Composition of the mantle lithosphere beneath south-central Laurentia:
Evidence from peridotite xenoliths, Knippa, Texas

Urmidola Raye1,*; Elizabeth Y. Anthony2; Robert J. Stern1; Jun-Ichi Kimura1; Minghua Ren2; Chang Qing3; and Kenichiro Tani3

1Department of Geosciences, University of Texas at Dallas, 800 W. Campbell Road, Richardson, Texas 75080, USA
2Department of Geological Sciences, University of Texas at El Paso, 500 W. University Avenue, El Paso, Texas 79968-0555, USA
3Institute for Research on Earth Evolution (IFREE), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka, 237-0061, Japan

ABSTRACT

Mantle xenoliths in ~83 Ma basanites from south-central Texas provide a rare opportunity to examine the lithospheric mantle beneath southern Laurentia. These peridotites represent lithosphere at the boundary between Mesoproterozoic continental lithosphere and transitional Gulf of Mexico passive margin. Here we report petrographic, mineral, and major element data for 29 spinel peridotite xenoliths from Knippa and use these to characterize the lithospheric mantle beneath south central Texas. The xenoliths comprise spinel-bearing lherzolites and harzburgites with coarse, equigranular textures. Some peridotites contain veins of lizardite. There are no pyroxenites or eclogites. The peridotites contain olivine (Fa89-92), orthopyroxene (En89-92), clinopyroxene (Wo40-45En45-49Fs3-5), and spinel. Spinel Cr# (Cr/(Cr+Al)) distinguishes lherzolites (Cr# = 0.25–0.36) and harzburgites (Cr# = 0.14–0.21) and harzburgites of the harzburgites at ~1 to +0.61 and lherzolites at 0 to –2.6 log units with respect to fayalite-magnetite-quartz (FMQ) buffer, similar to lightly metasomatized spinel peridotites elsewhere. The degree of melt depletion and oxidation of the Knippa peridotites are consistent with present data for slightly metasomatized lherzolitic mantle and/or harzburgites rather than forearc settings. Equilibration temperatures range from 824 to 1058 °C (mean = 916 °C), calculated at reference pressure of 2.0 GPa.

Calculated mean seismic velocities Vs = 4.44 km/sec and Vp = 7.87 km/sec show no systematic difference between lherzolites and harzburgites, and agree with present geophysical measurements of upper mantle velocity beneath Texas. The seismic velocities calculated for these samples will provide important constraints for interpretation of EarthScope and other geophysical data sets.

INTRODUCTION

Mantle xenoliths entrained in alkaline magmas are an important source of information about the composition and physical state of subcontinental mantle. Abundant localities are found in western North America (Wilshire et al., 1990). The majority of these samples are located in the Basin and Range Province where Mesozoic and Cenozoic tectonic elements have overprinted Precambrian lherzolitic formation. Very few sample localities are found in tectonic provinces that represent the southern edge of Laurentia. The Knippa locality, located in central Texas, is one such example. The locality lies within the Balcones igneous province (Fig. 1) at the nexus of Mesoproterozoic and transitional lithosphere of the Gulf coastal plain. The lithosphere was affected by the Mesoproterozoic accretion and subsequent Paleozoic tectonism. Characterization of these samples therefore informs us of a very different set of events and permits comparison of subcontinental mantle across a broad region.

This study reports petrographic descriptions, major-element whole-rock analyses, and mineral compositions for these spinel-peridotite xenoliths. We characterize the depletion history, thermometry, oxidation state, and seismic velocities. These results complement a recent trace-element study from the same locality by Young and Lee (2009).

GEOPHYSICAL SETTING

The continental crust of Texas—and much of southern Laurentia—was generated as part of the ~1.37 Ga southern granite-rhyolite province (Fig. 1) (Anthony, 2005; Barnes et al., 2002; Bickford et al., 2000; Reese et al., 2000; Whitmeyer and Karlstrom, 2007). In the southeastern part of the Llano uplift (Fig. 1), dioritic and tonalitic gneiss are inferred to represent a 1.33–1.30 Ga allochthonous magmatic arc (Mosher, 1993; Roback, 1996). This arc is thought to have accreted to Laurentia during the Grenville orogeny at ~1.1 Ga due to N-dipping subduction beneath Laurentia (Mosher, 1998). Young and Lee (2009) studied trace-element compositions of Knippa peridotites and found enrichments in fluid-mobile trace elements (e.g., La) relative to fluid immobile trace elements (e.g., Nb). They concluded that these trace-element patterns were caused by subduction-related fluid metasomatism that modified previously melt-depleted continental lithosphere. They suggested that the continental lithospheric mantle represented by these xenoliths may have been the upper plate during Mesoproterozoic subduction.

Following Mesoproterozoic subduction and the Grenville orogeny, the lithosphere of southern Laurentia was affected by three major tectonic events during Phanerozoic time—two episodes of rifting and ocean opening separated by continental collision (Thomas, 2006). The first rifting episode in Early Cambrian time (~530 Ma) was associated with opening of the Iapetus Ocean. During or shortly after this, a continental sliver that ultimately became the Precordillera of Argentina rifted away (Thomas and Astini, 1996). Associated with early Paleozoic ocean opening (~530 Ma) was the formation of the Ouachita orogeny during Pennsylvanian

*uraye@utdallas.edu

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Composition of the mantle lithosphere beneath south-central Laurentia

time (~350 Ma). Late Triassic uplift (~225 Ma; Dickinson et al., 2010) heralded rifting in what was then the interior of Pangea. This culminated in Late Jurassic seafloor spreading to form the Gulf of Mexico (165–140 Ma; Bird et al., 2005; Stern et al., 2011). The Gulf of Mexico opening also established the present passive continental margin of SE Texas (Fig. 1).

The Balcones Igneous Province (Fig. 1) lies above the transition that separates Mesoproterozoic crust from the Pennsylvanian Ouachita orogenic lithosphere. The Balcones Igneous Province trend also approximates the southern and western limit of attenuated transitional crust beneath the Texas Gulf coastal plain, a result of the Jurassic opening of the Gulf of Mexico (Mickus et al., 2009; Sawyer et al., 1991). This lithospheric transition was most recently reactivated by Miocene faulting (~25–10 Ma) (Galloway et al., 1991).

We do not have a clear picture of the nature of transitional crust, largely because it is buried beneath thick sediments of the Gulf of Mexico coastal plain. This crust could be composed of one or more of the following components: (1) metamorphosed sediments and crust of the Paleozoic passive margin, deformed during the Ouachita orogeny (Mickus and Keller, 1992); (2) fragments of Gondwana, left behind when Gondwana separated from Laurentia in Jurassic time (Rowley and Pindell, 1989); (3) juvenile mafic crust of Jurassic age (Mickus et al., 2009); and (4) thinned crust of southern Laurentia. The underlying lithospheric mantle may have a similarly complex history.

Knippa peridotite xenoliths are hosted by basanites of the Balcones Igneous Province, which is characterized by isolated, monogenetic igneous centers that formed numerous small plugs, laccoliths, sills, tuff rings, and lava lakes (Barker et al., 1987; Spencer, 1969). Balcones Igneous Province basanites give 40Ar/39Ar ages of ~81.5–83.5 Ma (Griffin et al., 2010). The xenoliths are spinel peridotites. The absence of garnet- and plagioclase-peridotite indicates derivation from a depth range of 40 to 85 km, i.e., within the upper part of the subcontinental lithospheric mantle.

SAMPLE DESCRIPTION

Spinol-peridotite xenoliths were collected from the Vulcan quarry, situated in Knippa, Uvalde County, Texas (29.278°N, 99.657°W). Host basanites are dense, black, and fresh. These lavas are aphric to sparsely phric in hand specimen, and in thin section have scattered phenocrysts (90% olivine and 10% clino-pyroxene). The black groundmass contains finely dispersed clinopyroxene, plagioclase, olivine, nepheline, titaniferous magnetite, melilite, zeolite, amphibole, phlogopite, and apatite. Mg# (= Mg/Mg + Fe) of the basanites range from 0.67 to 0.75, have low Ni and Cr abundances, and show strong, light rare-earth element (LREE) enrichment, with chondrite-normalized (La/Yb)N = 19–24 (Griffin et al., 2010).

The ultramafic xenoliths are dispersed in the basanite, where they comprise 5%–10% of the total rock volume. They have subspherical or ellipsoidal forms, with long axes ranging from 1 to 6 cm. They are usually well rounded, although some are polygonal. Host rock-xenolith contacts are sharp in most cases, but some show reaction rims suggesting interaction with basanite magma.

PETROGRAPHY

Knippa xenoliths are Type 1 peridotites (Frey and Prinz, 1978). They consist of olivine, orthopyroxene, clinopyroxene, and the aluminous phase is spinel (Fig. 2). All constituent phases are homogeneous, without chemical zoning. Spinel are brown, elongate, and are mostly in contact with clinopyroxene. Mineral boundaries vary from straight to gently curved, and commonly form 120° triple junctions, indicating recrystallization under equilibrium conditions. Olivines are typically fractured, and some grains display kink banding and undulose
extinction. Sparse spinel grains are distributed around margins of large silicate minerals. Some clinopyroxene and spinel show reaction rims along common grain boundaries. None of the Knippa xenoliths contain accessory amphibole, phlogopite, or silicate glass. Serpentine veins (Fig. 3) are dominated by lizardite (Satsukawa et al., 2010); these are found in some of the peridotite xenoliths. These veins follow grain boundaries as well as cracks in olivine grains. Serpentine-rich veins also contain apatite, pentlandite, and pyrrhotite (Fig. 3), but most olivines and orthopyroxenes are unaffected away from the reaction boundaries.

Following the International Union of Geological Sciences (IUGS) classification for ultramafic rocks (LeBas and Streckeisen, 1991), Knippa xenoliths are lherzolites (modal clinopyroxene >5%) and harzburgites (<5% clinopyroxene) as shown in Figure 4. Lherzolites are more abundant than harzburgites. Lherzolites are predominantly equigranular (Fig. 2), and olivine is 1–4 mm, orthopyroxene is 1–2 mm, clinopyroxene is 0.25–1 mm, and spinel is ~0.15 mm. This variation in mineral grain size is also shown by thin-section X-ray scan map (Fig. 2F). Harzburgites are moderately fractured and have clinopyroxenes that are smaller (~0.1 mm) than those in lherzolite. Table 1 lists modal analyses of Knippa peridotites, 70% of which are lherzolites, with up to 12% clinopyroxene. Modes were also calculated using the method of Lee (2003) (Calculated Mode, Table 1). Bulk chemical compositions and mineral compositions were used to determine mineral mass proportions. Calcium oxide, MgO, FeO, Al₂O₃, and SiO₂ were used for the inversion. In these calculations, homogeneous four-phase mineral compositions (i.e., orthopyroxene, clinopyroxene, olivine, and spinel) were assumed. Accessory phases were not considered. Mineral mass proportions (Xᵢ) were determined by matrix inversion via \( X = (C^T C)^{-1} C^T B \), where X is the column matrix consisting of mineral mass proportions (Xᵢ), C is the mineral composition matrix, Cᵀ is the transpose of C, and B is the bulk composition column matrix. The calculated modes were also checked by MINSQ program of Herrmann and Berry (2002), which produced similar results. Agreement between visual and calculated modes is excellent.

**ANALYTICAL PROCEDURES**

The xenoliths were trimmed to remove all adhering basanite and cut into two similar halves. One part was cut into rectangular slabs 0.5 cm thick and sent for thin-section preparation. Visual modes (Table 1) are estimates from thin-section examination. The other half was crushed into rock chips to be pulverized. Considering xenolith grain size, texture, and homogeneity, 5–10 g of the crushed rock provided a representative whole-rock sample of each xenolith. Aliquots of the crushed material were ground to a fine powder in agate jars from thin-section examination. The other half was crushed into rock chips to be pulverized. Considering xenolith grain size, texture, and homogeneity, 5–10 g of the crushed rock provided a representative whole-rock sample of each xenolith. Aliquots of the crushed material were ground to a fine powder in agate jars

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**Figure 2. Photomicrograph of Knippa peridotites showing**

(A) elongated spinel (Sp) grain surrounded by orthopyroxene (Opx) and clinopyroxene (Cpx); (B) olivine (Ol) grains showing triple junctions along with Opx and Cpx; (C) lizardite veins along grain boundaries and within cracks of olivine grains; (D) backscattered-electron image of thick lizardite veins within Ol grains and thin veins within Opx grains; (E) zoom-in image of lizardite veins within Ol grains; (F) X-ray scan image (including Ca, Fe, Si, and Cr elements) showing grain-size variations between Ol, Opx, Cpx, and Sp, respectively.

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**Supplemental Table File. Excel file of four tables: Table S1: Representative Microprobe Analysis of Olivine Compositions; Table S2: Representative Microprobe Analysis of Orthopyroxene Compositions; Table S3: Representative Microprobe Analysis of Clinopyroxene Compositions; and Table S4: Representative Microprobe Analysis of Spinel Compositions.**

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Composition of the mantle lithosphere beneath south-central Laurentia

Figure 3. Backscattered-electron image of accessory phases within lizardite veins. Common accessory phases are apatite and pentlandite. Numbers show representative microprobe analyses listed in the table below.

<table>
<thead>
<tr>
<th></th>
<th>Lizardite</th>
<th>Pentlandite</th>
<th>Apatite</th>
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<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>Avg(n=5)</td>
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<tr>
<td>SiO₂</td>
<td>37.09</td>
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<td>37.73</td>
</tr>
<tr>
<td>TiO₂</td>
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<td>0.00</td>
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<tr>
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<td>0.00</td>
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<tr>
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<td>0.06</td>
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<td>0.24</td>
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<tr>
<td>MgO</td>
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<td>37.82</td>
</tr>
<tr>
<td>CaO</td>
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<td>0.00</td>
<td>0.15</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td>84.42</td>
<td>83.89</td>
<td>83.85</td>
</tr>
</tbody>
</table>

Figure 4. Modal mineralogy of Knippa peridotites obtained by visual estimates. Following International Union of Geological Sciences classification for peridotites (LeBas and Streckeisen, 1991), Knippa xenolith suite consists of lherzolites (Lhz; modal Cpx >5%) and harzburgites (Hzb; <5% Cpx). Data from Young and Lee (2009) also shown. Ol—olivine; Opx—orthopyroxene; Cpx—clinopyroxene; Serp—serpentine.
average of five or more analyses of each grain and of several grains from different parts of the same sample; these results are summarized in Table 2. In order to examine the equilibrium among mineral phases, attention was paid to evaluating phase homogeneity. Minerals in Knippa peridotite xenoliths are homogeneous with little grain-to-grain chemical variation except near contacts with host basalt where some reaction is evident. All of the compositions we report were measured far from these contacts.

Major-element composition of Knippa xenoliths (Table 1) was determined in two separate labs. Nine samples were sent to Activation Laboratories Ltd., Lancaster, Ontario, and analyzed by tetraborate fusion–inductively coupled plasma (ICP) method, while 20 samples were analyzed by...
RESULTS

Mineral Chemistry

Major phases in Knippa peridotites are compositionally homogeneous and do not show significant grain-to-grain chemical variations. Olivine compositional range is Fo$_{89}$ to Fo$_{92}$ with one exception of Fo$_{88}$ (Table 2; Fig. 5). The Fo content of Knippa olivines falls in the range expected for Proterozoic (Fo$_{92}$ to Fo$_{93}$) and especially Phanerozoic (Fo$_{91}$ to Fo$_{92}$) lithospheric mantle (Gaul et al., 2000). Harzburgite olivines are slightly more magnesian (Fo$_{96}$–Fo$_{97}$) than lherzolite olivines (Fo$_{88}$–Fo$_{91}$).

Orthopyroxenes are enstatite with a composition of Wo$_{12}$En$_{19}$Fs$_{69}$ (Table 2; Fig. 5). Orthopyroxene Mg# ( = 100*Mg/[Mg + Fe$^2+$]) correlates with coexisting olivine Mg# (Fig. 6A). Lherzolite orthopyroxenes have higher Al$_2$O$_3$ (3%–4%) and lower Cr$_2$O$_3$ (0.1%–0.4%) content than harzburgite orthopyroxenes (2%–3% Al$_2$O$_3$; 0.67%–1.08% Cr$_2$O$_3$) (Fig. 6B).

Clinopyroxenes are apple-green diopsides, with a composition of Wo$_{68}$En$_{24}$Fs$_{6}$ (Table 2; Fig. 5) with Mg# between 90 and 93. Al$_2$O$_3$, MgO, and Cr$_2$O$_3$ in lherzolite clinopyroxene range from 2% to 6% and 0.5% to 1.1%, respectively, while those in harzburgite clinopyroxene range from 3% to 5% and 0.67% to 1.08%.

Spinels are summarized in Table 2. Based on Cr# ( = Cr/Cr + Al), there are two distinct spinel compositions (Fig. 5). Harzburgite spinels have higher Cr# (mean = 0.29) than lherzolites (mean = 0.17).

Serpentine is lizardite, and thin serpentine veins contain small grains of pentlandite ([Fe,Ni]$_n$Si$_x$), apatite (Ca$_5$[PO$_4$]$_3$), and trace amounts of pyrrhotite (Fe$_7$S$_8$). Pentlandite contains 29.88–40.39 atomic% Ni, 24.31–35.18 atomic% Fe, and 31.78–34.89 atomic% S. The contents of CaO and P$_2$O$_5$ in apatite are 33–34 and 38–39 wt%, respectively, and are fluorapatite (Ca$_5$[PO$_4$]$_3$F) with 2.5–3 wt% fluorine (Fig. 3).
### Whole-rock Geochemistry

Whole-rock major-element composition of Knippa xenoliths (Table 1) agree with those calculated by Young and Lee (2009) from mineral modes and compositions. The whole-rock contents of Al\(_2\)O\(_3\) and CaO in Knippa peridotite xenoliths anticorrelate with MgO content (Fig. 7). For comparison, the composition of primitive (undepleted) upper mantle (Hart and Zindler, 1986; Jagoutz et al., 1979; McDonough and Sun, 1995), forearc peridotite (Parkinson and Pearce, 1998; Parkinson and Arculus, 1999; Pearce et al., 2000) and backarc basin (BAB) peridotite (Michibayashi et al., 2009) are also shown. The Knippa peridotites have high whole-rock MgO and low CaO and Al\(_2\)O\(_3\) compared to fertile model–primitive mantle compositions. Negative correlations of Al and Ca oxides with MgO are consistent with Knippa peridotites representing the residue of previous melt depletion. Both lherzolites and harzburgites follow melt-depletion trends.

### Seismic Velocity

Seismic velocities were calculated at standard temperature and pressure (STP) (25 °C and 1 atm) using the method described by Lee (2003) (Table 3). V\(_p\) (Primary wave velocities) for Knippa xenoliths range from 8.24 to 8.31 km/sec and V\(_s\) (Secondary wave velocities) range from 4.77 to 4.84 km/sec. There is no systematic difference in seismic velocities between Knippa lherzolites and harzburgites.

The velocities calculated by the method of Lee (2003) correspond to temperatures that are lower than those in the upper mantle. For this reason, seismic velocities were also calculated using the method of Hacker and Abers (2004) and mineral equilibration temperatures between 900 and 1060 °C. Table 3 shows that V\(_p\) range from 7.80 to 7.97 km/sec and V\(_s\) range from 4.34 to 4.52 km/s. No systematic differences exist between the seismic velocities of lherzolites and harzburgites calculated by this method.

### DISCUSSION

The following section discusses the implications of the compositional data reported above. We focus on the equilibration temperatures of Knippa xenoliths, the oxidation state of the mantle beneath Knippa, and estimates of partial melting and depletion of the peridotites. Finally, we compare the calculated seismic velocities to geophysical seismic-velocity models for this part of southern Laurentia.
Composition of the mantle lithosphere beneath south-central Laurentia

Temperature

Mantle temperatures can be estimated using thermometric techniques on equilibrated samples. Equilibrium between mineral phases is essential for such estimates. Attainment of equilibrium among mineral phases of the Knippa xenoliths and absence of disturbance during serpentinization and after entrainment in basanite melt are inferred from the correlation between olivine and orthopyroxene Mg# with a nearly constant slope (Fig. 6A). In addition, as described in the sections on petrography and mineral chemistry, homogeneity among constituent phases is also evident from absence of chemical zoning and grain-to-grain chemical variations as well as by the recognition of typical equilibrium textures in thin section.

Several methods have been proposed for estimating the equilibrium temperatures of spinel-peridotite mineral assemblages. Four of the most commonly used geothermometers (with abbreviations in parentheses) are: (1) the two-pyroxene thermometer of Brey and Kohler (1990) (T/BKN), (2) the Ca-in-orthopyroxene thermometer of Brey et al. (1990) (T/BK_Ca), (3) the thermometer of Witt-Eickschen and Seck (1991) based on Cr-Al partitioning between orthopyroxene and spinel coexisting with olivine (T/WS), and (4) the thermometer of Wells (1977) based on iron solubility in coexisting pyroxenes (T/Wells). Knippa xenoliths have equilibrium temperatures of 824–1058 °C for T/BKN, except for two samples with temperatures of 760 and 1150 °C (Table 3). The T/BKN and T/Wells geothermometers give similar results that closely correlate, with \( r^2 = 0.917 \) (Fig. 8), but with somewhat higher minimum temperature of 890 °C. These temperatures denote thinner and warmer lithosphere than typical cratonic lithosphere but cooler than Phanerozoic lithospheric mantle as discussed by Young and Lee (2009). No significant temperature differences exist between Knippa lherzolites and harzburgites.

These temperature estimates pertain to the Late Cretaceous time of xenolith entrainment. The thermal structure of the upper mantle may have been disturbed by Balcones Province igneous activity, in which case the temperature estimates may be higher than conditions that exist today. Alternatively, the lithospheric thermal structure may not have changed significantly since that time, due to the brevity of the Balcones Igneous Province event and the thermal inertia of the lithosphere.

Oxygen Fugacity

The oxidation state of the upper mantle, which can be calculated from the equilibrium reaction involving coexisting olivine, orthopyroxene, and spinel, has been extensively applied in spinel peridotites (Ballhaus et al., 1991; Mattioli and Wood, 1988; Nell and...
Raye et al.

Wood, 1991; O’Neill and Wall, 1987; Wood, 1990; Wood and Virgo, 1989). The equilibrium reaction is as follows:

$$6 \text{Fe}_2\text{SiO}_4 + \text{O}_2 = 3\text{Fe}_2\text{Si}_2\text{O}_6 + 2\text{Fe}_3\text{O}_4.$$  

Olivine Orthopyroxene Spinel

The oxygen-fugacity values for Knippa xenoliths were calculated using electron microprobe analyses, which yield total iron content of spinels. The distribution of Fe$^{2+}$ and Fe$^{3+}$ in spinel was inferred from stoichiometry. The mantle fugacity values obtained by this method (Ballhaus, 1993; Mattioli et al., 1989) differ little from those obtained by direct determinations of Fe$^{3+}$.

Calculated oxygen-fugacity values (Table 3) are given relative to the fayalite-magnetite-quartz (FMQ) buffer at 2.0 GPa. The oxygen fugacity relative to FMQ buffer is little affected by changes in estimated pressure within the range of the spinel-lherzolite stability field (Wood, 1990). Changing the pressure to 1.5 GPa causes a shift of oxygen fugacity of <0.001 log units. Oxygen-fugacity values of Knippa xenoliths fall in a relatively narrow range from below the FMQ buffer ($D\log fO_2 = –2.6$ to $0.61$; Fig. 9). The harzburgites show slightly higher oxygen fugacity than the lherzolites. The $D\log fO_2$ values for lherzolite are 0 to $–2.6$; whereas for harzburgite, the values are $–1$ to $+0.61$ (Fig. 9). Mean oxygen-fugacity value and standard deviation (relative to FMQ) for unserpentinized harzburgite is $0.00 \pm 0.64$ and for lherzolite is $–0.94 \pm 0.70$. Serpentinization did not affect oxygen fugacity: oxygen fugacity for unserpentinized harzburgite ($0.00 \pm 0.64$) is indistinguishable from that of serpentinized harzburgite ($–0.62 \pm 0.49$). Similarly, serpentinized lherzolite ($–1.6 \pm 1.45$) has an oxygen fugacity that is indistinguishable from that of unserpentinized lherzolite ($–0.94 \pm 0.70$).

Comparing Knippa peridotite oxygen-fugacity estimates with the oxygen-fugacity range of global Proterozoic and Phanerozoic subcontinental lithospheric spinel peridotites (Ballhaus at al., 1991; Ballhaus, 1993), the Knippa peridotites plot in the field of lightly metasomatized peridotites (Fig. 9).

### Table 3. Temperature, Oxygen Fugacity, and Seismic Velocity of Selected Samples Calculated at P = 20 kbar

<table>
<thead>
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<th>Sample no.</th>
<th>T/Wells (°C)</th>
<th>T/BKN (°C)</th>
<th>$D\log fO_2$</th>
<th>Vp (STP) (km/s)</th>
<th>Vs (STP) (km/s)</th>
<th>Vp (T) (km/s)</th>
<th>Vs (T) (km/s)</th>
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<td>4.81</td>
<td>7.82</td>
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<tr>
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<td>969</td>
<td>950</td>
<td>–</td>
<td>8.30</td>
<td>4.84</td>
<td>7.88</td>
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<tr>
<td>Kn3</td>
<td>991</td>
<td>987</td>
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<td>8.30</td>
<td>4.83</td>
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<td>Kn4</td>
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Note: STP—standard temperature and pressure; T/BKN—two-pyroxene thermometer of Brey and Kohler (1990); T/Wells—thermometer of Wells (1977); T(936 °C)—Mean Knippa temperature; Vp—primary wave velocity; Vs—secondary wave velocity.
peridotites overlap the abyssal and backarc basin peridotite field (Arai and Ishimaru, 2008) and have lower oxygen fugacities compared to forearc peridotites.

**Partial Melting and Depletion of the Knippa Lithospheric Mantle**

The Cr# versus TiO₂ in spinel (Fig. 10) distinguishes between spinels that experienced melt-rock interaction and those defining a partial melting trend (Arai, 1992; Zhou et al., 1996). Figure 10 shows a partial melting trend, starting from fertile mid-ocean ridge basalt (MORB) mantle with 0.18% TiO₂, and is superimposed on published experimental results of Johnson et al. (1990). Details of the method are explained in Pearce et al. (2000). Ti, being an incompatible element, should rapidly decrease as the degree of melting increases and Cr# increases. The trend for Knippa peridotites toward higher Ti, especially for harzburgites, therefore implies melt-mantle interaction through reaction or melt impregnation by a Ti-rich melt (Edwards and Malpas, 1996; Kelemen et al., 1995). This reaction would have followed depletion of the host harzburgite as origin of the Ti-rich trend point to the most Cr#-rich melting trend of the peridotite. No significant difference is seen between serpentinized and unserpentinized peridotites, again confirming that the serpentization is probably a late-stage, low-temperature phenomenon.

Spinel Cr# correlates with Fo content of coexisting olivines and Cr contents of coexisting orthopyroxene and clinopyroxene. These compositional variations are interpreted to have been caused by extraction of a basaltic partial melt and have been observed in xenolith suites worldwide (Bonatti and Michael, 1989; Frey et al., 1985; Frey and Prinz, 1978; Hauri and Hart, 1994). Knippa xenoliths plot within the olivine-spinel mantle array (OSMA; Fig. 11), interpreted as a mantle-peridotite restite trend (Arai, 1994). With greater extents of partial melting, olivine Fo increases greatly, defining the olivine-spinel mantle array. Peridotites from different tectonic settings occupy distinct parts of the array. Melting curves from Pearce et al. (2000) based on experimental studies of Jaques and Green (1980) show that Knippa lherzolites were produced by <10% melting, whereas harzburgites were produced by 10%–15% melting, which is consistent with the estimate based on Cr# versus TiO₂ plot. As noted above, spinel Cr# is a much more sensitive index of melt extraction than olivine Mg#. Hellebrand et al. (2001) calculated fractional melt percentage as a function of spinel Cr#, yielding the relationship: F = 10×ln (Cr#)+24, where F = melt percentage. This relationship is thought to be valid for spinel Cr# between 10 and 60. Based on Hellebrand et al.’s (2001) model, Knippa lherzolites reflect 5%–9%, and harzburgites reflect 11%–14% melt extraction from a primitive mantle source (Fig. 12). These melt-depletion signatures are less than current data sets for forearc peridotite (Parkinson and Pearce, 1998; Parkinson and Arculus, 1999; Pearce et al., 2000) but quite consistent with backarc basin peridotite (Arai and Ishimaru, 2008; Ohara et al., 2002).

The whole-rock compositions are consistent with the results obtained from mineral composition and reflect moderate extraction of partial melts. As melt depletion increases, whole-rock compositions show decreasing Al₂O₃ and CaO and increasing MgO. With progressive melting, Al₂O₃ in orthopyroxene decreases (Fig. 6B), olivine Fo content increases, modal olivine increases, and modal clinopyroxene decreases. The whole-rock contents of Al₂O₃ and CaO, which reflect variations in melt extraction from primitive (undepleted) upper mantle (PUM; Hart and Zindler, 1986; Jagoutz et al., 1979; McDonough and Sun, 1995), are plotted as a function of MgO (Fig. 7). Experimental batch and fractional melting curves of Asimow (1999) are plotted starting from PUM compositions.

**Figure 8. Equilibration temperature for Knippa peridotites.** Temperature was calculated at 2 GPa using the two-pyroxene thermometer (T/BKN) of Brey and Kohler (1990) and the thermometer of Wells (1977) (T/Wells). Knippa xenoliths have equilibrium temperatures of 824–1058 °C (T/BKN). The two approaches agree with r² = 0.91. There are no significant temperature differences between lherzolites (Lhz) and harzburgites (Hzb) or between serpentizated versus fresh peridotites, suggesting that these lithologies are mixed in the lithosphere beneath Texas. Serp—serpentine.

**Figure 9. Oxygen fugacity of Knippa peridotites. Oxygen fugacities fall near the fayalite-magnetite-quartz buffer (Δlog fO₂FMQ = −2.6–0.61).** Knippa lherzolites and harzburgites plot in the field of lightly metasomatized spinel peridotites (Bailhaus, 1993). In contrast, forearc peridotites have distinctly higher Cr# and oxygen fugacity. Forearc peridotite data are from Parkinson and Pearce (1998), Parkinson and Arculus (1999), and Pearce et al. (2000), and backarc basin (BAB) peridotite data are from Arai and Ishimaru (2008). The less oxidized forearc samples are from, for example, Pali Aike. See text for further discussion.
which again indicate that lherzolites reflect less melt depletion than do harzburgites. Note that the harzburgite samples with TiO₂-rich spinel that follow the melt-rock reaction trend in Figure 10 plot around the highest MgO-end of the whole-rock trend (Fig. 7), implying that melt depletion formed the harzburgite first, and melt impregnation occurred later. Effect of melt reaction to the depleted harzburgites shown by Cr# versus TiO₂ in Figure 10 is not identifiable in other plots, suggesting negligible effect on the estimates of melt extraction based on major and compatible elements. However, the effect should not be underestimated for incompatiible elements such as Ti or rare-earth elements (REEs). According to the tectonic model shown in figure 7 of Mosher (1998), the mantle beneath Knippa would have underlain a forearc during late Mesoproterozoic time. However, Knippa peridotites have major-element and mineral compositions that are different from forearc peridotites and are consistent with metamorphosed continental lithosphere (Young and Lee, 2009) or backarc peridotites (Arai and Ishimaru, 2008). Peridotites from different tectonic settings plot in different parts of this trend. Knippa peridotites plot within the continental field. Melting curve (dashed line with % melting) from Pearce et al. (2000) based on experimental studies of Jaques and Green (1980) indicate that the lherzolites were produced by <10% melting, whereas the harzburgites were produced by 10%–15% melting. All forearc peridotite data are from Parkinson and Pearce (1998), Parkinson and Arculus (1999), and Pearce et al. (2000), and backarc basin (BAB) peridotite data are from Arai and Ishimaru (2008) and Ohara et al. (2002). FMM—fertile MORB mantle; MORB—mid-ocean ridge basalt; Serp—serpentine.

Seismic-Velocity Structure beneath Texas

Calculated velocities were compared with geophysical measurements of seismic velocity beneath the region. Rayleigh wave-dispersion experiments carried out by Keller and Shurbet (1975) using different stations in Texas (Corpus Christi, Edinburg, Laredo, San Marcos, and Houston, Fig. 13A) show that crustal structure is generally similar along all profiles extending from the Llano uplift southeastward to the Gulf of Mexico. A generalized crustal structure model proposed by Keller and Shurbet (1975) is shown in Fig. 13B. Based on Rayleigh wave-dispersion data, the upper layers (Vp ≤5.2 km/s) are interpreted to be Mesozoic and Cenozoic sedimentary rocks, the upper crustal layer (Vp >5.2 km/s) is interpreted to consist primarily of Paleozoic metamorphic rocks, and the lower crustal layer (Vp ≤6.9 km/s) is interpreted to comprise mafic

Figure 10. Chromium is compatible in spinel and increases with melt extraction, while titanium is incompatible and decreases with melt extraction. Increase of Ti content in the Cr# versus TiO₂ wt% of spinel is thus indicative of an early melt-extraction event followed by subsequent melt-rock reaction. The harzburgites appear to have undergone more melt-rock reaction than the lherzolites.

Figure 11. Knippa peridotite compositions plotted on the olivine-spinel mantle array (OSMA) of Arai (1994). OSMA is a mantle-peridotite restite trend. Peridotites from different tectonic settings plot in different parts of this trend. Knippa peridotites plot within the continental field. Melting curve (dashed line with % melting) from Pearce et al. (2000) based on experimental studies of Jaques and Green (1980) indicate that the lherzolites were produced by <10% melting, whereas the harzburgites were produced by 10%–15% melting. All forearc peridotite data are from Parkinson and Pearce (1998), Parkinson and Arculus (1999), and Pearce et al. (2000), and backarc basin (BAB) peridotite data are from Arai and Ishimaru (2008) and Ohara et al. (2002). FMM—fertile MORB mantle; MORB—mid-ocean ridge basalt; Serp—serpentine.

Figure 12. Melt depletion of Knippa peridotites, based on Cr# of spinel. Chromium being compatible in spinel, increases in the residue with increasing melt extraction. Hellebrand et al. (2001) calculated fractional melt percentage as a function of spinel Cr#, yielding the relationship F = 10-3ln (Cr#) + 24, where F = melt fraction. This relationship is valid for spinel Cr#s between 0.1 and 0.6. Knippa lherzolites (Lhz) are formed by <10% melt extraction and harzburgites (Hzb) by ~15% melt extraction. All forearc peridotite data are from Parkinson and Pearce (1998), Parkinson and Arculus (1999), and Pearce et al. (2000), and backarc basin (BAB) peridotite data are from Arai and Ishimaru (2008) and Ohara et al. (2002). Serp—serpentine.
of the mantle lithosphere beneath south-central Laurentia

Figure 13. (A) Index map showing Knippa (star), seismograph stations: LAR—Laredo, COR—Corpus Christi, EDN—Edinburg, SAM—San Marcos, HOU—Houston (Keller and Shurbet, 1975), C—Cram (1961, 1962), D—Dorman et al. (1972), H—Hales et al. (1970) refraction line and gravity profiles 1, 2, 3, and 4. T1 (stations 2, 4, and 5), T2 (stations 1, 2, and 3), and T3 (stations 1, 3, and 4) are tripartite locations. (B) Generalized crustal structure model proposed by Keller and Shurbet (1975). (C) Crustal structure as interpreted from seismic velocities. Our calculated upper mantle seismic velocity agrees well with those velocities obtained from geophysical experiments.

CONCLUSIONS

Peridotite xenoliths in Cretaceous basanites from the Knippa quarry of south-central Texas are among a few mantle samples from the southern margin of Laurentia and thus provide constraints on the nature of this lithospheric mantle. Based on our petrographic, mineral-chemical, and whole-rock chemical studies, we estimate that equilibration temperatures at the time of entrainment were 824–1058 °C and that Δlog fO2 values are 0 to –2.6 for lherzolite and –1 to +0.61 for harzburgite. Melt depletion was less than 10% for lherzolite and 10%–15% for harzburgite. This melt-depleted mantle subsequently underwent melt-mantle interaction through reaction or melt impregnation by a Ti-rich melt. No significant difference between serpentinized and unserpentinized peridotites confirmed that the serpentinization was a late-stage, low-temperature phenomenon. The combination of these characteristics suggests that this mantle was either a slight metasomatized continental lithosphere and/or backarc basin rather than a forearc setting.

Calculated seismic-velocity data are consistent with geophysical profiles from the Llano uplift southeastward to the coastline of the Gulf of Mexico. Our velocity calculations will be useful to constrain improved geophysical models generated by Earthscope’s new data set.

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