	0.08	0.53	0.03	0.50	0.02	0.64	0.07	0.59	0.04	0.84	0.14	0.66	0.05	1.16	0.09
Zr	1.68	0.79	0.77	0.25	0.78	0.18	0.19	0.02	0.32	0.06	1.25	0.35	1.03	0.70	1.06	0.39	3.36	0.31
La	0.022	0.014	0.005	0.001	0.017	0.017	0.024	0.005	0.005	0.001	0.020	0.005	0.015	0.015	0.005	0.001	0.032	0.030
Ce	0.083	0.027	0.023	0.012	0.067	0.052	0.065	0.011	0.012	0.007	0.079	0.008	0.046	0.015	0.031	0.018	0.116	0.064
Nd	0.068	0.006	0.031	0.015	0.045	0.017	0.022	0.008	0.016	0.003	0.054	0.011	0.075	0.046	0.050	0.021	0.143	0.056
Sm	0.020	0.012	0.014	0.007	0.011	0.008	0.005	0.007	0.009	0.004	0.014	0.008	0.016	0.004	0.025	0.020	0.058	0.019
Eu	0.009	0.002	0.006	0.001	0.006	0.002	0.003	0.001	0.004	0.001	0.005	0.002	0.008	0.002	0.008	0.004	0.024	0.006
Gd	0.035	0.010	0.031	0.004	0.019	0.003	0.012	0.003	0.028	0.004	0.025	0.009	0.028	0.010	0.044	0.019	0.093	0.017
Dy	0.066	0.018	0.102	0.012	0.061	0.003	0.050	0.004	0.078	0.006	0.064	0.012	0.086	0.010	0.078	0.020	0.169	0.022
Er	0.067	0.010	0.140	0.019	0.078	0.008	0.067	0.004	0.093	0.013	0.086	0.009	0.120	0.017	0.097	0.019	0.149	0.014
Yb	0.114	0.027	0.252	0.038	0.140	0.011	0.127	0.006	0.160	0.013	0.170	0.014	0.201	0.029	0.149	0.023	0.206	0.010
Lu	0.021	0.005	0.048	0.007	0.026	0.003	0.024	0.001	0.032	0.005	-	-	0.043	0.008	-	-	0.034	0.003
Hf	0.026	0.015	0.020	0.010	0.014	0.006	0.005	0.001	0.015	0.003	0.021	0.015	0.013	0.010	0.012	0.006	0.094	0.006

Table 3

Table 3 - Clinopyroxene, Orthopyroxene, and Whole Rock Hf isotope compositions

	CPX	¹⁷⁶ Hf/ ¹⁷⁷ Hf	2se	εHf	OPX	¹⁷⁶ Hf/ ¹⁷⁷ Hf	2se	εHf	Whole-rock	¹⁷⁶ Hf/ ¹⁷⁷ Hf	2se	εHf
07EB1.01 ^a		0.283892	0.000015	39.6		0.283808	0.000067	36.6		0.283640	0.000049	30.7
07EB1.05 ^a		0.283267	0.000007	17.5								
07EB2.03 ^a		0.283580	0.000029	28.6								
07EB4.01 ^a		0.283104	0.000007	11.7		0.283116	0.000037	12.2				
07EB4.05 ^a		0.283223	0.000005	15.9						0.2831987	0.000036	15.1
07EB4.21 ^a		0.283541	0.000006	27.2						0.283559	0.000047	27.8
07EB1.06		0.284944	0.000026	76.8								
07EB1.11		0.284969	0.000034	77.7								
BELB 4-30		0.283487	0.000008	25.3		0.283487	0.000008	25.3				
BELB 4-5		0.283244	0.000007	16.7								
CC07-1-06		0.283564	0.000013	28.0						0.283152	0.000034	13.4
CC07-1-09		0.285274	0.000012	88.5								
CC07-1-14		0.284548	0.000015	62.8								
CC07-1-22		0.291387	0.000044	304.7								
CC07-1-24		0.285031	0.000021	79.9								
CC07-1-35		0.284439	0.000013	59.0								
CC07-1-51		0.284385	0.000015	57.0								
CC07-2-01		0.283273	0.000007	17.7		0.283115	0.000015	12.1		0.283007	0.000026	8.3
CC07-3-01		0.284804	0.000006	71.9		0.283898	0.000075	39.8		0.283329	0.000022	19.7

^a Cpx Hf isotope compositions originally reported in Byerly and Lassiter, 2014

Table 4

Table 4 - Clinopyroxene, Orthopyroxene, and Whole Rock Nd isotope compositions

	CPX	¹⁴³ Nd/ ¹⁴⁴ Nd	2se	εNd	OPX	¹⁴³ Nd/ ¹⁴⁴ Nd	2se	εNd	Whole Rock	¹⁴³ Nd/ ¹⁴⁴ Nd	2se	εNd
07EB1.01 ^a		0.514017	0.000006	26.9		0.513911	0.000102	24.8		0.513704	0.000006	20.8
07EB1.05 ^b		0.513094	0.000004	8.9								
07EB1.09 ^a		0.513223	0.000005	11.4								
07EB2.03 ^b		0.513466	0.000005	16.2								
07EB4.01 ^a		0.513067	0.000006	8.4		0.512946	0.000068	6.0		0.513031	0.000005	7.7
07EB4.05 ^a		0.513168	0.000005	10.3						0.513087	0.000027	8.8
07EB4.21 ^a		0.513717	0.000010	21.1						0.513543	0.000007	17.7
07EB1.11		0.512830	0.000008	3.7								
BELB 4-30 ^a		0.513005	0.000010	7.2		0.512996	0.000017	7.0		0.512847	0.000016	4.1
BELB 4-5		0.512958	0.000004	6.2								
CC07-1-06 ^a		0.512955	0.000003	6.2						0.512930	0.000004	5.7
CC07-1-09		0.512962	0.000004	6.3								
CC07-1-14		0.512978	0.000006	6.6								
CC07-1-20 ^a		0.512942	0.000003	5.9						0.512821	0.000026	3.6
CC07-1-22		0.513140	0.000005	9.8								
CC07-1-35 ^a		0.512899	0.000007	5.1								
CC07-1-41		0.512902	0.000005	5.1								
CC07-1-51 ^a		0.512933	0.000004	5.8								
CC07-2-01 ^a		0.512880	0.000004	4.7		0.512910	0.000013	5.3		0.512899	0.000005	5.1
CC07-3-01 ^a		0.513007	0.000022	7.2		0.513059	0.000048	8.2		0.512933	0.000006	5.8

^a Cpx Nd isotope compositions originally reported in Byerly and Lassiter, 2012

^b Cpx Nd isotope compositions originally reported in Byerly and Lassiter, 2014

Table 5

Table 5 - Mineral Modal Abundances

	Olivine	OPX	CPX	Spinel	sum	ssq residuals
07EB1.01	60	21	18	2	101	0.1
07EB1.05	63	14	19	2	98	0.1
07EB2.03	55	31	12	4	102	0.2
07EB4.01	52	30	17	3	102	0.1
07EB4.05	53	28	17	2	100	0.2
07EB4.21	57	29	13	2	101	0.1
07EB1.11	72	23	3	1	99	0.1
CC07-1-06	57	32	7	4	100	0.9
CC07-1-09	67	13	16	4	100	0.1
CC07-1-14	66	26	8	1	101	0.1
CC07-1-20	56	37	7	2	102	0.1
CC07-1-22	66	21	12	2	101	0.6
CC07-1-35	59	25	12	2	98	0.1
CC07-1-51	65	25	9	1	100	2.2
CC07-2-01	62	26	10	2	100	0.1
CC07-3-01	69	16	13	2	100	0.1