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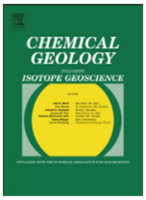

Trace element partitioning and Lu–Hf isotope systematics in spinel peridotites from the Rio Grande Rift and Colorado Plateau: Towards improved age assessment of clinopyroxene Lu/Hf–^{176}Hf/^{177}Hf in SCLM peridotite

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ABSTRACT

Our study of Colorado Plateau and Rio Grande rift spinel peridotite xenoliths determined bulk Lu–Hf budgets and cpx, opx, and whole rock ^{176}Hf/^{177}Hf to evaluate the potential age significance of Lu/Hf–Hf isotope correlations in sub-continental lithospheric mantle (SCLM) derived xenoliths. The samples have fertilities (spinel Cr# range from 0.1 to 0.5), and equilibration temperatures (950–1050 °C) that overlap with those of spinel peridotites commonly used in Lu–Hf dating studies. The Lu/Hf of clinopyroxene (cpx) and its associated whole rock (WR) are similar in fertile samples, but cpx has a lower Lu/Hf than that of the WR in refractory samples. Orthopyroxene (opx) has systematically higher Lu/Hf than cpx, but in many samples, the opx and cpx have identical ^{176}Hf/^{177}Hf, suggesting that the Hf isotope composition of these minerals is supported by the Lu/Hf of the WR rather than that of the individual minerals. Many opx fractions and whole rocks have less radiogenic ^{176}Hf/^{177}Hf than their corresponding cpx (but similar to that of the host magma), reflecting contamination. Because the ^{176}Hf/^{177}Hf of cpx is supported by the WR Lu/Hf, it is necessary to use the latter rather than the cpx Lu/Hf for isochron dating. However, because the actual WR Lu/Hf values are susceptible to secondary overprinting, we recommend using model WR Lu/Hf values (determined from mineral Lu and Hf concentrations and modal abundances) to construct external cpx isochrons. Model WR and measured cpx ^{176}Hf/^{177}Hf are correlated ($r^2 = 0.98$) in a suite of eastern Colorado Plateau xenoliths and yield an apparent age of 1.2 Ga (versus 1.5 Ga when – incorrectly – using cpx Lu/Hf). Despite the good correlation between Lu/Hf and ^{176}Hf/^{177}Hf, we do not find correlations between indicators of melt depletion and Lu/Hf or ^{176}Hf/^{177}Hf. This suggests that Lu/Hf–^{176}Hf/^{177}Hf correlations are not the result of melt depletion. Instead, we propose that Lu/Hf–^{176}Hf/^{177}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}Hf/^{177}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 (Schmidberger et al., 2002; Carlson et al., 2004; Wittig et al., 2006; Shaw et al., 2007; Choi et al., 2008, 2010; Chu et al., 2009; Choi and Mukasa, 2012; Lazarov et al., 2012; Liu et al., 2012; Bianchini et al., 2014). 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}Hf/^{177}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 (Salters and Zindler, 1995; Schmidberger et al., 2002; Ionov et al., 2005; 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}Lu/^{177}Hf$_{cpx}$ and ^{176}Hf/^{177}Hf$_{cpx}$ 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}Lu/^{177}Hf$_{cpx}$ and ^{176}Hf/^{177}Hf$_{cpx}$

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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 $^{176}Hf/^{177}Hf$ 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 $^{176}Hf/^{177}Hf$ 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–$^{176}Hf/^{177}Hf$ 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. Ionov et al., 2006; Wu et al., 2006; Bianchini et al., 2007; Yu et al., 2009; Wittig et al., 2010) 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–$^{176}Hf/^{177}Hf$ 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 Al_2O_3 ~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 sd). 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 $^{143}Nd/^{144}Nd$ of 0.512070 ± 0.000010 (2 sd—external). The BHVO-2 standard was also analyzed throughout the study and produced an average $^{143}Nd/^{144}Nd$ of 0.512970 ± 0.000010 (2 sd—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 $^{176}Hf/^{177}Hf = 0.282160$. A solution of BHVO-2 was run as a secondary standard throughout the study and had an average $^{176}Hf/^{177}Hf$ of 0.283096 ± 0.000020 (2 sd) 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, $^{187}Os/^{188}Os$ analyses, and some cpx trace element and $^{143}Nd/^{144}Nd$ 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 (Fig. 1a, b). The asthenosphere-derived samples are LREE depleted ($(La/Sm)_N$ ranges from 0.04 to 0.42). The lithosphere-derived samples are LREE enriched. Excluding one sample whose $(La/Sm)_N$ is 0.7, the lithosphere-derived samples have $(La/Sm)_N$ 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. $Hf/Hf^* < 1$, where $Hf^* = \sqrt{Nd_N \cdot Sm_N}$). Orthopyroxene fractions display a complementary enrichment in HFSE (e.g. $Hf/Hf^* > 1$) 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 $^{176}Hf/^{177}Hf$ are similar to or less radiogenic than the $^{176}Hf/^{177}Hf_{cpx}$ from the same sample.